

**THE PHYSICO-MECHANICAL AND MORPHOLOGICAL
PROPERTIES OF α -CELLULOSE-FILLED POLYSTYRENE (PS)
AND POLYVINYL ACETATE (PVAc) BLENDS**

By

PAUL ANDREW MAMZA

**B. Sc (Hons) Chem., M. Sc (POLYMER SCI. and TECH.) (ABU.),
(PGNS/UJ/0017/06)**

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DECLARATION

I hereby declare that this work is the product of my own research efforts; undertaken under the supervision of Professor B. T. Nwifo and has not been presented elsewhere for the award of a degree or certificate. All sources have been duly distinguished and appropriately acknowledge.

Signature/Date

Paul Andrew Mamza
(PGNS/UJ/0017/06)

CERTIFICATION

This is to certify that the research work for this thesis and subsequent preparation of thesis by Paul Andrew Mamza (PGNS/UJ/0017/06) were carried out under my supervision.

Professor B. T. Nwifo

Signature/Date

Endorsement by the Head, Department of Chemistry,

Dr. S. J. Salami

Signature/Date

DEDICATION

This research is dedicated to Paul John Flory, the Father of Modern Polymer Chemistry, who gave Polymer the meaning of scientific research.

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ABSTRACT

Studies of physico-mechanical and morphological properties of pure and α -cellulose reinforced blends of polystyrene (PS) and poly (vinyl acetate) (PVAc) are reported in this work. The compression moulded articles of the blends of different compositions (10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20 and 90:10, PS/PVAc) were tested for mechanical performance, absorption behaviour, void activity and morphological arrangements. Comparison of mechanical properties such as tensile strength, modulus of elasticity and elongation at break revealed apparent compatibility domains for 20:80 and 10:90, PS/PVAc for both pure and reinforced blends. However, the α -cellulose filled blends have enhanced tensile strength for all the compositions. From the values of the breaking load (in kilonewtons-KN) Vs composition of the blends, there was considerable strength improvement with α -cellulose filler content. The equilibrium sorption in four different solvents, showed a declining order in accordance to acid > water > base > acetone. However, solvent absorption increased with filler content in all the solvents, because the filler increased the gelation level, hence the sorption rise except in acetone which showed a sharp reduction in % absorption in the presence of α -cellulose filler. The acetone seems to dissolve the crystalline portion of the blends and cannot be used to detect the differences between the polymer blends

and their molecular structure. The void activity in the blend were estimated by density measurements, and they showed a definite pattern except that the filler increases the densities of the blends 30/70, 20/80, and 10/90, PS/ PVAc having the highest values than other compositions. Also, photo micrographs of the certain blends showed a two phase system appearing bright (PVAc phase) and the other appearing opaque (PS phase) in virtually all the micrographs, even though the heterogeneity due to phase inversions (phase changes) was relevant for some compositions. For other compositions, a domain distribution showed considerable miscibility within the range of compositions.

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND WITH COMMERCIAL EXAMPLES

Blending procedures had been employed since time immemorial. The principle of blending is geared towards achieving property averaging. A blend is therefore the physical mixture of two or more substances, without a chemical bond.

Linseed oil, a triglyceride of unsaturated fatty acids, is heated with a brittle resin, usually an unsaturated C₂₀ mono carboxylic acid (Mantell, Kopf, Curtis and Rogers, 1942). The resin itself could be used as a coating, but the linseed oil is incorporated to reduce the brittleness of the product. On the other hand, the linseed oil by itself forms an oily, slow-to-harden coating. Thus, the principle of property averaging (blending) was recognized a long time ago. The resin contains unsaturation and, presumably during the heating with the oil and the subsequent oxidative cross-linking, is incorporated covalently. Nevertheless, no segregation occurs and clear, tough, films of high molecular weight result. Many modern vanishes use phenol-formaldehyde resins rather than natural resins. Modification of the basic phenol structure is required in order to obtain solubility of the resin in the linseed oil. parasubstitution with tert-butyl, phenyl, and other hydrocarbon groups increases the aliphatic character (reduces solubility parameter) enough to achieve solubility.

In the non-convertible coatings (lacquers) area, the importance of polymer-polymer systems was recognized as soon as it was found that cellulose nitrate required plasticization to obtain adequate toughness for coatings. Shellac, a natural resin obtained from insects, was an early example of a polymeric additive to cellulose nitrate. The mixture forms clear, tough films and “the two appear to act as mutual plasticizers” (OCCA, Manual, 1961). Later it was observed that poly (vinyl acetate), poly (vinyl methylether), and poly (vinyl ethyl ether) performed the same function. As cellulose acetate made inroads into cellulose nitrate markets, it was found that not all the plasticizers for the later were suitable for the former. Phenolic resins, poly (α -methylstyrene) and poly (vinylacetate) gave clear coatings with cellulose acetate. The coatings chemists also discovered the concept of using a third component to improve the miscibility of the two others. Phenolic resin, shellac, and styrene-co- α -methylstyrene was an example of such a ternary mixture (Olabisi, , Robeson and Shaw, 1979).

1.2 Definition of polymer blends

These are mixture of chemically different polymers and or copolymers with no covalent blending between them. Polymer blends can be classified as homologous, miscible, immiscible, partially miscible, compatible, non-compatible, interpenetrating polymer networks (IPN) or polymer alloys. Homologous polymer blends are a subclass of chemically identical polymers which

exhibit single-phase behaviour. Immiscible polymer blend encompasses those blends, which exhibit two or more phases at all composition and temperatures.

Partially miscible polymer blends are a subclass of polymer blend including those blends that exhibit a 'window' of miscibility i.e. they are miscible only at some concentration. Compatible Polymer blends are a utilitarian term indicating commercially useful materials, mixture of polymer with strong repulsive forces that is homogenous to the eye.

Interpenetrating Polymer Network (IPN) are a subclass of polymer blend reserved for a mixture of two polymers where both components form continuous phases and at least one is synthesized or cross linked in presence of the other while polymer alloys are a class of polymer blends, heterogeneous in nature with modified controlled, interfacial properties and/or morphology (Utracki, 1987). The polymer blends and alloys however must be distinguished from polymeric composites, which are defined as follows (Mathews, 1912)

- i. It (composite) consists of two or more physically distinct and mechanically separable materials.
- ii. Mixing the materials in such a way that the dispersion of one material in the other can be done in a controlled way to achieve optimum properties.

The properties are superior and possibly unique in some specific respects to the properties of the individual components.

1.3 Two-component systems: definitions

1.3.1 Blends-two phase and single phase

An important case where the polymer-polymer mixture exhibits miscibility or solubility has provoked recent interest as miscible polymer blends are increasingly reported in the technical polymer literature. Until now, polymer-polymer miscibility has been treated as a special case in the field of polymer blends or alloys with the recent commercialization of new polymer-polymer miscible blends combined with very definite advances in the thermodynamics of polymer-polymer phase behaviour, the necessity for a treatise specifically related to polymer-polymer miscibility has therefore evolved. Several reviews of miscible polymer mixtures have been published in the past decade with listings of up to 50 mixtures exhibiting some degree of miscibility (Buckley, 1967, Bohn, 1968, Krause, 1972 and Krause, 1978). The most comprehensive reviews have been authored by Krause (1972 and 1978) and provide an excellent listing of both miscible and immiscible blends. The literature search for this treatise has revealed over 100 different mixtures with the necessary criteria to be considered miscible polymer mixtures. Polymer miscibility is not only important in the case of simple polymer mixtures, but also determines the physical

nature of block and graft copolymers, interpenetrating networks, and thermosetting networks of polymer mixtures. It is evident that classification of the use of the term “miscibility” to describe single-phase, polymer-polymer blends is necessary. Prior studies and reviews have generally used the term “compatible” to describe single-phase behaviour. However, “compatibility” has been used by many other investigators involving various studies of polymer-polymer blends behaviour to describe good adhesion between the constituents, average of mechanical properties, behaviour of two-phase block and graft copolymers, and ease of blending. The term “solubility” which is more descriptive and exact than “compatibility”, could be another choice for describing molecular mixing in polymer-polymer blends. For single-phase, solvent-solvent and polymer-solvent mixtures, solubility is the accepted term. With polymer-polymer blends, ideal or random molecular mixing may not adequately describe the true nature of the blend even though the physical parameters of the blend would suggest true solubility. After much deliberation and discussions with many investigators involved with polymer-polymer blend research, the term miscibility has been chosen to describe polymer-polymer blend with behaviour similar to that expected of a single-phase system. The term miscibility used does not imply ideal molecular mixing but suggests that the level of molecular

mixing is adequate to yield macroscopic properties expected of a single-phase material.

The level of molecular mixing existing in polymer blends that exhibit macroscopic properties indicative of single-phase behaviour is commanding considerable attention without widespread agreement. For specific blends, recent studies have been able to provide experimental evidence of the level of molecular mixing. Until recently, only microscopic (i.e. electron microscopy), techniques were utilized to provide further insight into the level of mixing. In some blends, heterogeneous structure was observed at high levels of magnification even though macroscopic properties implied single-phase behaviour. Heterogeneous structures (domains), however, have been observed in amorphous homopolymers (i.e. atactic polystyrene), thus confusing the interpretation of polymer blend miscibility (Geil, 1975). These conflicting conclusions from macroscopic and microscopic experiments have resulted in research directed toward answering a specific question (Couchman and Karasz, 1977 and Kaplan, 1976): How large is the size of a domain required to be in order to yield macroscopic properties (i.e. glass transition temperature) distinctly different from other domains of different molecular structures? In early investigations of the thermodynamics of polymer mixtures, serious deficiencies were observed with the application of methods used successfully for

predicting solvent-solvent or solvent-polymer solubility. The single value solubility parameter approach was found to be quite unsuccessful in predicting polymer-polymer miscibility and new techniques that offered more promise were investigated. Equation of state thermodynamics has been applied recently to polymer phase behaviour and the result qualitatively agrees with the experimentally observed phase behaviour of polymer mixtures. This approach reveals definite differences from those one would expect via extrapolation of techniques commonly applied to solvent-solvent and solvent-polymer mixtures. Indeed, the thermodynamics of polymer-polymer mixtures requires much more rigorous treatment than the previously accepted methods for solvent-solvent and solvent-polymer mixtures.

Although the miscible blends of poly (vinyl chloride) (PVC) and butadiene acrylonitrile copolymers have been commercial since the 1940s (Emmet, 1944 and Reed, 1949), recent interest has been provoked by the commercialization of a blend of poly (2,6-dimethyl-1, 4-phenylene oxide) (PPO) and polystyrene (PS) (Cizek, 1968) under the trade name Noryl, as well as the need for more permanent (i.e. polymeric) plasticizers for PVC (Graham, 1975, and Hammer, 1977). The best commercial advantages of a miscible polymer blend can best be summarized by the word "versatility". With a specific polymer, the number of

possible variations in usable properties is limited without resorting to composition changes. Random, block and graft copolymerization, polymer blends, and composites offer significant property diversification (Olabisi et al, 1979). With polymer blends exhibiting two-phase behaviour, definite advantages can be derived (e.g. impact polystyrene and acrylonitrile-butadiene-styrene (ABS) if mechanical compatibility is assured and a property compromise between the constituents is therefore achieved. With miscible polymer mixtures, mechanical compatibility is assured and a property compromise between the constituents is therefore achieved. Thus, with a miscible polymer-polymer blend, a range of price/performance characteristics between the component polymers can lead to a large number of potentially useful and different products. The versatility places miscible polymer blends into a unique situation with potential commercial importance. Single-phase polymer blend, the two-phase system must be defined and contrasted with miscible systems to delineate the two subjects and to establish the criteria for excluding what is certainly the vast majority of polymer-polymer mixtures. In most instances, the critical property will be the glass transition; blend with a single glass transition will be classified as miscible, blends of components having similar glass transition temperatures will provide ambiguous cases and other techniques must be employed. But experience has shown that immiscibility in

polymer blends is rarely well concealed, revealing itself as opacity, delamination, double glass transition, or combination of these properties.

From a thermodynamic point of view, every polymer has some solubility in every other polymer, but the magnitude in most cases is exceedingly low. For example, if polystyrene is fluxed on a mill with poly (methylmethacrylate), a two-phase mixture results, no matter how long or intensive the mixing. One could, in principle (but with difficulty in practice), separate the two phases, analyze the composition of each, and arrive at values for the mutual solubilities. In this case, as with hexane in water, the solubilities would be less than 1%(Okada, 1977).

On the other hand, if one fluxes polystyrene on a mill with poly (2,6-dimethyl-1, 4-phenylene oxide) as the second component, one phase results. It is thermodynamically stable because no matter how slowly the mixer runs or how long one waits there is still only one phase (Ogawa, Kanaya and Matsuba, 2008).

Consider a third example: polystyrene plus poly (vinyl methyl ether) (PVME), if PS is fluxed with an equal amount of PVME on the mill at 80°C, a clear, one-phase mixture results. However, if the temperature is raised to 140°C, two phases appear. A return to 80°C restores one phase. This behaviour has been

summarized for a range of compositions by the experimental cloud-point curves (Olabisi, Robeson and Shaw, 1979).

These three examples provide an excellent basis on which to build a definition of polymer miscibility and hence polymer blend. The first represents an example of an immiscible blend, the second is a miscible blend; the third illustrates that miscibility and immiscibility can be exhibited by the same mixture depending on the ambient condition. Furthermore, the third example demonstrates that the driving forces for the transition from the one-phase (miscible) to the two-phase (immiscible) state are thermodynamic in origin and do not depend, for example, on the extent or intensity of mixing.

In spite of the seemingly unquestionable behaviour described in these examples, an exact definition of miscibility in polymer mixtures is a subject of considerable debate because it represents different characteristics to different investigators. For the investigator interested in macroscopic properties useful on practical industrial problems, a miscible polymer mixture is that which exhibits a single glass transition temperature (T_g) and it is irrelevant whether or not changes of state occur during the preparation of the sample or during measurement. Here, miscibility implies homogeneity of the mixture up to a scale whose dimension is similar to the segmental size responsible for the major glass transition.

However, for the investigator interested in statistical thermodynamics, miscibility implies homogeneity on a scale equivalent to the range of intermolecular forces. Miscibility in this sense is not necessarily satisfied by the T_g criterion. Miscibility is not even absolutely satisfied by the usual qualitative criterion given in several texts that the Gibb's free energy of mixing, ΔG^M , must be negative for a system to be thermodynamically stable. Such criterion is only a degenerate form of Gibb's criteria, because it neither distinguishes unstable from stable states nor gives any understanding of the concept of metastability, which is so important in phase separation phenomena. Furthermore, it is known (Konigsveld and Kleintjens, 1976) that mixtures are often unstable at negative ΔG^M (not relative to the pure constituent but to some intermediate composition and that the ΔG^M becomes more negative as the mixtures phase-separate further.

1.4 Trends in the science and development of polymer blends

The oldest reference to blends of solid polymers appropriately is to impact resistant polystyrene which is today the poly blend in largest commercial production. In 1912, in a British patent, Mathews stated that the addition of rubber to polystyrene "gives hardness and toughness thereto in accordance with the

proportion added.” Ostromislensky (1927) was issued a patent which describes the preparation of impact polystyrene by a method which today is termed a “graft copolymerization”. However, the first commercial blend was produced in 1846 by Sir Thomas Hancock, the discoverer of mastication by mixing natural rubber with *gutta percha*. It was used to apply on clothes for water proofing and was patented in the said year. This was the first rubber/plastics blend. The next in the series came only in 1942 almost about a century later when it was discovered that acrylonitrile butadiene rubber could plasticize polyvinyl chloride (PVC) permanently. This spurred the rapid development of commercial thermoplastics-rubber blends. In the subsequent years, plasticised PVC was added to vulcanized nitrile butadiene rubber (NBR) to improve ultraviolet (UV) and oxidative stability. They are still utilized in sponge, wire, cable, footwear, belt and hose applications/appliances. This yielded compositions offering resistance to plasticizer migration in adverse environments such as oil and water containment and food contact applications. This blend is found to be miscible. Other high molecular weight Polymers have since been used as permanent plasticizers for PVC such as ethylene/vinylacetate/acrylonitrile (EVA) copolymer containing 65 – 70 wt % vinylacetate and polyester based thermoplastic polyurethane (TPU). These blends are also found to be miscible. In 1942, Dow Chemical Corporation, introduced an alloy

“Stralloy-22” an interpenetrating network (IPN) of polystyrene and polybutadiene. In 1944, R.F. Boyer polymerised styrene in the presence of styrene – butadiene rubber (SBR) to obtain high impact polystyrene (HIPS).

In 1946, a mechanical mixture of NBR and poly (styrene-co-acrylonitrile) was produced to obtain acrylonitrile – butadiene – styrene (ABS) type Polymers (Nando, 2002).

In 1947, a series of miscible blends were developed. Nitrocellulose with polyvinyl found a miscible pair. Similarly, nitrocellulose with polymethyl methacrylate (PMMA) gave rise to a miscible blend. Polystyrene with benzylcellulose also formed a miscible pair.

In 1951, the impact properties of crystalline, polypropylene (PP) was improved by blending with polyethylene or by copolymerizing with ethylene. The year 1960 saw rapid growth in the field of engineering polymer alloys and blends. Polystyrene was found to be miscible with poly (2, 6, dimethyl 1:4 phenylene ether) and this helped to process the PPE easily. The density as well as mechanical properties of the blends is found to be higher than that obtained by the additivity rule, exhibiting a significant synergistic behaviour. This densification has been assumed to be due to specific interaction between the blend constituents, which also increased the blend viscosity

above that of log-normal additivity rule. A series of commercial blends were produced in 1965 by Mayer & Salwer General Electric Company in the name of Noryl. The upper use temperature of ABS polymer is 90°C. This temperature can be improved by adding α -methylstyrene acrylonitrile copolymer to ABS which also improves its load bearing capability. An azeotropic methyl styrene acrylonitrile has a Tg of 25°C higher than the SAN matrix of ABS. This is known as 'High heat ABS' developed in 1962. Similarly, α -methyl styrene acrylonitrile is miscible with PVC. It has great demand in high heat resistance applications. ABS/PVC blends have been commercialized since 1969. In the same year, PP and ethylene / propylene/ diene monomer (EPDM) blends have been discovered by Coran and Patel and later commercialized by Monsanto, Chemical Co., in the name of 'Santoprene'. It improves the impact resistance of PP. They were widely used as bumpers, in automotive parts, suitcases, sports, thermoplastic rubbers and as construction materials.

Polystyrene (PS) has a heat distortion temperature at 90°C. Its Tg can be increased significantly by adding poly (2, 6 dimethyl 1:4 phenylene oxide) (PPO) with a Tg of 210°C. These blends are used in appliances, business machines, housing, electronic equipment, pump components and automotive applications.

Blends of ABS/PVC was marketed in 1969 by Borg Warner. They are thermoformable, possessing good moldability and flame retardancy. Also they bear good weatherability. They are used in electronics housing, business machines and electronic parts.

Super touch nylon was developed by Dupont in 1975 by blending Nylon66 with an elastomer. It becomes tougher and fracture behaviour changes on incorporating rubber. It is basically used in automotive applications. It was followed by toughening of polyethylene terephthalate (PET) by adding a small quantity of the polyolefinic elastomer. When reinforced with glass fibres (31%), it is used to make automotive body parts.

In 1976, blends of PET with polybutylene terephthalate (PBT) were developed by General Electric Co., USA (Valox 500 or 700), and, when reinforced with glass fibres, provided good dimensional stability. Glass fibres were used to the extent of 65%.

Borg Warner first introduced blends of polycarbonate (PC) and ABS in 1977 (Banerjee, 2002), which was commercialized by Mobay Chemical Co., U.S.A. These blends were used in automotive applications, electronics and medical parts. When

reinforced with glass fibres and aluminium, it attained excellent impact strength, and higher dimensional stability. These blends possess excellent moldability and are most suitable for injection moulding. They possess good low temperature impact strength and also sometimes used in electrical and electronic parts. ABS/PC blends confer high heat and impact resistant properties. In 1979, General Electric Co. introduced impact modified blends of PC with PBT and/or PET, under the trade name Xenoy. A 50:50 blend of PC: PBT improved the low temperature properties and when reinforced imparted good tensile strength and flexural modulus. Therefore, they are used in car bumpers, automobile and electronic components. When PC is blended with PET, and reinforced with glass fibres, it is used in car bumpers and in sports. The percent of glass fibre is limited to 30%. Celanese Co. in 1980, introduced toughened blends of elastomer with PBT (Celanex 500) and polyoxymethylene (POM) – Celcon-400. PBT/elastomer blends are used in car bumpers, automotive and electronic components and possess high impact resistance properties. They are quite often reinforced with glass fibres and other short fibres and mica. Blends of PBT/PET with glass fibre reinforcements are used in computer and other appliances.

POM-elastomer blends are used for low temperature impact strength property and POM with PBT/TPU are used for

automotive and electronic industries. Quite often they are reinforced with particulate as well as fibrous fillers. In 1980, Union carbide, USA introduced blends of ABS with Polysulfone (PSO) which improved the processability and the blends imparted good hot water resistant property.

In 1981, blends of (polypropylene ether) (PPE) copolymer and PS were introduced by Borg Warner for low temperature impact strength. It is also reinforced with glass fibres. They are used for equipment housing, office equipment and in electronics. They possess good processability, excellent impact strength and can be used continuously at a temperature of 100°C. PPE/PS blends were found to be miscible due to specific interaction. Densification and increased blend viscosity above the log-normal additivity rule evidences this. It improves flame resistance and solvent resistant properties too.

Monsanto Chemical Co. in 1981 introduced blends of poly(styrene-co-maleicanhydride) (SMA) with ABS and Arco Chemical Co. introduced blends of SMA with polycarbonate (PC). The former blend improved moldability and paintability, whereas the later blend is transparent and is used in food contact applications. In 1982, Dupont introduced Selar, a modified and compatibilised amorphous polyamide to be used as an additive to polyolefins. It reduced the permeability of

polyolefins. PA-6, 12/Elastomer and PA-66/Elastomer blends found applications in automotive and recreational apparatus (sports) when reinforced with 15 – 50% of glass fibres, its stiffness and impact resistant property increased. PA-6, 6/inomer blends are used in low temperature, impact strength, tubing and in cables. They improve moldability PA-6, 12/inomer blend is used for low water absorption also. In 1983, blends of PPE and PA by General Electric Co. started a new family of high performance blends called Noryl GTX or Noryl plus. PA:PPE in the ratio of 70:30, with filler reinforcement give rise to composites for auto panels, wheels and fenders. When reinforced with glass fibre, it found applications in automotive parts. PPE/PA blends are also used for high temperature impact resistance and electrical as well as in mechanical components. Quite often they are reinforced with carbon fibres and glass fibres. Blends of PBT/EVA/polymer ether block-amide (PEBA) and PA/PEBA are used for powder coating and in sports goods.

In 1984, Mobay Chemical Corporation developed blends of polyurethane elastomer (TPU) with polycarbonates (PC). It was found to be basically useful in automobile industry and as a thermoplastic rubber. In the same year, Borg Wagner developed blend of poly acrylates (PA) and acrylonitrile-styrene-butadiene (ABS) rubber for automotive body panel as they possess high heat, impact and chemical resistance properties. In 1985,

terblends of PC with ASA i.e., poly (acrylate-co-styrene-co-acrylonitrile) were introduced by General Electric Co. and BASF. These blends are used in automotive and household applications. The coating industry has utilized miscible polymer systems for years to enlarge their market base. Nitrocellulose and cellulose acetate, butyrates were modified with natural products such as shellac and other synthetic polymers e.g. phenolics, poly (vinyl acetate) etc to improve their performance. Specific adhesive formulations based on miscible polymer blend systems have been developed e.g. nitrile rubber formulations with vinylchloride, co - and terpolymers and phenolic resins. For commercial applications weatherable films and poly (methyl methacrylate) – poly (vinylidene fluoride) have been proposed. Poly electrolyte complexes such as poly (vinyl benzyltrimethyl ammonium chloride) and sodium poly (styrene sulfonate) have been utilized for diverse applications such as titrations of macromolecules, battery separators, homodialyzers (artificial kidneys) and as a matrix for slow release of implantable drugs (Nando, 2002).

The commercial importance/development of Polymer blends and alloys is driven by more favourable economics than in the more conventional chemical routes to new products. Blend systems, comprising existing materials, can be developed about twice as rapidly as new polymers, allowing manufacturers to respond

more rapidly at reduced cost, to new market requirement. Since the properties of an existing blend system are functions of composition, an existing blend can be easily and quickly modified to meet performance and cost objectives required by new or changing markets. Discounting research and development cost, new blend systems are particularly attractive when one of the compounds is much less expensive than the others because this allows the blend to be procured at a lower cost than that of the higher costing ingredient. Blends can also be commercially rewarding, even though the ingredients are comparably valued, if the blend offers improvements in processibility, performance and find some special application. Polymer blends are required to share the common goal of reducing the weight and dimensions of the moulded articles, of achieving multi-functionality and greater design freedom, better performance and improving cost efficiency.

New trend of polymer technology has appeared to make products having high resistance to heat, cold and chemicals. For purposes of miniaturization, manufacturers of electronic equipment particularly in the field of data processing, office machine and information technology are particularly interested in good resistance to heat, dimensional stability and excellent electrical properties. Medical technology requires light, reliable and sterilisable equipment. The aeronautics industry requires

low weight, excellent mechanical properties, flame resistance, low smoke density in the event of fires and low toxicity smoke. The increased usage of instrumentation in all branches of industry has led in particular to the increased use of dimensionally stable polymer blends (Banerjee, 2002). The last few years have seen a remarkable increase in both the usage of polymer blend (Hess, 1993) as well as the development of many new types of blends which include elastomeric alloys (Coran, 1980, 1990, 1992) and IPN (Mc Donel, 1978).

1.5 Structure development in polymer blends

It is convenient to classify Polymer blends are either miscible or immiscible. From rheological point of view, the miscible blend can be modeled as either solutions or homologous polymer blends. On the other hand, suspensions, emulsion and block copolymers can be used as models for immiscible blends (Ultracki, 1972).

1.6 Preparation and manufacture of polymer blends

Polymer blends may be manufactured by variety of technique such as (Shaw, 1985 and Eanthos, 1991)

- i. Melt blending
- ii. Solution blending
- iii. Latex or dispersion mixing

Melt blending in intensive mixing extrusion equipment is the predominant commercial method of blend preparation.

1.6.1 Melt blending

In melt mixing, two or more polymers plus any derived fillers, reinforcement and additives are referred by weight into a sheer intensive extruder. The constituents are mixed at elevated temperatures (i.e. above the melting points of the polymer constituents) by extruder screw, which exerts mechanical shearing forces and ensures even distribution and thorough blending of blend elements. The entire process of compound has four stages involving:

- a. Preparation of ingredients (drying, sizing, heating, etc)
- b. Premixing (dry blending, homogenization, breakage of agglomerates, fluxing etc)
- c. Melt mixing in dispense and distributive fields (usually with degassing) and
- d. Chopping e.g. granulating, peletizing or dicing.

The most frequently used applications are single-screw extruders (usually with preblending stage), two screw extruders, intensive blenders and other machines. The advantages of single screw extruder are its price, wide commercial choice of the type and size; the disadvantage are poor adjustability of the pressure field and residence time and low degree of deformation. The twin

screw extruders do not have this disadvantage. Excellent adjustment of the temperature and flow profiles, short residence time and flexibility can be achieved with them but their price is relatively high. Both extruders with one-screw and twin screws are continuous blenders, which can easily be built into a method with several phases in the case of high volume production. General purpose extruders have been produced recently having high performance mixing heads for single-screw extruders for Polymer blends. The other types of blending appliances for Polymer blends are batch sigma or internal blenders. Their advantage is uniform shear and deformation. Their disadvantage are price, low productivity, long blending cycle and low reproductivity of certain phases of production. Melt blending has several advantages over solution blending and latex mixing. A liquid blending or dispersion agent is eliminated thus reducing cost associated with solvent removal, recovery and losses. Additionally by combining only those elements desired in the final mixture, melt blending reduces the likelihood of contamination in the blend. The use of elevated temperatures in melt blending however, poses the possibility of considerable cross linking or grafting of the polymers. Further polymer degradation caused by chain scission can result in color shifts and poor mechanical properties if processing temperatures are not carefully controlled.

1.6.2 Casting from common solvent

Casting of blend from common solvent is the simplest mixing method available and is practiced widely. Very small quantities of Polymers can be handled easily. If pure solvent and clear glass wares are used, contamination can be precluded. As temperatures never exceed ambient so degradation is not a problem. Contaminations of the blend with residual solvent and potential for phase separation or selective precipitation are hazards for this preparation method.

1.6.3 Latex or dispersion mixing

This uses coagulation to give an intimate blend mixture. Films can also be cast. Mixing requires no extensive equipment, no high temperatures are required. Dispersion mixing is followed with melt mixing (or compounding) to produce polymer stands for pelletizing.

1.6.4 Compounding and mixing processes

Mixing and compounding are terms used interchangeably by different authors. Compounding is a major processing operation in fabricating plastics and their products. It is essentially simple mixing in which particles of two or more components are rearranged into a more random distribution without reducing the ultimate particle size (Mascia, 1974). The purpose of mixing in polymer processing is to attain an acceptable degree of

homogeneity or uniformity of composition, (Holmes-Walker, 1975). According to reports, optimum results in mixing can be obtained when the mixing parameters, for example, time of mixing, temperature and speed are taken into account during speed mixing, (Titow, 1984). The expected degree of mixing is in most cases identified by visual appearance of the mix and the homogeneity of the product after subsequent processing. Several types of machines such as roll mills, high-speed mixers, extruders and others are used in mixing. Each method of mixing imposes its own pattern and degree of severity on the matrix materials and additives. The conventional warring blender will be used in this study for compounding the blends.

1.6.5 Uses of polymer blends

Polymers blend is used to increase ductility and toughness of brittle polymers or to increase the stiffness of rubbery polymers and can be quickly and easily modified to meet performance and cost, objective required by new and changing markets.

1.6.6 Basic thermodynamics

Equilibrium – phase behavior of mixtures is governed by the Gibbs free energy of mixing,

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \quad (1)$$

ΔH_{mix} = Enthalpy of mixing, ΔS_{mix} = Entropy of mixing and T is the temperature.

Depending on how ΔS and ΔH are affected by composition and temperature (T) for miscibility, ΔG_{mix} must be negative and satisfy the additional requirement:

$$\left(\frac{\delta^2 \Delta G_{\text{mix}}}{\delta \phi_i^2} \right)_{T,P} > 0 \quad - \quad - \quad - \quad - \quad - \quad (2)$$

In order to ensure stability against phase segregation (P = pressure), the volume fraction ϕ of component i is employed.

1.6.6(i) Flory – Huggins' Theory

The thermodynamic treatment of phase behaviour of mixtures becomes more useful when specific models for the enthalpic and entropic terms are used. The example of such model, which introduces the most important elements needed for polymer blends is that developed by Flory and Huggins originally for the treatment of polymer solutions (Flory, 1953). It assumes that only contribution to the entropy of mixing is combinatorial in origin and approximated by:

$$\Delta S_{\text{mix}} = -R(V_A - V_B) \left(\frac{\phi_A}{V_A} \ln \phi_A + \frac{\phi_B}{V_B} \ln \phi_B \right) \quad - \quad - \quad (3)$$

ϕ_i refers to the volume fraction (i) in the mixture and \bar{V}_i is the molar volume of i, which is related to molecular weight and density. For simplicity each component is assumed to be monodispersed, as more complex expressions result when polydispersity is considered. The Flory - Huggins treatment assumes that the heat of mixing follows a Van-Laar type relation.

$$\Delta H_{\text{mix}} = (V_A + V_B)B \phi_A \phi_B \quad (4)$$

B is the interaction energy for mixing segments of the two components and it is expressed as χ - parameters (Schrer and Chinai 1955), where R is the gas constant.

$$B/RT = \frac{\chi_A}{V_A} = \frac{\chi_B}{V_B} = \chi_{AB} \quad (5)$$

Where χ_A is the interaction parameter of polymer A, χ_B is the interaction parameter of polymer B and χ_{AB} is the interaction parameter of polymer blend AB.

Application of the thermodynamic requirement for phase stability to this model reveals that miscibility of two polymers occurs only when B is less than a critical value given by equation (6)

$$B_c = \frac{RT}{2} \left[\left(\frac{\rho_A}{M_A} + \frac{\rho_B}{M_B} \right)^{1/2} \right]^2 \quad (6)$$

ρ_A and ρ_B are densities of A and B, and M_A and M_B molecular weights of A and B and R is the gas constant, T , the temperature.

Some important conclusion can be learned from this simple model. First, it shows that ΔH_{mix} does not depend on polymer molecular weight, whereas ΔS_{mix} does. Endothermic mixing, where $B > 0$, does not favour miscibility. Thus, forming a homogeneous mixture requires that molecular weights must be low enough that the favourable entropic contribution offsets the unfavourable enthalpic effect. For exothermic mixing, where $B < 0$, this theory predicts that the condition for miscibility will be satisfied no matter how large the molecular weights are. Thus, miscibility of high molecular weight polymers is only assured when mixing is exothermic. When the interaction energy density is positive, the polymer blend phase diagram is not predicted by this simple theory, unless B is temperature-dependent, in which case basic thermodynamic relations reveal that this quantity is not strictly an enthalpic parameter as defined in equation (6).

1.7 Polystyrene

Polystyrene is brittle, rigid, transparent, easy to process (shrinkage is low), free from odour and taste. It is thermally stable, with excellent electrical properties. All these properties are responsible for the commercial success of polystyrene.

Polystyrene is sometimes referred to as crystal Polystyrene, these refers to the clarity of the finished product and does not imply that the molecular structure responsible for many of the good properties of polystyrene such as clarity of products, the low energy input required for processing and ease of processing with low shrinkage.

1.7.1. Properties of polystyrene

i. General

Polystyrene is an amorphous thermoplastic with a density of 1.05 g/cm^3 with an extremely low moisture absorption (0.05%). Styrene polymers have some unique properties which makes them useful in a wide range of products. The single most important characteristic of general purpose polystyrene is that it is a glass like solid below 100°C . Above this temperature, commonly called the glass – transition temperature, the polymer chain (on a molecular level) has rotational freedom which allows large – chain – segment mobility. The polymer is thus fluid enough to be easily shaped into useful forms. Below the glass transition temperature, polystyrene possesses considerable mechanical strength, allowing it to be used in load bearing tasks in thousands of applications.

Rubber – modified polystyrene is a two phase system consisting of a dispersed rubber phase and a continuous polystyrene phase. This system uses a unique feature of polystyrene –

elongation by the formation of energy absorbing crazes. The dispersed rubber particles initiated large numbers of crazes without crack formation, thus contributing to the development of very tough products. In addition to toughening, the rubber particles also increase the environmental stress – crack resistance because the microscopic rubber particles are placed in tension as they are cooled after fabrication, compressing the rigid phase. The particles try to shrink more than the rigid phase because rubber has a greater coefficient of expansion than polystyrene. Modern micrographic and analytical tools have been developed to measure and predict the complex interactions of these two – phase systems.

Styrene readily copolymerizes with a variety of other monomers. The first well known copolymer was styrene – butadiene synthetic rubber. Other significant copolymers include tough, solvent – resistant copolymers with acrylonitrile; heat, resistant polymers with maleic anhydride; and rubber – modified, transparent systems with methyl methacrylate. Although there have been many studies concerning, multiple (more than two) comonomers, few significant commercial products exist.

Since styrene polymers are non polar, chemically inert, resistant to water, and easy to fabricate, they are the products of choice for electronic, medical, food packaging, appliance and

automotive applications. Recent manufacturing trends provide improved processability and further decrease trace impurities. High – speed, efficient fabrication equipment is both reducing the cost of manufacturing and increasing the strength of the fabricated parts.

Polystyrene molecules can be oriented during fabrication. Modern processing equipment uses controlled orientation to produce tougher fabricated parts. Tensile strengths may double and elongation may increase by up to two orders of magnitude, resulting in tremendous increases in toughness. Toughening by orientation contributes to the success of polystyrene foam, now widely used in both insulation and as foam sheet in food packaging, and to the success of clear, thermoformed, biaxially oriented polystyrene. Pure polystyrene does not absorb ultra violet light in the terrestrial sunlight spectrum and would apparently have better ultraviolet stability if it were not for the presence of ultraviolet absorbing trace impurities. The presence of rubber tends to decrease the out door stability; this is countered by incorporating special rubbers and stabilizers. Anionic polymerization produces a more thermally stable polymer which can be made even more stable by proper selection of the end group, because most degradation begins at chain ends. Because of the commercial interest in polystyrene, its polymerization ease, and its relatively simple linear

structure, polystyrene is one of the most thoroughly investigated polymer systems in the world. (Mark, Bikales, Overberger and Menges, 1989).

ii. Mechanical Properties

Polystyrene is hard, stiff and dimensionally stable but relatively inextensible material with a high tensile strength and low elongation at break. The mechanical strength is affected to a large degree by the processing conditions. The highest value can be obtained with free flowing materials at a low processing temperature.

Table 1: Some mechanical properties of Polystyrene and their values

Property	Approximate value
Tensile strength	55 – 80NM/m ²
Tensile modulus	3-4 GN/m ²
Elongation of break	<10%
Flexural strength	50-100MN/m ²
Notched impact strength	50 – 100MN/m ²
Specific heat	<3KJ/m ²
Glass transition temperature	100°C
Compressibility	220 x 10 ⁶ MPa ⁻¹
Transparency	Transparent
Mould shrinkage	0.001 – 0.005m/m
Melting temperature	240°C

Source: (Kirk-Othmer, 1996)

iii. Chemical resistance

Polystyrene has good chemical resistance. It is resistant to alkalis, dilute mineral acids, water and aqueous solution.

iv. Resistance to stress cracking

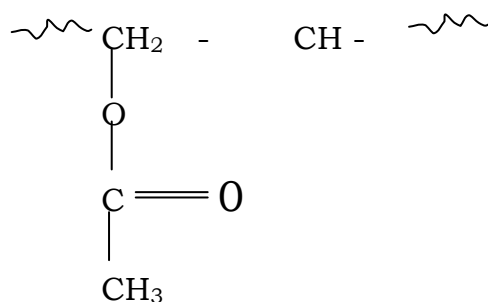
Polystyrene is susceptible to stress cracking parts with internal stresses can form stress cracks even in the resistant. It is therefore advisable to produce injection-moulded parts with a few internal stresses as possible.

v. Advantages and limitations

Polystyrene has good chemical properties, low cost, easy to process, low shrinkage, however, it has limitations, which include negligible mechanical properties above 70°C, brittle at room temperature and degrade rapidly in outdoor use due to ultraviolet light.

1.7.2 Polyvinylacetate (PVAc)

Poly (vinyl acetate) is an amorphous, thermoplastic Polymer



Some of the properties of polyvinyl acetate are reproduced below

Table 2 Physical Constants for Poly (Vinyl acetate)

Property	Value
Absorption of water at 20°C for 24 – 144h,	3-6
% coefficient of thermal expansion, K ⁻¹ cubic cm ³	6.7 x 10 ⁻⁴
Linear, below T _g	7 x 10 ⁻⁵
Linear, Above T _g	22 x 10 ⁻⁵
Cohesive energy density, (MJ/m ³) ^{1/2a}	18.6 – 19.09
Compressibility, cm ³ /(g.kPa) ^b	17.8 x 10 ⁻⁶
Decomposition temperature, °C	150
Density, g/cm ³	
At 20°C	1.191
25°C	1.19
50°C	1.17
120°C	1.11
200°C	1.05
Dielectric constant at 2 MHz	
At 50°C	3.5
120°	8.3
Dielectric dissipation factor, at 2 MHz, tan δ	
At 50°C	150
120°C	260
Dielectric strength, V/L	
At 30°C	0.394
6°C	0.307
Dipole moment, C.m ^c per monomer unit	
At 20°C	2.30
150°C	1.77
Dynamic mechanical loss peak at 100Hz, °C	70
Elongation at break, at 20°C and 0% rh, %	10 – 20
Glass-transition temperature, T _g , °C	28 – 31
Pressure dependence, °C/100 MPa ^d	0.22
Hardness, at 20°C, Shore units	80 – 85
Heat capacity, at 30°C, J/g ^a	1.465
Heat distortion point, °C	50
Heat of polymerization, Kj/mol ^a	87.5
Refraction index, n _D	
At 20.7°C	1.4669
30.8°C	1.4657
52.1°C	1.4600
80°C	1.4800
142°C	
Interfacial tension, mN/m (=dyn/cm)	
At 20°C with polyethylene	14.5
20°C with polydimethylsiloxane	8.4
20°C with polyisobutylene	9.9
20°C with polystyrene	4.2
Internal pressure, MJ/m ^{3a}	
At 0°C	255
28°C	397.8
60°C	418.7
20°C	284.7
40°C	431.3

Source: (Schrer , 1955; Daoust , 1952; Managaraj , 1965, Gardon, 1965 and Burell, 1970), (VanHelden, 1968, Petroleum Refiner, 1959 and Volger, 1968)

Poly(vinyl acetate) (PVAc) polymer resins are manufactured in a variety of molecular weights.

With increasing molecular weight, properties vary from viscous liquids to low melting solids to tough, horny materials. They are neutral, water-white to straw-coloured, tasteless, odourless, and non-toxic. The resins have no sharply defined melting points but become softer with increasing temperature. Due to their solubility parameter, they are soluble in organic solvents, e.g. esters, Ketones, aromatics, halogenated hydrocarbons, carboxylic acids etc, but are insoluble in the lower alcohols (excluding methanol) glycols, water, and non polar liquids such as ether, carbon disulfide, aliphatic hydro carbons, oils, and fats. Alcohols, e.g., ethyl, propyl, and butyl, containing 5-10w% water dissolve PVAc; butyl alcohol and xylene, both of which only swell the polymer at normal temperatures, dissolve it when heated. The electrical properties are strongly affected by the ability of poly (vinylacetate) to absorb water. Whereas dried resin has a dielectric constant ϵ^1 of $0.08+0.02$ at 35°C and 60Hz, after exposure to 100% relative humidity the number become 10 and 0.7, respectively (Mead , 1941 and Morgan , 1940).

As with many thermoplastic resins, strength properties increase with molecular weight, tensile strengths up to 50.3MPa (730psi) may be obtained. The softening point, as determined by the

ring-and-ball method or by the Kraemer and Sarnow method, also increases with molecular weight (Fikentscher, 1932 and Kraemer, 1938) Poly(vinyl acetate) resin is commercially available in pure, dry form as beads, granules, or lumps and is graded according to viscosity at 20°C of a 1M solution in benzene (86.09g or one mole of repeating units of the resin delivered in benzene to make a liter). On cooling below room temperature, poly(vinyl acetate) become brittle. The brittle point may be lowered by plasticization or copolymerization. When heated above room temperature and above the polymer glass - transition temperature (30°C), all viscosity, grades become very flexible and at 50°C become limp.

The glass-transition temperature of PVAc is depressed by the incorporation of moisture causing the polymer to be more flexible under humid conditions.

Poly(vinyl acetate) can be heated at 125°C for hours without changing, but at 150°C it gradually darkens, and at over 225°C it liberates acetic acid forming a brown insoluble resin which carbonizes at a much higher temperature. The products of thermal decomposition of PVAc are at 150 – 200°C acetic acid, and at 300 – 350°C aromatic compounds, i.e., benzene, toluene, naphthalene, etc (Ballisteri, 1980). PVAc resists oxidation and degradation by UV and VIS radiation, therefore its aging qualities are excellent.

The NMR spectrum of PVAc in carbon tetrachloride solution at 110°C shows absorption at 4.86 δ (pentad) of the methine proton; 1.78 δ (triad) of the methylene groups; and 1.986 δ , 1.96 δ and 1.94 δ , which are the resonances of the acetate methyls in isotactic, heterotactic, and syndiotactic triads, respectively. Poly (vinyl acetate) produced by normal free-radical polymerization is completely atactic and non crystalline. The NMR spectra of ethylene vinyl acetate copolymers have also been obtained (Okada, 1977). The IR spectra of the copolymers of vinylacetate differ from that of the homopolymer depending on the identity of the comonomers and their proportions.

The chemical properties of PVAc are those of an aliphatic ester. Thus, acidic or basic hydrolysis produces poly(vinyl alcohol) and acetic acid or the acetate of the basic cation. Industrially, poly(vinyl alcohol) is produced by a base catalysed ester interchange with methanol, where methyl acetate forms in addition to the polymeric product. The chemical properties of PVAc can be modified by copolymerization. When a comonomer having a carboxylic acid or sulfuric acid group is used, the copolymer becomes soluble in dilute aqueous alkali or ammonia. These copolymer becomes soluble in dilute aqueous alkali or ammonia. These copolymers also adhere better to metals than homopolymers or neutral copolymers because of

the interaction between the acid groups and the metal surface. Copolymerisation with monomers such as butyl acrylate can improve flexibility and provide specific adhesion to surface (Kirk Othmer, 1997).

The mechanical properties of poly(vinyl acetate) depend on the molecular weight (Burrell, 1970). Poly(vinyl acetate) is elastic and its mechanical properties can be varied with the control of molecular weight.

1.8 Blend formulations and processing

The formulation of polymer blends has been an active area research for the past three decades owing to the enhancement in the physical and mechanical properties of the blends achieved via synergism (Ultracki, 1988, Walsh, 1985 and Coleman, Graf and Painter, 1991). The physical as well as chemical properties of the blend depend on the degree of miscibility of the blend components. Although even immiscible or partially miscible blends have found commercial applications, the complete miscibility of the components in the blend is desirable because mixing on molecular scale results into superior physical as well as mechanical properties with change in composition (Thakore, Desai, Sawade and Devi, 2001, Thakore, Desai and Devi, 1999, Zaccaria and Ultracki, 2003). A variety of experimental techniques are

used to prepare and characterize polymer blends (Olabisi, Robeson and Shaw, 1979; Macknight, Karasz and Fried, 1978, and Paul, 1985). Some of more important ones are briefly reviewed here, with particular emphasis on those dealing with establishing the equilibrium phase behaviour and the energetic interactions between chain segments responsible for miscibility. This information is necessary for the development of the role of molecular structure in segmental interactions.

1.8.1 Mixing

Mixing in the melt state is often the method of choice for the preparation of polymer blends. It offers the advantage of this reason and also because of the speed and simplicity of melt mixing; it has primary commercial blending method. By using proper equipment, it is possible to obtain excellent dispersion of the components. Temperature, time and environment for the mixing can be carefully controlled. The melt components are either batch or continuous type. The former require lower investment cost, are more labour-intensive, have low output and poor batch-to-batch reproducibility. Some of these traditional disadvantage are mitigated by the recent development in process control and autoimmunization. Two-roll mills, interval and kinetic energy mixers are the batch mixers. The two-roll mill has an open construction allowing for observation of the mixing process. Since the gap can be adjusted during mixing, the stresses can be tailored to the variable processing

conditions. Modern mills can be programmed to perform automatically. Internal mixers, like two-roll mills, were originally developed for the rubber industry. Today, they find use in mixing not only rubbers but also a diversity of plastics formulations, blends, master-batches, and filled/reinforced system. Some of internal mixers are also fully automatic.

The continuous mixers require high capital investment but are easily robotizable. They can provide high output with good reproducibility and can be run with a statistical loop control. To this group belong.

1. Twin-shaft continuous mixers
2. Single-screw extruders
3. Twin-screw extruders
4. Specialty mixers

The twin-shaft continuous mixers or continuous internal mixer combines high intensity mixing with continuous operation. The unit provides solid conveying, melting and mixing function. The material is continuously pumped from one total chamber to another. The maximum stress, randomization and total mixing time can be controlled. There are more than thirty types of motionless mixers (or static mixers), which are efficient in blending and homogenizing the molten materials.

The single-screw extruders are a simple, inexpensive distribution and relatively long residence time. Buss Kneader or

Barmag extruders and single screw extruders equipped with special mixing screws are the exceptions to rule. The Buss kneader has constant channel depth screw with interrupted flights and three rows of stationary pins in the barrel. During operation, the screw rotates and axially oscillates providing good self-wiping of the blades.

The residence times distribution is relatively broad. It is easy to clean service, analyze and optimize the process in this machine. It is used for blends, PVC formulations, engineering resins, food stuffs, etc. Planetary gear extruder and the FN-plasticizers are the other single screw extruders. In the planetary gear extruder, the planetary spindles provide both the dispersive and distributive mixing. For blends and high performance resins, i.e. planetary extruder that continuously rolls and folds melt into 200 to 300 μ m thin layers was introduced into market recently. Twin-screw extruders are the most popular compounding machines. For large volume production, the twin-screw compounders out-perform the single screw extruders.

1.8.2 Processing of blends

i. Compression Moulding: This process forms the essential part of polymer processing, which is applicable to both thermoplastics and thermosets with the latter forming a larger proportion of articles produced. Products form by this method

includes films, sheets and laminates. Its principle involves heating the blend in a closed mould thereby the resin softens and takes the shape of the mould. Temperature, pressure and time will depend on the nature of the material, size and shape of the mould, Holmes- Walker (1975).

1.8.3 Test methods

i. Solvent Sorption Measurement: Solvent sorption is one of most widely used techniques in characterizing structural changes in polymers. According to Gray and Gilbert (1975), the rate of solvent absorbed at equilibrium all depend on the type of polymer and its thermal or shear history. Illers (1977), reported that in semi crystalline polymers, solvent sorption behaviour is directly proportional to the amount of crystallinity and the available free volume in a polymer. Measurements of the equilibrium sorption of vapours or of gases in miscible blends can, in principle, give information about the interaction energy parameter. The rate of sorption of a liquid by a resin following Fick's diffusion law is given by the well-known equation, Vergaud (1991),

$$\frac{M_t}{M_\infty} = \frac{m_t - m_0}{m_\infty - m_0}$$

$$= 1 - \frac{8}{\pi^2} \sum_{i=0}^{\infty} (1/2i + 1)^2 \exp [-(2i+1)^2 \pi^2 D_s t / L^2] \text{----- (7)}$$

M_t is the accumulate mass of the diffusing liquid at time t , M_∞ the mass of the sorbed liquid at equilibrium (after infinite time), m_0 , the mass of the dry disc, m_t , the mass of the disc at time t , m_∞ , the mass of the specimen at equilibrium, L , the thickness of the disc, and D_s , the diffusion coefficient of the liquid during the sorption process.

Analogous to the Fickian sorption, the Fickian desorption of a liquid can be expressed by the following equation.

$$\frac{M_t}{M_\infty} = \frac{m_t - m_0}{m_\infty - m_0} = 1 - \frac{8}{\pi^2} \sum_{i=0}^{\infty} (1/2i + 1)^2 \exp(-(2i+1)^2 \pi^2 D_d t / L^2) \text{----- (8)}$$

Here D_d is the diffusion coefficient of the liquid during the desorption process, m_0 , the mass of the disc saturated with liquid, while m_∞ is the equilibrium mass of the disc at the end of the desorption.

The diffusion coefficient of a liquid during its sorption or desorption process can be determined by means of an interactive method developed by Sideridon, Karabela, Vonvondi and Papanstasiou, (2008). The basic principles of this method are described below.

In the case of the sorption of a liquid, equation (7) can be rewritten as

$$M_t = m_\infty - \frac{8}{\pi^2} (m_\infty - m_0) \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp \left[-\frac{(2i+1)^2 \pi^2 D_s t}{L^2} \right]$$

This is an equation of the form

$$M_t = a - b \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp \left[-\frac{(2i+1)^2 ct}{L^2} \right] \quad \text{-----} \quad (9)$$

$$\begin{aligned} M_t &= a - b \left(\frac{8}{\pi^2} \right) \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp \left[-\frac{(2i+1)^2 ct}{L^2} \right] \\ &= a - b \left(\frac{8}{\pi^2} \right) \left(\exp(-ct) + \frac{1}{9} \exp(-9ct) + \frac{1}{25} \exp(-25ct) + \dots \right) \text{-----} (10) \end{aligned}$$

Where

$$\begin{aligned} a &= m_\infty \\ b &= \frac{M_\infty - m_0}{m_\infty - m_0} \text{-----} (11) \\ C &= \pi^2 D_s / L^2 \end{aligned}$$

In the case of desorption of the liquid equation (8) can be rewritten as

$$M_t = m_\infty - \frac{8}{\pi^2} (m_\infty - m_0) \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp \left[-\frac{(2i+1)^2 \pi^2 D_d t}{L^2} \right] \text{-----} (12)$$

Namely

$$\begin{aligned} m_t &= a + b \left(\frac{8}{\pi^2} \right) \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp \left[-(2i+1)^2 ct \right] \\ &= a + b \left(\frac{8}{\pi^2} \right) \left(\exp(-ct) + \frac{1}{9} \exp(-9ct) + \frac{1}{25} \exp(-25ct) + \dots \right) \text{-----} (13) \end{aligned}$$

Where

$$\begin{aligned}
 a &= m_{\infty} \\
 b &= m_0 - m_{\infty} \\
 c &= \frac{\pi^2 D_d}{L^2} \text{-----} (14)
 \end{aligned}$$

The parameters a, b and c of equations (10) and (13) can be determined by fitting the appropriate experimental plots $m_t = f(t)$ to equations (10) and (13). Then, m_{∞} , m_0 and D can be calculated by means of equation (11) and (14). In this treatment, a non linear curve fitting technique, based on the so-called Lavenberg-Marquardt algorithm, Levenberg (1944) and Marquardt (1963) was used. The algorithm starts with the initial guesses for the unknown parameters (a, b, and c) that are supplied by equation (10) and (13) and it calculates the sum of the squared deviation between the original data and the calculated fit. The algorithm then varies the values of the parameters slightly and re-evaluates the sum of the squared deviation until it finds the best fit. The sums of the infinite series of equations (8) and (12) were approximated by a partial sum including l terms so that

$$\sum_{i=0}^{\infty} (1/2i + 1) \exp(-(2i+1)^2 \pi^2 D_t / L^2) - \sum_{i=0}^{l-1} (1/2i + 1)^2 \exp(-(2i+1)^2 \pi^2 D_t / L^2) < 10^{-16} \text{-----} (15)$$

where l takes values from a, b and c elements and i is an integer, $l \geq \lambda$ for $i = 1$ (λ is a numerical coefficient)

It should be noted that this iterative method was applied to simulated as well as to experimental values of sorption data

with known values of the parameters a, b, and c. With the values of m_{∞} and m_0 for the sorption and desorption process,, the following thermodynamic parameters concerning the equilibrium state can be calculated:

$$\begin{aligned} \text{WS\%} &= \frac{100(m_{\infty}(\text{s}) - m_0(\text{s}))}{m_0(\text{s})} \\ \text{WS\%} &= \frac{100(m_{\infty}(\text{D}) - m_0(\text{D}))}{m_0(\text{D})} \text{-----(16)} \end{aligned}$$

Where WS% is the percentage of the sorbed liquid during sorption process, WP% is the percentage of the desorped liquid during the desorption process and SL% is the extracted amount of monomer known as “solubility” of the resin as the liquid under consideration.

ii. Density Measurement

According to reports, three techniques are widely used to measure densities of polymer sample these include density gradient column, dilatometry and pycnometry, Tager (1978). Density gradient column is probably the most convenient way of estimating the degree of crystallinity in semi crystalline polymers. In this method, density is determined by matching the buoyancy of the unknown solid and the surrounding liquid so that the solid floats freely for an extended length of time. The gradient is determined, by calibration, which are accurate to $\pm 0.0002\text{g/cm}^3$ at a fixed temperature. According to experimental

values, densities of melt crystallized polymers of semi-crystallised polymers are based on two phase systems (crystalline and amorphous) and each phase may be characterized by a unique density, [Sheldon (1963) and Wunderlich (1973)]. It can be shown that, the weight fraction crystallinity, x can be expressed as a function of the density through the following derivations.

$$m = m_c + m_a \text{ ----- (17)}$$

Here m is the mass of a polymer and m_c and m_a are the masses of the crystalline and amorphous regions, respectively; but $M_t = C_0 (D/V + V_t)$ (Gilbert and Mulla, 1983) where

$$C_0 = M_\infty/V_0 \text{ -----(18)}$$

Where M_t = mass of solvent absorbed per unit area of sample at time t (s) and M_∞ is mass of solvent absorbed at equilibrium, D is the average diffusion coefficient, V is the velocity of the solvent from and V_0 is the initial volume of the immersed sample, by substitution equation (18) becomes

$$d_v = d_c V_c + d_a V_a \text{ ----- (19)}$$

where d and V terms refer to the densities and volumes of the relevant regions. By definition, the volume fraction crystallinity, X_v is V_c/V and when substituted in equation (18), the following equation is obtained

$$d_v = d_c V X_v + d_a V (1 - X_v) \text{ -----=----- (20)}$$

$$X_v = \frac{d - d_a}{d_c - d_a} \text{ ----- (21)}$$

Similarly, the weight fraction crystallinity can be expressed as:

$$X_m = \frac{V - V_a}{V_c - V_a} \text{-----} \quad (22)$$

The density of the processed sample alone is obtained by correlating the measured density with the densities of additives using the relationship:

$$d_c = \frac{100 + \frac{\sum l_i}{d_i}}{100/d_c^1 + \sum l_i/d_i} \quad (23)$$

Here d_c is the measured density, l_i 's are additive weight fractions in parts per hundred (Phr), the d_i 's are densities of additives, d_c^1 is the actual density of the processed sample.

iii. X-ray analysis: X-ray analysis is widely used to study the internal arrangement of polymer molecules and the changes that occur on the Polymer structure due to heat effects and mechanical effects, Clark (1963) and Tager (1978). According to Billmeyer (1973) and Edward (1973). X-ray analysis of crystalline polymers have revealed the presence of both ordered and disordered regions which are manifested in the form of sharp and diffused features. Various x-ray techniques are employed in the study of processed samples; these include wide-angle x-ray diffraction (WAXD), small-angle x-ray diffraction (SAXD) and small-angle x-ray scattering (SAXS) each covering different Bragg angle, (Clark (1961) and Carrega (1977)). According to Alexander (1967), crystalline fraction, X , of polymer

sample can be determined from the separate intensities due to crystalline scattering, I_c and amorphous scattering, I_a , thus:

$$X = \frac{I_c}{I_a - I_c} \text{-----} (24)$$

Ruland (1961), presented a simplified method for quantitative analysis of the x-ray diffraction trace to obtain the crystalline fraction as:

$$X = \frac{I_c}{I_a + KI_c} \text{-----} (25)$$

The scattering intensity of the choosing crystalline reflections occurs at a different angular distribution than the amorphous region, since K is a correction factor.

iv. Tensile measurement

Tensile testing instruments are widely used to study the mechanical properties of the plastic material. These properties which include, tensile stress, % elongation and Young's modulus all depend on the basic properties of the polymer chain molecule and other factors such as processing and environmental conditions. Mechanical properties of polymer blends normally determine its applicability. Nelson (1974) reported that the response of a polymer to applied stresses would depend upon its gross morphology and molecular behaviour. One of the most accessible way of determining mechanical properties of polymeric materials is by the stress-

strain curve experiment and Instron Tensile Tester is the most common instrument being used (Martin (1965), Billmeyer (1971) and Edward (1973)). Tensile stress and % elongation are calculated using the following equations.

$$\text{Tensile stress} = \frac{\text{maximum breaking load (N)}}{\text{Original cross-sectional area of test sample (m}^2\text{)}} \quad \text{--(26)}$$

$$\% \text{ elongation} = \frac{\text{Chart extension}}{\text{Guage length}} \times \frac{\text{chart to cross head}}{\text{speed ratio}} \times 100 \quad \text{--}$$

(27)

The Young's modulus (E) is the tangent over which the stress-strain curve is constant. It is a measure of the intrinsic stiffness of the polymer material.

1.9 Fillers as additive in polymer blends

A wide variety of particulate fillers such as carbon black, silica and calcium carbonate are used intensively in the rubber / polymer industry to improve and modify the physical properties of polymer materials (Bakobza, and Rapoport, 2002). The addition of filler usually leads to increase in abrasion and tear resistance. Essentially two classes of particulate fillers have been found to offer significant reinforcing, effects: Carbon black and high – structured silica (Leblance, 2002). Carbon black can be incorporated as reinforcement filler in NR/LLD PE blends (Ahmad , Mohd and Abdullah, 2002). Carbon black has a unique ability to enhance the physical properties of elastomers

(Donnet, Bansal and Wang, 1993). This well documented phenomenon (Donnet and Voet, 1976 and Kraus, 1965) termed as “reinforcement”, has a profound effect on the current tyre and rubber industries. However, carbon black is used in plastics to alter the key physical properties of compound, which determines application in given market segment (Donnet, 2002). Carbon black reinforcement had become a subject of scientific interest as early as in the 1940s. Silica reinforcement started to be considered in the 1980s when the benefits of surface treatment with silanes was recognized, with the need for lower rolling resistance tyre, being an important driving force in recent research efforts. The interaction between carbon black and elastomer occurs spontaneously but in the case of silica, it is chemically modified (Lablance, 2002).

The effects of carbon black filler loading on the mechanical properties of polymer blends were widely reported in the literature (Banik, 2000 and Katbab, 2000). However, there is no study reported on the additive effects of polystyrene/ polyvinyl acetate blends in the presence of α – cellulose filler.

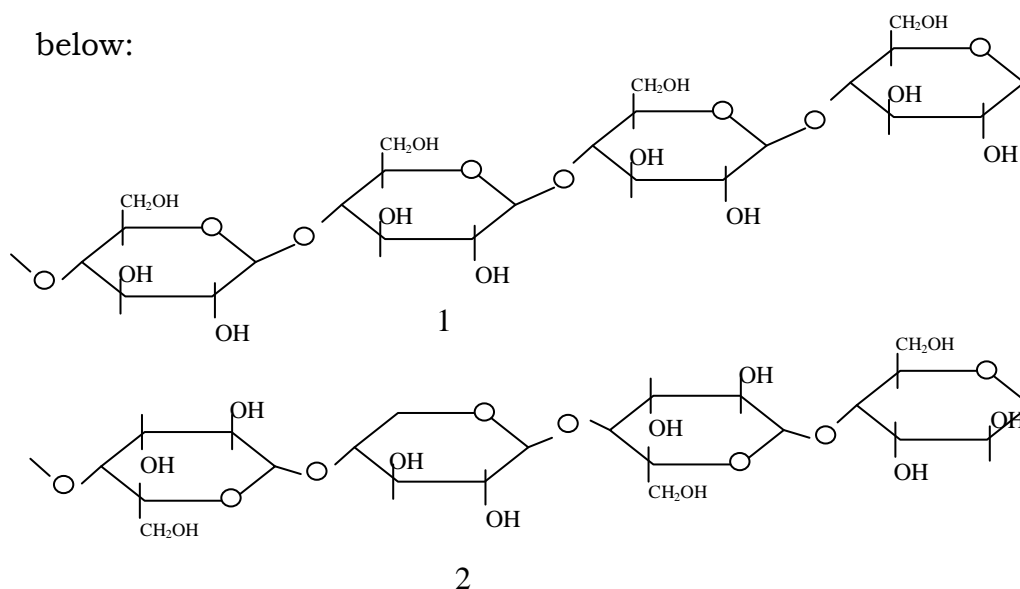
1.9.1 α (alpha) -Cellulose as a filler in polymer cellulose, structure and properties

Cellulose, the principal polysaccharide in plant cell walls, was named by Payen (Payen, 1838) who first recognized the isomerism of cellulose and starch. Early workers in the cellulose

field included Nageli, who promulgated the middle structure of cellulose, Mercer, who used alkali to heat cellulose before chemical reaction (Mercerization), and Schweizer, who developed the processes leading to the establishment of the rayon industry (Mark, Bikales, Overberger and Merges, 1989).

Representation and terminology

In a strict scientific sense, the term cellulose applies only to the β (Beta)-(1 \rightarrow 4) D-glucan isolated from plant cell walls. This material has a structure that may be represented by (1) or (2) below:



Although (2) more nearly represents the actual three-dimensional structures of cellulose, i.e. every other D-glycosyl residue rotated 180⁰, structure (1) is more commonly used to represent this polymer. Material described as cellulose typically also includes smaller amounts of hemicelluloses and lignin. Ideally, material designated as cellulose should be identified by source and physicochemical treatments received (Wise, 1952)

Pure cellulose, also known as α -cellulose (Ranby, 1952) is soluble in 17.5% NaOH, β -cellulose and γ (gamma) -cellulose are not true cellulose. β - cellulose, believed to be degraded low degree of polymerization α -cellulose (Ranby, 1952) is soluble in 17.5% NaOH, but precipitates upon acidification. γ -cellulose is completely soluble at any pH and is thought to be the hemicellulose, i.e. xylans, mannans, galactans, etc.

1.10 Blend morphology

In many instances, phase - separated blends are the preferred means of achieving useful results. For example, such a polymer - polymer composites yield materials whose stiffness can be adjusted, in principle, to any value between those of the component polymers. However, tailoring blends to achieve this or any other characteristics requires, among other things, control over the spatial arrangement or morphology of the phases, and some degree of stability once they are formed. These arrangements may consist of one phase dispensed as simple spheres in a matrix of the other polymer. On the other hand, the dispersed phase may take the form of platelets or fibrils with varying aspect ratios. Another distinct morphology consists of both phases simultaneously having a continuous character (Paul, 1978) or an interpenetrating network of phases (Gergen, Davision and Lutz, 1986). The typical dimension of the phases are important in all these morphologies.

1.10.1 Morphology generation and control

Homogenous mixtures of two polymers may phase – separate upon a change in the temperature or removal of the solvent (Mc Master, 1975, Kwei and Wang, 1978, Degennes, 1980, Hashimoto, Kumaki and Kawai, 1983, 1984, Sasaki and Hashimoto , 1984, Strobl, 1985 and Ronca and Russell, 1985). In most commercially significant blends, however, the component polymers are immiscible, and the morphology of the dispersed phase is often generated by either added block and graft copolymer compatibilizers or chemical reactivity of the two principal components. Such blends are typically prepared by extrusion - melt blending.

The morphology generated during mixing depends on the interfacial tension between the phases and the viscosity and elasticity (Paul and Barlow, 1980, Van Oene, 1978, Plochocki, 1978, White, 1982, 1985, Han, 1981 and Nelson , Avgeropoulos, Weissert and Bohm, 1977). The component occupying the most space tends to assume the role of the continuous phase. The size of the dispersed phase is determined by the balance between drop breakup (Elmendorp and Maalike , 1985) and coalescence processes (Roland and Bohm, 1984) which in turn are governed by the deformation field imposed by the mixing device, interfacial tension, and the rheological characteristics of the components. The shape of the dispersed phase may be

deformed from spheres into fibrils by uniaxial elongational flow, e.g. extension through a die or into platelets by biaxial stretching, e.g. blow molding.

The component with the lower viscosity tends to encapsulate the more viscous (or more elastic) component (White, 1985) during mixing, because this reduces the rate of energy dissipation. Thus the viscosities may be used to offset the effect of the proportions of the components to control which phase is continuous (Paul and Barlow, 1980 and Nelson, Avgeropoulos, Weissert and Bohm, 1977). Frequently there is an intermediate situation where a continuous or interpenetrating network of phases can be generated by careful control of composition, microrheology, and processing condition. Rubbery thermoplastic blends have been produced by this route (Kresge, 1978).

The morphology created during processing is a dynamic structure that may be subject to further changes during subsequent processing steps, as can be observed in a number of blends e.g. polyethylene – PS systems (Fayt, 1981, Paul, 1978 and Fayt, Hajiandreou and Teyssie, 1985). In these blends, appropriate polystyrene – containing block copolymers improve the morphology and its stability. Another example relates to the morphology of near – miscible PC – SAN (Matrix of ABS) blends,

but they have poor morphological stability at melt temperatures (Cheng, Keskkula and Paul, 1992).

Compatibilization with appropriate graft or block copolymers or via chemical reactivity during melt blending should give rise to a more stable morphology. Melt blended nylon – 6 – elastomer compositions that are chemically reactive or are compatibilized with a reactive third component are very tough and typically have a more stable phase morphology. Other unique features or morphology development are involved in formulating toughened PVC, PP, PPO and polyesters.

In situ polymerization and the use of the core – shell impact modifiers are additional approaches to forming heterophase blends.

1.10.2 Morphology characterization

Electron microscopy has become one of the most widely used technique for characterizing blend morphology (Shaw, 1985). Scanning electron microscopy (SEM) offers the simplest procedure (White, 1984). Because it only reveals surface features, the internal structure of blends is investigated by viewing fracture surfaces are used at ambient or cryogenic temperatures. At low temperature, yielding is suppressed during the fracture process. Photo micrographs of this type often give

information about the extent of adhesion between phases. To aid the identification of phases and enhance morphological features, one of the phases may be selectively extracted by a solvent, leaving the other phase to be viewed in the microscope. Further by solvent extraction the matrix polymer can be selectively removed in materials such as high impact polystyrene (HIPS) leaving the particulate rubber phase intact for viewing by SEM (Keskkula and Traylor , 1978).

Transmission electron microscopy (TEM) requires viewing thin sections of material. Normally, TEM is not directly useful for polymer blends because of insufficient contrast between most organic polymers in the electron beam, hence, staining methods to enhance contrast are of the used. Osmium tetroxide, O_5O_4 , is a useful stain for rubber – modified polymers (Kato, 1965). The rubber phase, through its unsaturation, reacts with O_5O_4 , whereas the matrix phase does not. This can produce sufficient contrast between them owing to the high electron density of the former phase. The use of O_5O_4 , is primarily limited to polymers with double bonds or other reactive sites. For modified PVC and other saturated polymers, chemical etching methods are utilized, (Keskkula, 1982). Reaction with O_5O_4 , causes hardening, which facilitates microtoming of ultrathin sections for viewing. In addition, this, stain makes the craze structure visible in stress – whitened polymers.

1.11 Property relationships in polymer blends

The relationship between the physical properties of a blend and those of its components can depend on the thermodynamic interaction between the components and many other factors. Some generalizations are possible, but exceptions are common and fundamental understanding for some properties remains incomplete in spite of the central importance of this issue in blend technology (Kirk – Othmer, 1996).

Fully miscible blends generally represent the simplest case. In the absence of crystallinity, most properties follow some additive relationship, miscible blends are similar to random copolymers in this regard. The glass transition temperature, and hence the softening point is generally a monotonic function of composition. As a rule, most mechanical properties, permeation (Logarithmic scale) to small molecules, etc, follow nearly linear relations with composition in such systems, but exceptions are known (Joseph, Lorenz, Barlow and Paul 1982, Yee, 1977, Hopfenberg and Paul , 1978, Maeda, 1985 and Kambour, 1987). Of course, if the blend converts from rubbery to glassy with composition, the usual changes in properties at the glass transition become super- imposed on the relationship. Crystallization of one of the components changes properties in similar ways, as would be expected for a single – component

polymer (Murff, Barlow and Paul, 1986 and Preston, Barlow and Paul, 1984).

For blends where the components form separate phases, properties depend on the arrangement of these phases in space and the nature of the interface between the phases. Immiscible blends behave like composite materials in many respects. Properties like softening temperature, modulus, permeation, etc are dominated by the properties of the component that forms the continuous phase (Hopfenberg and Paul, 1978). Failure properties, especially those related to ductility e.g. elongation at break and impact strength, often depend on the dimensions of the phases and the degree of interfacial adhesion between the components. The nature of the interface is related to the thermodynamic interaction between the components (Callaghan, Takakuwa, Paul and Padwa, 1994), which then governs morphology generation in the melt via interfacial zone and the degree to which chains from the two phases entangle. When the thermodynamic affinity is very low, the blend can exhibit a degree of toughness well below that of either component and is regarded as incompatible. Improvement of this property response is often called compatibilization.

1.12 Statement of Problem

Polystyrene(PS) is a brittle polymer with limited mechanical properties, while Polyvinyl Acetate (PVAc) is highly elastic. The individual polymers had limitations in high density and mechanical applications, moreso other aspects of end – use like optical stability and environmental resistance. The blends of the two polymers is expected to have moderate properties required for some household applications. The present study is to established the most convenient blend composition that is desirable for such applications through the mechanical, sorption, density and morphological studies of these blends, first as pure PS/ PVAc blends and secondly as α - cellulose modified PS/ PVAc blends .

1.13 Aim and scope of research

Polymers have shortcomings in terms of one property or other under different applications, hence blending of different polymers is essential to compromise these shortcomings, in order to improve the properties and performance characteristics. The limitations of polystyrene (PS) are its brittleness and limited mechanical stability at elevated temperatures, while polyvinyl acetate (PVAc) is highly elastic. A blend of this polymer pair is expected to have improved mechanical properties. The use of a selected filler, incorporated into the polymer-polymer matrix in particular may offer improved applicability in Structure-

property modification for a particular end use. The upsurge in the study of polymer blends both in industrial laboratories and in Universities and research institutes has been due largely to the use of polymeric materials in increasingly demanding applications like polystyrene (PS) – polypropylene ether (PPE) blend, for example finds applications in Dashboards, steering wheel coverings, casing parts – for heating and ventilation, teleprinters, faxes, telex machines casings for electrical devices, distribution boxes, TV rear panels, TV and Video chasis, heat exchangers etc. The search for a cost effective technique and technically superior product makes the study of Polymer blends more comprehensible concepts.

1.14 Significance and limitation of this study

The synthesis of new polymers is cumbersome and capital intensive, hence the need for extensive research on the modification of the already existing polymers. Plastics are fast replacing traditional materials such as glass, metals and ceramics because of its high technical advantages and low economic cost. With proper monitoring of conditions for processing of polymer blends, new materials can open a window for various industrial and domestic applications based on its end-use properties. This study is tailored towards achieving this objective. However, the limitations of this study are lack of adequate equipments for an all-encompassing research on the

microscopic and macroscopic structures and the dependence of such structures on the end-use applications.

1.15 Scope of research

The polymer blends composed of polystyrene (PS) and poly (vinyl acetate) (PVAc) have been widely investigated. Kaczmarek (1995) studied the photodegradation of PS/PVAc blends irradiated both with UV and fluorescent light and found that the processes of photo-oxidation and photodegradation in blends can be accelerated compared to pure PS and PVAc homopolymers. The composition of blends and morphology exerted an obvious influence on the course of photo-oxidative degradation. By density and viscometric measurements of the solutions of PS/PVAc blend, Mamza and Folaranmi (1996) concluded that PS and PVAc composition shows considerable compatibility level. Rawal and Devi (1992) determined the viscosity of the solutions of PS/PVAc blends of various compositions and observed that the ternary polymer-solvent systems are miscible, although PS and PVAc are immiscible. In this work, a detailed study of the physico-mechanical properties in relation to structure-property relationship of various PS/PVAc blends will be conducted to assess its applicability in the industries.

However, even though much work has been done on the PS /PVAc blends, no work has been reported on the blends reinforced by a α -cellulose as filler.

The original scope of this investigation includes the following:-

- Preparation of varying compositions of polyblends of PS and PVAc by dry blending
- Addition of α -cellulose as filler to the blend mixtures, so as to monitor the reinforcing effect of α -cellulose on the structure-property relationships in the different compositions of the blend.
- Preparation of polymer sample by pressing in a compression moulding machine (varying pressure, temperature and time).
- Measurement of the mechanical properties: stress-strain relationship, modulus of elasticity, tensile strength vs composition and load vs extension.
- Measurement of density, sorption properties: determination of morphology and x-ray diffraction parameters.

The ultimate goal is to produce a novel polymer blend with high mechanical performance and other usable properties that can be utilized in the polymer industries for various applications.

1.16 Justification

The principal limitations of polystyrene are its brittleness, non-biodegradability and limited mechanical stability at elevated temperatures. Poly (vinyl acetate) is highly elastic. Both are

neutral, water-white to stray-coloured, tasteless, odourless, and non-toxic. The resins have no sharply defined melting points but become softer with increasing temperature. Both are soluble in organic solvents, e.g. esters, ketones, aromatics. A blend of this polymer pair is expected to have improved mechanical properties and other superior properties for industrial applications under appropriate blending conditions and incorporation of filler in the polymer-polymer matrix through the study of its morphology.

CHAPTER TWO

LITERATURE REVIEW

2.1 REVIEW OF PAST RELATED WORKS

Properties of a given polymer can be improved in various ways such as blending with other polymers or by incorporation of reinforcing fillers. Reinforcement of polymer blends is particularly useful in those cases where blending produces improvement of some properties with simultaneous determination of other properties such as mechanical strength, modulus, stiffness, etc, thus in order to retain the advantage of blending, it becomes necessary to compensate for the loss of properties by reinforcement with suitable fillers [Gupta (2002)].

Nwufo, Griffin and Ekpenyong (1984) studied the extrusion of starch-extended water-soluble poly(vinyl Alcohol) and asserted that the method is relatively faster in estimating the physico-mechanical properties of the virgin polymer and its composite, thereby enabling the prevention of the extrudate so produced during extrusion from water effects. While studying the microscopic arrangement/appearance of fractured surfaces and some mechanical properties of starch-extended poly (vinyl alcohol), Nwufo and Griffin (1985), with the aid of scanning electron microscopy (SEM), showed that the composite with 0% starch content reflected only fracture lines, whereas composites with 10% w/w starch content in Mowiol (an industrial

plasticized poly(vinylalcohol) showed fracture lines as well as some pitting, indicative of starch beds. The mechanical properties of the composites revealed that the impact strength decreases with increase in starch content, in comparison to the matrix impact property. They explained that the swelling of starch in the matrix brings about a further increase in the percentage of starch resulting in a break, however, the breaking strength decreased progressively with increase in the starch content. Also, the flexural modulus showed increase with increase in starch content.

Kolawole and Agboola (1982) conducted some mechanical property studies on polystyrene (PS) and its blends with acrylonitrile-butadiene-styrene, PVC and polybutadiene and observed an increase in modulus with exposure time while the elongation decreases.

Olayemi and Ibiyeye (1986) evaluated the mechanical properties of blends of poly (vinyl acetate) and poly (ethyl methacrylate) and observed improvements in the mechanical properties of the polymers due to blending. These were considered to be as a result of the presence of favourable and strong (PVAc – PEMA) intermolecular interactions which reveals miscibility and compatibility of the polymers. In this study, a lower critical value (M_v) of 4.9 was found, above which phase separation would be expected on blending these two polymers to the extent

of 20% weight of PEMA. The stress-strain curves for the PVAc and PEMA samples and some of their blends indicate a somewhat rubbery, soft and weak characteristic of PEMA as the percentage of the latter was increased in the blend. Also, the dependence of tensile strength (TS) of films of the polymers on blend composition, shows an increase from that for PVAc with a peak, followed by a decrease to a minimum, then a final increase to the value for PEMA, with increase in percentage PEMA, in the blend. Some areas above and below the additivity straight line joining $(TS)_{PVAc}$ to $(TS)_{PEMA}$ were observed in the study. However, they concluded that twenty percent PEMA produces the optimum effect on TS, initial modulus (IM) and % elongation at break of the films obtained from the blends. Films from blends with up to 30% PEMA, and, in particular, those with 20% PEMA, have high values of TS, IM and % elongation at break, and are, on the basis of the mechanical properties studied, significantly superior to the individual polymers that constitute the blends.

Folaranmi and Zayyan (2002) studied some properties of polystyrene (PS) – polyisobutylene (PIB) rubber blends and observed that at higher concentrations of PIB in the blend the transparency was impaired and phase separation was observed. The results of the mechanical test on some selected films showed a higher value of yield stress and ultimate strain and a

larger area under the stress-strain curve for blends than for PS, suggesting that PS was toughened by blending with the PIB rubber samples. They observed the highest value of Young's modulus for 95/5 blend with subsequent decrease for blends with higher rubber content. It was concluded from the study that PS was semi-compatible with PIB at low percentage concentration of rubber in the blend and at low solid content of solution. There was also a tendency of the blend to demix at higher rubber content of the blend as reported from the film morphology study. Toughening of PS with PIB rubber must therefore be at fairly low rubber concentrations, preferably < 10% of the total weight.

Mamza and Folaranmi (1996) carried out compatibility studies on solution of polystyrene (PS) and polyvinyl acetate (PVAc) blend by density and viscometric methods. The studies revealed that experimental densities of the blends were found to be lower than the calculated values assuming additivity of volumes of polymers and solvent, while the plots of relative viscosity (η_{rel}) with composition are of the S-type, indicating two-phase formation with phase separations at intermediate compositions and the comparison of the calculated (using the Krigbaum – Wall equation for both solvents) and observed intrinsic viscosities shows higher calculated values, thereby suggesting that PS and PVAc are an incompatible pair.

Ashraf, Ahmad , Riaz, Devi and Singhal, (2007) studied and highlighted the utilization of linseed oil epoxide (LOE) (a product from a sustainable resource), to obtain blends of LOE with polystyrene (PS) forming tough and flexible free-standing films. The mechanical properties of LOE/PS blend films were found to match with those of LDPE at composition LOE/PS, 65/35. The potential applications for such sustainable resource-based blend included packaging films and production of biodegradable plastic sheets which can be formed into products such as bio-bags. It was observed in this study that the blends of LOE with PS were miscible in solution phase in the composition range of LOE/PS, 85/15 to 45/55 as confirmed by viscosity and density measurements. At composition LOE/PS, 35/65 phase separation takes place which indicates the onset of immiscibility. The morphological investigation revealed a two-phase system in the case of LOE/PS, 85/15. The toughness of the films was found to increase with increasing content of PS in the blend. The mechanical properties of LOE/PS blend films were found to match with LDPE at composition LOE/PS, 65/35. The study concluded that the linseed oil epoxy (a product from sustainable resource) can be substituted up to 65% or even higher with Polystyrene to obtain tough and flexible films.

Gupta and Singh, (2005) characterized by spectral, structural, thermal and electrical methods, polymer composites of O-

tolidine-iodine (1:0.75 molar ratio) charge-transfer complex with polystyrene prepared in different weight ratios. The polymer composites exhibit semi-conducting behavior. The current-voltage characteristics, frequency dependence of conductivities of these composites were determined. The frequency dependence of ac conductivity of these composites showed contribution from grain, grain boundary and electrode as a function of charge-transfer content. They observed that at low charge-transfer content, all the three contributions were present but at high content, only grain contribution was relevant.

Ogawa, Kanaya, Nishida and Matsuba, (2008) studied the phase separation and dewetting in polystyrene-poly(vinyl methyl ether) blend thin films in a wide thickness range using optical microscope (OM), atomic force microscope (AFM) and small-angle light scattering (LS). It was found that both phase separation and dewetting processes depend on the film thickness regions. In the first region above $\sim 15\mu\text{m}$ (micrometers) the spinodal decomposition (SD) type phase separation occurs in a similar manner to bulk and no dewetting was observed. They regarded the region as bulk. In the second region between ~ 15 and $1\mu\text{m}$, the SD type phase separation proceeds in the early stage, while the characteristic wavelength of the SD decreases with the film thickness. In the late stage dewetting was induced by the phase separation, whereas, in the third

region between $\sim 1\mu\text{m}$ and $\sim 200\text{nm}$ the dewetting was observed even in the early stage. They observed that dewetting morphology is very irregular and no definite characteristic wavelength is shown. They concluded that the irregular morphology was induced by mixing up the characteristic wavelengths of the phase separation and the dewetting. However, in the fourth region below $\sim 200\text{nm}$ the dewetting occurs after a long incubation time with a characteristic wavelength, which decreases with the film thickness. A layered structure was formed in the thin film during the incubation period which triggers the dewetting through the capillary fluctuation mechanism or the composition fluctuation one.

Thomas *et al* (2008) studied the miscibility, morphology, thermal and mechanical properties of DGEBA-based epoxy resin toughened with a liquid rubber. In the study, epoxy resin based on diglycidyl ether of bisphenol A and varying content of hydroxyl terminated polybutadiene were cured using an anhydride hardener. The ultimate aim of the study was to modify the brittle epoxy matrix by liquid rubber to improve the toughness characteristics. Chemorheological analysis of the modified network was performed to understand the physical transformation taking place during the cure polymerisation reaction. The delay in gel time on inclusion of rubber was explained by lower reactivity due to dilution and viscosity effect.

Tensile, flexural, and fracture toughness behavior of neat as well as modified networks have been studied in order to observe the effect of rubber modification. The morphological evolution of the toughened networks was examined by scanning electron microscope, and the observations were used effectively to explain the impact properties of the network having varying content of liquid rubber. Also, acoustic emission studies were performed on neat and certain modified systems. Based on acoustic emission results and morphological characteristics, toughening and failure mechanisms were discussed. The behaviour of the relaxation peaks were evaluated by dynamic mechanical analysis; the researchers also tried to explain the composition of networks. The thermal stabilities of the toughened epoxies were studied using thermogravimetric analysis (TGA). From this study, the activation energy for decomposition of neat and modified epoxies was estimated and compared. It was concluded that the reduction in cross-linking density of the thermoset upon modification can be confirmed and explained.

Wycisk, Trochimczuk and Matyb, (1990) studied the supermolecular structures of polyethylene (PE) / polystyrene (PS) blends using density, viscosity, mechanical and optical measurements and found that, depending on the composition of polystyrene, the morphology of the blends changed between that

of spherical domains of one component dispersed in a continuous matrix of the other, to a highly non-homogenous mixture of fibrous or cabbage-like macro-domains of both components. The presence of PS was also observed to affect the development of PE crystallites. The study of the dependence of specific volume on the blend composition revealed some non-additivity (Ca 2%, for PE – PS II, III and Ca 5% for PE – PS I) indicating the presence of some additional free volume (micropores). They observed that this resulted from high PE contraction (Ca 10 Vol %) on transition from the molten to the solid state and from the differences in viscosities of the melts of the components. It was also observed that the dependence of modulus of elasticity on PS content for PS I – II (two grades of processed polymer) had a strong influence on the PS molecular weight and the degree of dispersion before, as well as after the phase inversion. Before the phase inversion and for low molecular weight PS (PSI), relatively homogenous blends with spherical, separated PS domains of two distinct sizes viz; 0.2 – 0.4 and 1 - 5 μ m are obtained. As the molecular weight of PS increases, the small domains disappear while the other domains clearly enlarge. Highly non-homogenous structures are found with PS III (mainly Ca 10 μ m PS domains), meaning that the mixing efficiency is low.

An earlier work by Barensten and Heikens (1973) on the mechanical properties of polystyrene (PS) / low density polyethylene (LDPE) blends reveals that by adding a graft copolymer of polystyrene and low density polyethylene to the blends the impact strength and modulus of polystyrene graft copolymer blends could be made comparable to those of commercial rubber modified impact polystyrenes by adjusting the fraction of copolymer in the blend. They observed that the Young's modulus of the blends to which the copolymer was added did not differ from the modulus of the blends without copolymer. The yield strength and the elongation at yield increase, if the graft copolymer is added to the blends. These observations can be understood, if the graft copolymer is present at the interface between PS and LDPE and thus improving the adhesion. Electron scanning micrographs of the fracture surfaces show that the phase boundary of the dispersed LDPE particles and the holes from which the particles are pulled out are covered with small globules. The total volume of these irregularities agrees well with the amount of added copolymer. Addition of graft copolymer to the LDPE rich blends decreases the elongation at break also. It was concluded from observations of the electron scanning microscopy, phase contrast microscopy, and the stress whitening phenomena that after yield but well before break most PS particles are torn loose

from the surrounding highly oriented LDPE. Thus, at break porous LDPE is stressed just like in blends without copolymer.

Nicolais, Druilli and Landel, (1973) measured the Stress-Strain behavior of acrylonitrile-butadiene-styrene (ABS) containing up to 33.5 vol % of 10 - 40 μ m glass beads as filler estimated at one strain rate at room temperature. It was found that the beads eliminate the yielding and greatly enhance the ultimate elongation and work-to-break. The change in stress-strain response is associated with the dewetting and vacuole formation around the beads and with an increase in the amount of crazing,

At higher stresses, the unfilled material shows a well-defined yielding but the filled materials pass through a broad maximum with little change in the stress level. After this region of zero slope is attained, these samples continued to elongate with no further change in appearance and no necking. The electron scanning photomicrograph of the fracture surface of ABS containing 20 vol % glass beads strongly suggests the formation of elongated voids, such as are observed in filled elastomers.

Folaranmi, Ande and Umahi, (2001) reported the effect of polyisobutylene rubber concentration and molecular weight on density and relative and intrinsic viscosities of PMMA/PIB blend

solutions in toluene, as well as the morphology and tensile mechanical properties of some of the blend films.

Mishra and Luyt, (2008) reported the effect of organic peroxides on the morphological, thermal and tensile properties of EVA – organoclay nanocomposites. They observed a flocculated morphology and reduce Polymerclay interaction from the prepared nanocomposites. There is a good correlation between these morphologies and the thermal stabilities and total crystallinities of the nanocomposites. Also, clay incorporation and peroxide treatment did not significantly change the tensile properties.

Ahmad, Mohd and Abdullah, (2004) assessed the effects of filler (carbon black N110, silica and calcium carbonate) on the mechanical properties of natural rubber (NR)/Linear low – density polyethylene (LLDPE) blends. The mechanical and physical properties of the blends were found to be dependent on the filler characterization. Swelling index and elongation – at – break showed a decreasing trend with increasing volume percent of filler loading in the blend. The significant changes in other physical properties included the gel content, and bound rubber of the samples indicated a strong interaction between the filler particles and polymer matrix. In conclusion, mean agglomerate particle size and polymer-filler interaction are the factors determining the mechanical and physical properties of

NR/LLDPE blends. The reduction of elongation-at-break is due to stiffening of the polymer matrix by the filler. Further increase in filler loading causes the molecular mobility decrease due to extensive formation of physical bond between the filler particles and the polymer chain that stiffen the matrix. A progressively reinforced and hence lowered elongation –at-break at any filler loading greater than 20% was observed. They observed also that with good polymer-filler interactions, there would be increases in modulus as well as mechanical properties.

Razavi-Nouri, Jafarzadeh- Dogouri, Onomiehie and Langroudi, (2006) reported the mechanical properties and water absorption behavior of chopped rice husk-filled polypropylene composites. In the study the reinforcing effect of chopped rice husk (CRH) in polypropylene was studied. Composites containing different amounts of CRH with 0 to 40 parts per hundred part of polymer (php) were prepared using a co-rotating twin screw extruder and characterized by determination of their mechanical properties and also water absorption. In order to increase the interphase adhesion, polypropylene grafted with maleic anhydride was added as a coupling agent to all the composites studied. It was found that the tensile and flexural modulus of the composite containing 40php of CRH increased approximately by 33% and 100%, respectively. The results also showed that, while flexural strength was moderately improved by increasing of CRH into the

matrix, elongation-at-break and energy-at-break decreased dramatically. A reasonable adhesion between the main components was also observed in the spectra of the scanning electrons micrographs. Water absorption experiments, showed that although the diffusion coefficient increased with CRH loading, all the composites followed case 1 diffusion.

From their study, it is observed that the detrimental effect of CRH addition into PP containing MAPP (the matrix) became apparent such that CRH reduced the ductile behaviour of the matrix by making the composites more brittle. While the matrix showed ductile behaviour via a neck formation, the composites consisting CRH revealed brittle behaviour with no necking. Although the tensile strength of a composite is more sensitive to the matrix properties, its modulus is dependent on the fibre properties. To improve the tensile strength, a strong interface, low stress concentration and fibre orientation are required, whereas high fibre aspect ration and fibre wetting determine tensile modulus. The impact strength showed a slight decrease in value after addition of 10 php of CRH into the matrix. However, it leveled off when higher amount of CRH was added into the composite. The ductile deformation of the matrix is inhibited because of the presence of CRH. Three different mechanisms have been proposed for moisture penetration into the composite and the main process is the diffusion of water

molecules into the composite, while the main process is the diffusion of water molecules inside the microgaps between the polymer chains. The other two mechanisms are capillary transport of water into the gaps and flaws created at the interface of fibre and polymer matrix, because of incomplete wettability and impregnation and also diffusion of water molecules into the microcracks formed in the matrix during the compounding process (Lin, Q, 2002).

CHAPTER THREE

MATERIALS AND METHODS

3.1 MATERIALS AND THEIR SOURCES

Polystyrene (supplied by Philip Marris Ltd, England), poly(vinyl acetate), α -cellulose (filler), Hydrochloric acid, Sodium hydroxide (All supplied BDH Chemicals, Poole, England), Acetone (Supplied by M and B Chemicals Ltd), Hounsfield H5 KS Universal Testing Machine (Hounsfield, Red Hill, England) provided by the Department of Mechanical Engineering, Ahmadu Bello University, Zaria, compression moulding machine (Inc. U.S.A, MODEL M, S/No. 12000 - 137) and scanning electron microscope, n.j.k 120f (DEM, Joel, JSN-840 SEM) provided by the Department of Metallurgical Engineering, Ahmadu Bello University, Zaria).

3.2 Preparation of blend samples and testing

3.2.1 Sample preparation / blend formulations

Different blend compositions of polystyrene and poly (vinyl acetate) with a total solid content of 6.0g were prepared in the following weight percent compositions: 100:0, 90:10, 80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, 10:90 and 0:100. The samples were weighed on a digital mettler balance, AT400, with precision ± 0.0001 g. Each sample mixture was

thoroughly dry blended using a conventional warring blender, after manually mixing with spatula. The samples of dimension, 6cm x 2cm x 3mm were compression moulded at 190 – 200°C, applying 15 tons, pressure for 20 minutes. The compression moulded articles of specimens with the dimensions according to American standard for testing materials-ASTMD 638 model 3 were obtained for stress-strain measurements. Same process was repeated for α -cellulose filled (5g) blends of the same compositions.

3.2.2 Dry blending of blend formulations

Dry blends were prepared with a conventional warring blender. The blend compositions consisted of 5g of α -cellulose each added to the varying ratios of polystyrene and poly (vinyl acetate) and mixed with a spatula. The mixture was then transferred into the blender and mixed for three minutes. The temperature generated due to mixing rose to 70°C after three minutes. The content was finally discharged, cooled and kept in a polythene bag for subsequent compression moulding.

3.2.3 Compression Moulding of PS/PVAc dry blends

A compression moulding machine, model M, S/No. 12000 – 137, Inc U.S.A., was used. Each time, 6.0g of either pure PS, PVAc or dry blends of both were weighed separately and placed between two metal moulds of dimensions 6cm x 2cm x 3mm drilled in the mould. The mould pair containing the samples

were each transferred into the hot platens of the machine. The platens were then closed using the hydraulic lever. First the sample was pre-heated for one minute to equilibrate at 190-200°C without pressure to stabilize and to allow trapped air to escape. The pressure was then raised gradually to 15 metric tons for another minute after which the platens were removed and quenched with a water-soaked towel for a minute. The articles so produced were removed from the mould and kept in between large size filter paper for further studies.

3.2.4 Tensile strength measurements

A Hounsfield H5 KS Universal Testing Machine (Hounsfield, Redhill, England) provided by the Mechanical Engineering Department, Ahmadu Bello University, Zaria, was used to investigate the tensile strength, tensile modulus, elongation properties and stress-strain relationships of the unfilled and filled modified PS/PVAc blends. Samples of 6cm x 2cm x 3mm were used for tensile testing. Samples with a gauge length of 20mm were analysed at a cross head speed of 10mm.min⁻¹.

3.2.5 Sorption measurements

According to Liao, Chem, Han and Hsieh, (1997) the swelling ratio (S.R.) of a polymer can be calculated, assuming additivity of volumes, by

$$\text{S.R} = \frac{\frac{W_d}{\ell_{\text{polymer}}} + \frac{W_s - W_d}{\ell_{\text{solvent}}}}{\frac{W_d}{\ell_{\text{polymer}}}} \quad (28)$$

where W_d and W_s are the weight of dry and swollen polymers, respectively, and ℓ is the density (ℓ_p is the density of the dry polymer sample and ℓ_s is the density of the swollen polymer sample).

Further treatment of equation (28) gives

$$\text{S.R} = \left(1 + \frac{\Delta W}{W_d} \right) \frac{\ell_p}{\ell_s} \quad (29)$$

Where ΔW is the difference between dry mass W_d and masses of swollen polymers W_s . Equation (28) reduces to (29) for the percentage swelling quotient, $Q\%$, Sperling (1992) and Bamgbose, Dare Samuel and Ajaelu, (2007).

Assuming ℓ_p is constant, equation (29) becomes

$$Q\% = \left(\frac{\Delta W}{W_d} \right) \frac{100}{\ell_s} \quad (30)$$

However, in this work, the British Standard method 502F was used, briefly : The PS/PVAc processed blends were dried for 24 ± 1 hours at 51°C and then cooled for 20 minutes after which they were weighed to the nearest gram (W_1) using a digital metler balance AT400 with precision $\pm 0.0001\text{g}$. The weighed samples were then removed and dried with filter paper after which they were re-weighed within 1 minute of removal from the

distilled water (W_2). Thus, the water absorption was determined as $(W_2 - W_1)$ g and the % water absorption =

$$\frac{W_2 - W_1}{W_1} \times 100 \text{ ----- (31)}$$

The process was repeated in 0.05M hydrochloric acid, 0.05M sodium hydroxide and acetone (after redistillation) to determine the % solvent absorption levels of both the pure and reinforced polymer blends.

3.2.6 Density measurement of unfilled and filled PS/PVAc blends

The density of the blends (both unfilled and filled) was measured as mass per unit volume, according to British standards-BS2782 part 6. From the calculated volumes of the blends (6cm x 2cm x 3mm) and their weights or masses, the densities of the blends were calculated directly using the ratio of the mass to the volume. Graphs were plotted of density of unfilled and filled PS/PVAc blends versus blend compositions

3.2.7 Establishment of blend morphologies of unfilled and filled PS/PVAc blends.

The morphology of the cross-section of the blends of different compositions with or without the filler incorporated in the polymer – polymer matrix was examined by the scanning electron microscope, n.j.f. 120f (DEM, Jeol, JSN-840 SEM) at

magnification of 1000 x (acquired by the Department of Metallurgical Engineering, Ahmadu Bello University, Zaria)

3.2.8 FTIR, XRD and Surface Topography Characterization of the Blends

Experimental

(a) *Sample Preparation*

Different blends of PS and PVAc with a total solid content of 6.0g were prepared in the following weight:10:90, PS/PVAc, 20:80, PS/PVAc and 30:70, PS/PVAc blend compositions.

(b) *Material Characterization*

Fourier transform infrared (FTIR) spectra of the polymer blends with and without filler (in nujol) were recorded with an FTIR Shimadzu spectrometer in the 4500–500 cm^{-1} range, taking 10 scans at 2- cm^{-1} resolution. The indices of absorption for the polymer blends with and without filler were calculated using the formula [1]:

$$K = \frac{\alpha\lambda}{4\pi}$$

where K is the index of absorption, α is the absorption and λ is the wavelength of the scanned region of the infrared spectrum.

The surface topography and morphology of the polymer blends with and without filler were observed using optical microscope (model

NJF-120A) with a resolution of 400X and in conjunction with Image J; surface topography software, the surface topography and the particle sizes were determined. The ratio of crystalline/amorphous phase contents in the polymer blends with and without filler was determined by X-ray powder diffraction (XRD) analysis using MD-10 automated Diffractometer employing Cu K α ($\lambda=1.5402\text{\AA}$) radiation over the range $15^\circ \leq 2\theta \leq 75^\circ$. The crystallinity of the polymer blends with and without filler was calculated using the following

equation [3]:

$$\chi_c = \frac{\int_0^\infty S^2 I_c(s) d}{\int_0^\infty S^2 I(s) d}$$

where S is the magnitude of the reciprocal-lattice vector which is given by $S = (2 \sin \theta) / \lambda$, θ is one-half the angle of derivation of the diffracted rays from the incident X-rays, and λ is the wavelength; $I(s)$ and $I_c(s)$ are intensities of coherent X-ray scattering from both crystalline and amorphous regions and from only crystalline region of polymer sample, respectively, and d is the interlayer spacing. The average crystallite sizes D of the synthesized powders were estimated from the peak broadening effect using Scherrer formula [2]:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

3.2.9 Electrical Conductivity of the Filled and Unfilled PS/PVAc Blends

There are four possible mechanisms/models of electrical conduction as reported by Deshmukh *et al.*, (2007).

Poole – Frenkel mechanism

The current–voltage relationship for Poole–Frenkel mechanism is expressed as

$$J = B \exp \left(\frac{-\phi}{kT} + \beta_{PF} E^{1/2} \right)$$

$$\text{Where } \beta_{PF} = \frac{e}{kT} \left(\frac{e}{\pi \xi \xi_0 d} \right)^{1/2} = \text{constant} \dots \dots \dots (5)$$

where β is a constant and all other symbols have their usual meanings. The Poole – Frenkel mechanism predicts a field dependent conductivity as

$$\sigma = \sigma_0 \left(\exp \frac{\beta_{PF} E^{1/2}}{2kT} \right) \dots \dots \dots (6)$$

$$\text{or } \ln \sigma = \ln \sigma_0 + \frac{\beta_{PF} E^{1/2}}{2kT} \dots \dots \dots (7)$$

So that the Poole – Frenkel mechanism is characterized by the linearity of $\ln \sigma$ vs $E^{1/2}$ plots i.e. Poole – Frenkel plots predicted by (7) are linear with a +ve slope

Fowler – Nordheim mechanism

The Fowler – Nordheim relation (Fowler, 1928) for current density is

$$J = AV^2 \exp \left(\frac{-\phi}{kT} \right) \dots \dots \dots (8)$$

V

So that, $\ln \left(\frac{J}{V^2} \right) = \ln A - \phi/v$

and the $\ln J/V^2$ vs $1000/v$ plots is expected to be a linear straight line relation with a - ve slope

Schottky Plots

The Schottky - Richardson current voltage relationship is expressed as

$$J = AT^2 \exp\left[\frac{-\phi}{kT} + \beta_{SR} E^{1/2} \right] \dots\dots\dots(9)$$

β_{SR} being the field lowering constant given by

$$\beta_{SR} = e/kT \left(\frac{e}{4\pi\epsilon_0 d} \right)^{1/2} \dots\dots\dots(10)$$

and hence $\ln J = \ln AT^2 - \phi_s/kT + \beta_{SR} E^{1/2}$

and that $\ln J$ vs $E^{1/2}$ plots should be a straight line with a +ve slope. The results plotted with an axes marked in this way are referred to as Schottky plots and linear +ve slope on Schottky plots generally characterize Schottky - Richardson mechanism

Richardson mechanism

The Richardson current - voltage relation is expressed as

$$J = AT^2 \exp \left[\frac{AT^2 - \phi_s/kT + \beta_{SR} E^{1/2}}{kT} \right] \dots\dots\dots(11)$$

$$J/T^2 = A \exp \left[-\phi/kT + \beta_{SR} E^{1/2} \right]$$

$$\ln J/T^2 = \ln A + \left[-\phi_s/kT + \beta_{SR} E^{1/2} \right]$$

$$\ln J/T^2 = \ln A + \beta_{SR} E^{1/2} - \phi_s/kT \dots\dots\dots(12)$$

The graph between $\ln (J/T^2)$ vs $(1/kT)$ from this relation should be a straight line with a -ve slope. These plots are referred to as Richardson plots and Schottky - Richardson mechanism requires linearity of these plots

In this work the Arrhenius plots ($\ln (\sigma)$ vs. $1000/T$) at all values of applied voltage was adopted.

3.2.9.1 Film casting and measurement

Different composition of PS/PVAc blend solutions was prepared in Toluene. 20cm³ of the 2% solution of PVAc was poured carefully into a clean dry Petri dish placed on a flat surface in a fume cupboard and left for 24hours for the solvent to evaporate. 10cm³ of distilled water was then poured on the dry film in the dish. The dish with the content was left for 20minutes to allow the water penetrate the sides of the dish and allowed for the films to be removed easily. The film was repeated in turn for PS, and all the blend solutions. A micrometer screw gauge was used

to measure its thickness. Films of thickness of 70 μ m were used in this study.

3.2.9.2 Swelling Properties Measurement

The specimens were placed in a dessicator and transferred in to a preconditioning oven at 50 $^{\circ}$ c. After 24hours they were removed, stored in the dissector for 1hour and weighted to an accuracy of ± 0.0001 g using a Metler balance. This cycle was repeated until a constant mass (m_1) was obtained. Following, the films were immersed in water, HCl, NaOH and acetone at 50 $^{\circ}$ C. At fixed time intervals they were removed, blotted dry to remove excess liquid, weighted and returned to the solvent. The uptake of the liquid was recorded for time intervals up to 30hours.

3.2.9.3 Electrical Conductivity Measurements

A thermostatically controlled oven was used for heating purpose. The sample films with silver electrodes were sandwiched between two platinum electrodes (diameter, 2.5cm) and currents measured using an ammeter while the voltage was assessed from a voltmeter.

CHAPTER FOUR

RESULTS

4.1 Sorption test measurement for pure and filled PS/PVAc blends in water, acetone, 0.05M HCl and 0.05M NaOH.

Tables 3-9 give the sorption test measurement for pure and α -cellulose filled PS/PVAc blends. Table 3 gives sorption test in water for PS/PVAc blends without filler, while Table 4 gives sorption test in water for PS/PVAc blends with α -cellulose. Table 5 gives sorption test in acetone for PS/PVAc blends without filler and Table 6 gives sorption test for PS/PVAc with α -cellulose in acetone. Table 7 gives sorption test for PS/PVAc blends with α -cellulose filler in 0.05M HCl, while Table 8 gives sorption test in 0.05M HCl for PS/PVAc blends without filler and Table 9 gives sorption test in 0.05M sodium hydroxide for PS/PVAc blends without filler, while Table 10 gives sorption test for PS/PVAc blends with α -cellulose filler in 0.05M sodium hydroxide. There is an appreciable weight gain in water (Table 3), but from Table 4, the α -cellulose increases the rate of absorption for all the compositions. This is evident even in 0.05M hydrochloric acid and 0.05M sodium hydroxide (see Tables 7, 8, 9 and 10) except that

hydrochloric acid has the highest % solvent absorption for both the pure and reinforced. From the results, the order of % absorption is acid > water > base > acetone. However, the blends in acetone shows a dramatic decline in % absorption in presence of α -cellulose filler (table 6) and from the values of Tables 5 and 6) one can observe that it is loss of weight that is prevalent . These values is shown in figure 10, while Figure 9 gives the different series for % absorption.

Table 3: Sorption test in water for PS/PVAc blends without filler

Composition	W₁ (g)	W₂ (g)	Amount of absorbed(g)	% water absorption
100PS	1.0000	1.0002	0.0002	0.02
90/10PS/PVAc	1.0000	1.0013	0.0013	0.13
80/20PS/PVAc	1.0000	1.0080	0.0080	0.80
70/30PS/PVAc	1.0000	1.0102	0.0102	1.02
60/40PS/PVAc	1.0000	1.0132	0.0132	1.32
50/50PS/PVAc	1.0000	1.0232	0.0232	2.32
40/60PS/PVAc	1.0000	1.0133	0.0133	1.33
30/70PS/PVAc	1.0000	1.0188	0.0188	1.88
20/80PS/PVAc	1.0000	1.0568	0.0568	5.68
10/90PS/PVAc	1.0000	1.0717	0.0717	7.17
100PVAc	1.0000	1.0168	0.0168	1.68

Table 4: Sorption test in water for PS/PVAc blends with α - cellulose filler

Composition	W₁ (g)	W₂ (g)	Amount of absorbed (g)	% water absorption
100PS	1.0000	1.0011	0.0011	0.11
90/10PS/PVAc	1.0000	1.0044	0.0044	0.44
80/20PS/PVAc	1.0000	1.0053	0.0053	0.53
70/30PS/PVAc	1.0000	1.0201	0.0201	2.01
60/40PS/PVAc	1.0000	1.0235	0.0235	2.35
50/50PS/PVAc	1.0000	1.0298	0.0298	2.98
40/60PS/PVAc	1.0000	1.0315	0.0315	3.15
30/70PS/PVAc	1.0000	1.0412	0.0412	4.12
20/80PS/PVAc	1.0000	1.0615	0.0615	6.15
10/90PS/PVAc	1.0000	1.0870	0.0870	8.70
100PVAc	1.0000	1.0211	0.0211	2.11

Table 5: Sorption test in acetone for PS/PVAc blends without filler

Composition	W₁ (g)	W₂ (g)	Amount Desorbed (g)	% water absorption
100PS	1.0000	0.8500	0.1500	-15.00
90/10PS/PVAc	1.0000	0.8000	0.2000	-20.00
80/20PS/PVAc	1.0000	0.8000	0.2000	-20.00
70/30PS/PVAc	1.0000	0.6300	0.3700	-37.00
60/40PS/PVAc	1.0000	0.5250	0.4750	-47.50
50/50PS/PVAc	1.0000	0.4185	0.5815	-58.15
40/60PS/PVAc	1.0000	0.4012	0.5988	-59.88
30/70PS/PVAc	1.0000	0.2500	0.7500	-75.00
20/80PS/PVAc	1.0000	0.0713	0.9287	-92.87
100PVAc	1.0000	0.0007	0.9993	-99.93

Table 6: Sorption test in acetone for PS/PVAc with α - cellulose filler

Composition	W₁ (g)	W₂ (g)	Amount Desorbed (g)	% water absorption
100PS	1.0000	0.9025	0.0975	-09.75
90/10PS/PVAc	1.0000	0.8650	0.1350	-13.50
80/20PS/PVAc	1.0000	0.8413	0.1587	-15.87
70/30PS/PVAc	1.0000	0.8204	0.1796	-17.96
60/40PS/PVAc	1.0000	0.8000	0.2000	-20.00
50/50PS/PVAc	1.0000	0.8000	0.2000	-20.00
40/60PS/PVAc	1.0000	0.7213	0.2787	-27.87
30/70PS/PVAc	1.0000	0.5750	0.4250	-42.50
20/80PS/PVAc	1.0000	0.2570	0.7430	-74.30
100PVAc	1.0000	0.0011	0.9989	-99.89

Table 7: Sorption test in 0.05M Hydrochloric acid for PS/PVAc blends with α - cellulose filler

Composition	W₁ (g)	W₂ (g)	Amount of absorbed (g)	% water absorption
100PS	1.0000	1.0025	0.0025	0.25
90/10PS/PVAc	1.0000	1.0098	0.0098	0.98
80/20PS/PVAc	1.0000	1.0317	0.0317	3.17
70/30PS/PVAc	1.0000	1.0600	0.0600	6.00
60/40PS/PVAc	1.0000	1.0750	0.0750	7.50
50/50PS/PVAc	1.0000	1.0880	0.0880	8.80
40/60PS/PVAc	1.0000	1.0923	0.0923	9.23
30/70PS/PVAc	1.0000	1.1201	0.1201	12.01
20/80PS/PVAc	1.0000	1.2320	0.2320	23.20
10/90PS/PVAc	1.0000	1.3580	0.3580	35.80
100PVAc	1.0000	1.0250	0.0250	2.50

Table 8: Sorption test in 0.05M Hydrochloric acid for PS/PVAc blends without filler

Composition	W ₁ (g)	W ₂ (g)	Amount of absorbed (g)	% water absorption
100PS	1.0000	1.0013	0.0013	0.13
90/10PS/PVAc	1.0000	1.0085	0.0085	0.85
80/20PS/PVAc	1.0000	1.0220	0.0220	2.20
70/30PS/PVAc	1.0000	1.0316	0.0316	3.16
60/40PS/PVAc	1.0000	1.0475	0.0475	4.75
50/50PS/PVAc	1.0000	1.0632	0.0632	6.32
40/60PS/PVAc	1.0000	1.0800	0.0800	8.00
30/70PS/PVAc	1.0000	1.0917	0.0917	9.17
20/80PS/PVAc	1.0000	1.0999	0.0999	9.99
10/90PS/PVAc	1.0000	1.2019	0.2019	20.19
100PVAc	1.0000	1.0218	0.0218	2.18

Table 9: Sorption test in 0.05M Sodium hydroxide for PS/PVAc blends without filler

Composition	W₁ (g)	W₂ (g)	Amount of absorbed (g)	% water absorption
100PS	1.0000	1.0001	0.0001	0.01
90/10PS/PVAc	1.0000	1.0008	0.0008	0.08
80/20PS/PVAc	1.0000	1.0009	0.0009	0.09
70/30PS/PVAc	1.0000	1.0015	0.0015	0.15
60/40PS/PVAc	1.0000	1.0020	0.0020	0.20
50/50PS/PVAc	1.0000	1.0025	0.0025	0.25
40/60PS/PVAc	1.0000	1.0028	0.0028	0.28
30/70PS/PVAc	1.0000	1.0031	0.0031	0.31
20/80PS/PVAc	1.0000	1.0035	0.0035	0.35
10/90PS/PVAc	1.0000	1.0038	0.0038	0.38
100PVAc	1.0000	1.0005	0.0005	0.05

Table 10: Sorption test in 0.05M Sodium hydroxide for PS/PVAc blends with α - cellulose filler

Composition	W1 (g)	W2 (g)	Amount of absorbed (g)	% water absorption
100PS	1.0000	1.0002	0.0002	0.02
90/10PS/PVAc	1.0000	1.0011	0.0011	0.11
80/20PS/PVAc	1.0000	1.0025	0.0025	0.25
70/30PS/PVAc	1.0000	1.0060	0.0062	0.69
60/40PS/PVAc	1.0000	1.0075	0.0075	0.75
50/50PS/PVAc	1.0000	1.0087	0.0087	0.87
40/60PS/PVAc	1.0000	1.0090	0.0090	0.90
30/70PS/PVAc	1.0000	1.0120	0.0120	1.20
20/80PS/PVAc	1.0000	1.0250	0.0250	2.50
10/90PS/PVAc	1.0000	1.0320	0,0320	3.20
100PVAc	1.0000	1.0008	0.0008	0.08

4.2 Density of the pure and α -cellulose filled PS/PVAc blends

Table 11 gives the density of unfilled PS/PVAc polymer blends, while table 12 gives the density of filled PS/PVAc polymer blends.

From tables 11 and 12, it is evident that α -cellulose filler increase the density of the blends and that in 30/70%, 20/80% and 10/90%, PS/PVAc blends the densities are higher than the other compositions. There is an increase in density with filler content. The low densities of 60/40%, 50/50%, PS/PVAc is due to low compatibility of the blends. This representation can be clearly observed in figure 11 which shows the variation of the density of pure and reinforced blends with % composition

Table 11: Density of unfilled PS/PVAc Polymer Blends

% compositions	Mass (g)	Density(g/cm³)
100PS	0.2900	0.8056
90/10,PS/PVAc	0.6121	1.7002
80/20,PS/PVAc	0.8272	2.2978
70/30,PS/PVAc	0.6370	1.7694
60/40,PS/PVAc	0.2540	0.7056
50/50,PS/PVAc	0.2613	0.7258
40/60, PS/PVAc	0.4000	1.1111
30/70,PS/PVAc	1.7028	4.7300
20/80,PS/PVAc	1.1000	3.0556
10/90,PS/PVAc	1.0908	3.0300
100 PVAc	0.2801	0.7780

Table 12: Density of filled PS/PVAc Polymer Blends

% compositions	Mass (g)	Density(g/cm³)
100PS	0.3000	0.8333
90/10,PS/PVAc	0.6225	1.7292
80/20,PS/PVAc	0.8513	2.3647
70/30,PS/PVAc	0.6415	1.7819
60/40,PS/PVAc	0.2450	0.6806
50/50,PS/PVAc	0.2618	0.7272
40/60, PS/PVAc	0.5092	1.4144
30/70,PS/PVAc	1.7630	4.8972
20/80,PS/PVAc	2.3172	6.4367
10/90,PS/PVAc	2.0182	5.6061
100 PVAc	0.2913	0.8092

The structures and the microstructures were confirmed by the comparative FTIR, XRD, and Optical microscopy analyses of the polymer blends with and without filler: PS-10 (wt%)/PVAC-90(wt%)], PS-20 (wt%)/PVAC-80 (wt%) and PS-30 (wt%)/PVAC-70 (wt%). The results of the FTIR spectral analysis of the polymer blends including the characteristic absorption bands and their assignments are summarized in Table I3

Table 13: Characteristics FTIR Absorption band and their assignments for 10%PS-90%PVAc, 20%PS-80%PVAc and 30%PS-70%PVAc Polymer blends with and without filler

S/NO	Band Assignment	Absorption band (cm-1)					
		10%PS-90%PVAc		20%PS- 80%PVAc		30%PS- 70%PVAc	
		WITH FILLER	WITHOUT FILLER	WITH FILLER	WITHOUT FILLER	WITHOUT FILLER	WITH FILLER
1	O-Hstr Intermolecular H bonding (b)	3336	-	3349.50	3348.54	3353.36	3348.54
2	C-Hstr (m) (aliphatic)	2924.18	2923.22	2924.18	2923.22	2923.22	2924.18
3	C-Hstr vib (m)	2853.78	2852.81	-	-	-	-
4	C-Hstr (w) in oldehydes	-	-	-	2728.40	-	-
5	P-Hstr (w)	-	-	-	-	2347.45	2356.13
6	COOstr vib (non-conjugated) in amides	-	1654.98	-	-	-	-
7	C-NO2str (w) (asymmetric)	1557.57	1571.07	-	-	-	-
8	NOOstr (w)	-	-	-	-	1560.46	1559.50
9	C-Hbend vibration (w) in CH2	1464.02	1460.16	1460.16	1462.09	1462.09	1457.27
10	C-Hbend vib (w) in CH3	1377.22	1376.26	1376.26	1377.22	1376.26	1375.29
11	C-O-Cstr (w) vib. in ester	1193.98	1195.91	1199.76	1148.65	1190.12	1193.98
12	C-OHstr (w) in alcohol	-	-	-	-	1117.79	-
13	C-OHstr (w) in alcohol	1043.52	1042.56	1045.45	1042.56	1042.56	1042.56
14	C-H out plane bending vibration in substituted benzene	812.06	811.09	812.06	813.02	811.09	811.09
15	C-H out of plane deformation in substituted benzene	-	-	720.44	721.40	-	-
16	C-H twisting in ethylene	486.08	493.79	484.15	415.67	484.15	487.04

Table 14: Showing comparative XRD, microscopic and FTIR Analyses

Sample	2 θ (degree)	D (Å)	I _{max}	α_c (%)	D (Å)		Absorption Index (%)
					XRD	Particle size (μm) microscopy	
10% PS- 90% PVAc WITHOUT FILLER	22.19 32.97 45.93	4.00616 2.71626 1.97581	134.0 337.9 70.1	84.2	11.44	55.77	52.0
10% PS- 90% PVAc WITH FILLER	22.55 34.5 40.5 47.0 54.5 64.5	3.94224 2.28367 2.66545 3.07077 3.52609 4.10937	330.7 25 40 25 20 30	38.4	24.96	69.56	48.0
20% PS- 80% PVAc WITHOUT FILLER	26.21 28.81 29.69 30.86 33.33 34.02 40.82 47.11 58.03 64.74	3.39937 3.09864 3.00906 2.89741 2.68809 2.63493 2.2107 1.92892 1.58941 1.4398	71.7 29.9 25.7 5.6 36.8 69.4 7.0 34.9 7.3 14.2	64.6	20.5	47.39	56.0
20% PS- 80% PVAc WITH FILLER	33.5 34.21 41.26 47.09 58 63.86	2.67478 2.62097 2.18787 1.92997 1.59006 1.4576	68.5 46.5 5.8 24.8 5.5 1.8	34.8	33.01	117.14	51.0
30% PS- 70% PVAc WITHOUT FILLER	22.57 31.47 40.15 46.17 63.87	3.94 2.84259 2.24565 1.96606 1.45731	229.5 19.9 22.6 12.1 20.4	48.0	34.7	35.72	46.0
30% PS- 70% PVAc WITH FILLER	22.77 64.33	3.90515 1.44797	189.9 32.2	31.37	12.42	27.44	49.00

Figures 1 and 2 gives the stress versus strain results for PS/PVAc blends without and with filler respectively. The filler effect had adverse effect on the mechanical properties of the blends. However, the plot of load versus extension for the two systems (Figures 3 and 4) when compared with figure 5, 6, 7 and 8 i.e. with the tensile strength versus composition and % elongation versus compositions reveals the different interactions manifest in the mode of aggregation due to polymer-polymer and polymer-filler compatibility.

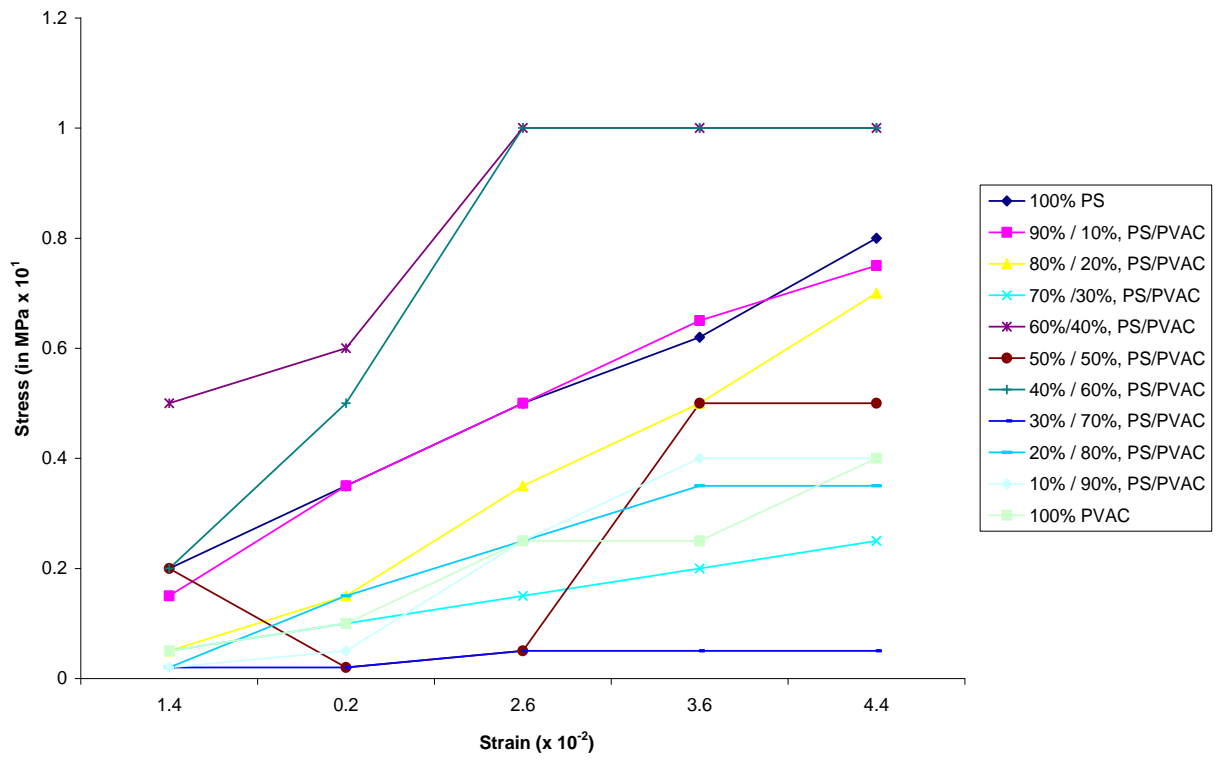


Fig.1 Plot of Stress versus strain for PS/PVAc Blend without filler

Fig. 1.2 Stress versus Strain for PS/PVAC blend with 5g alpha cellulose filler content

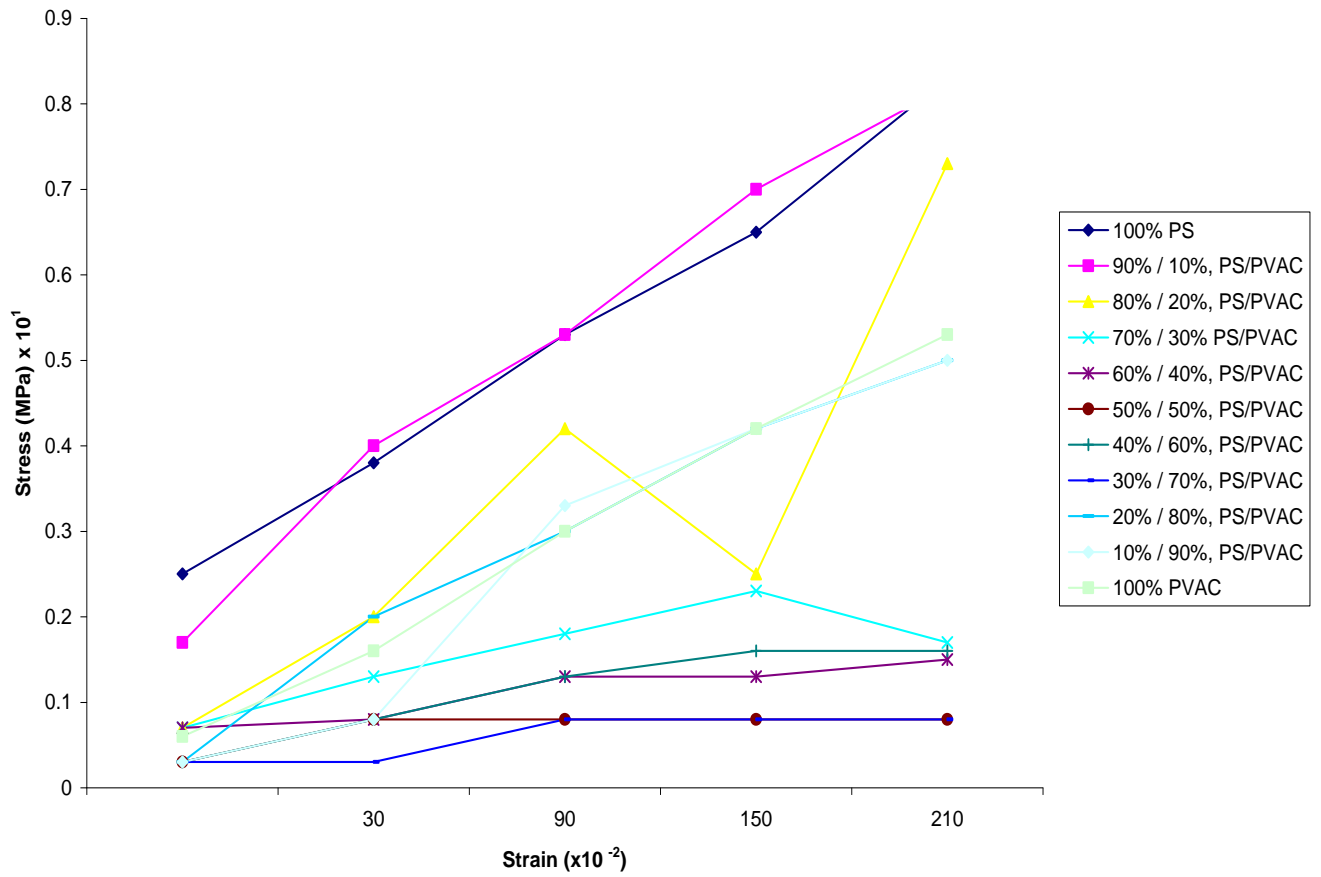


Fig. 2 Plot of Stress versus strain for PS/PVAc Blend with 5g alpha cellulose filter content

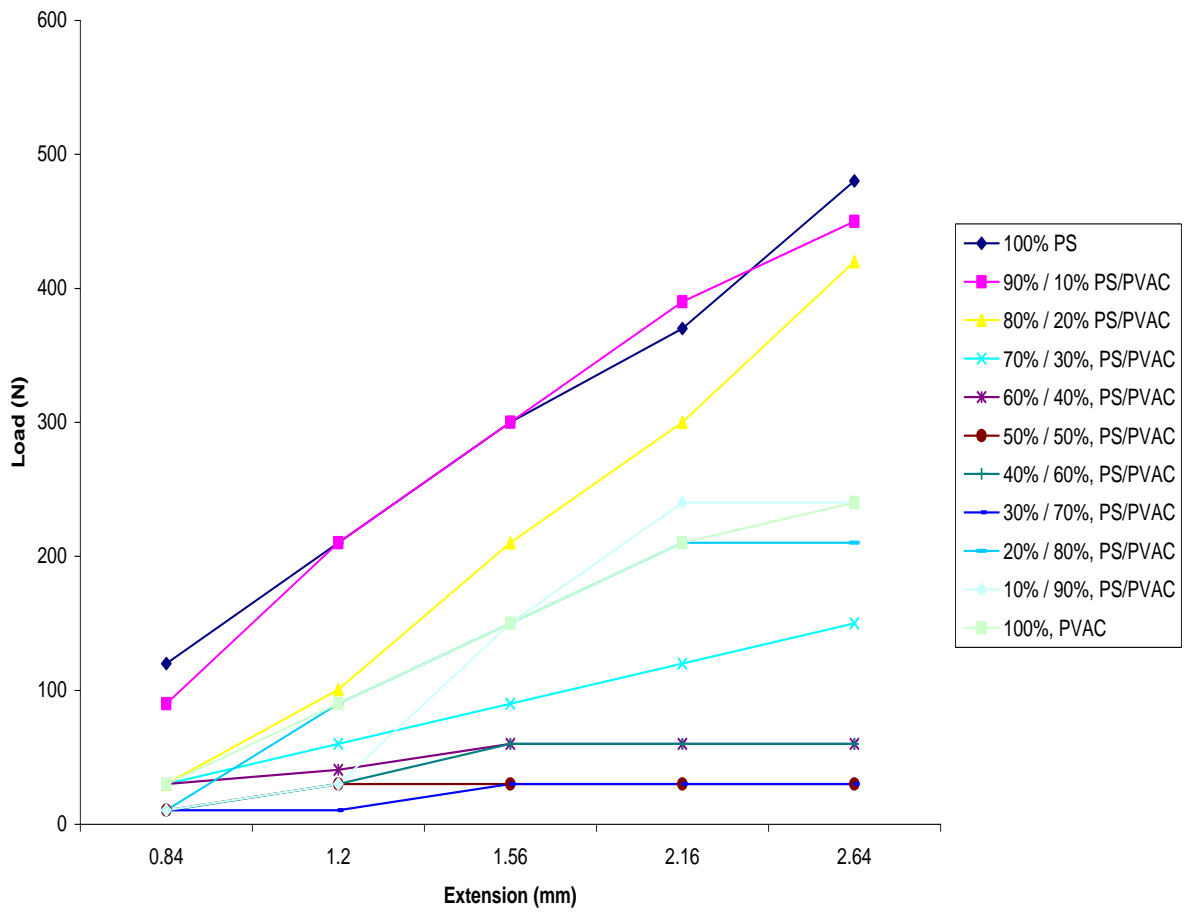


Fig. 3 Plot of Load Vs Extension for P.S/PVAc Blend without filler

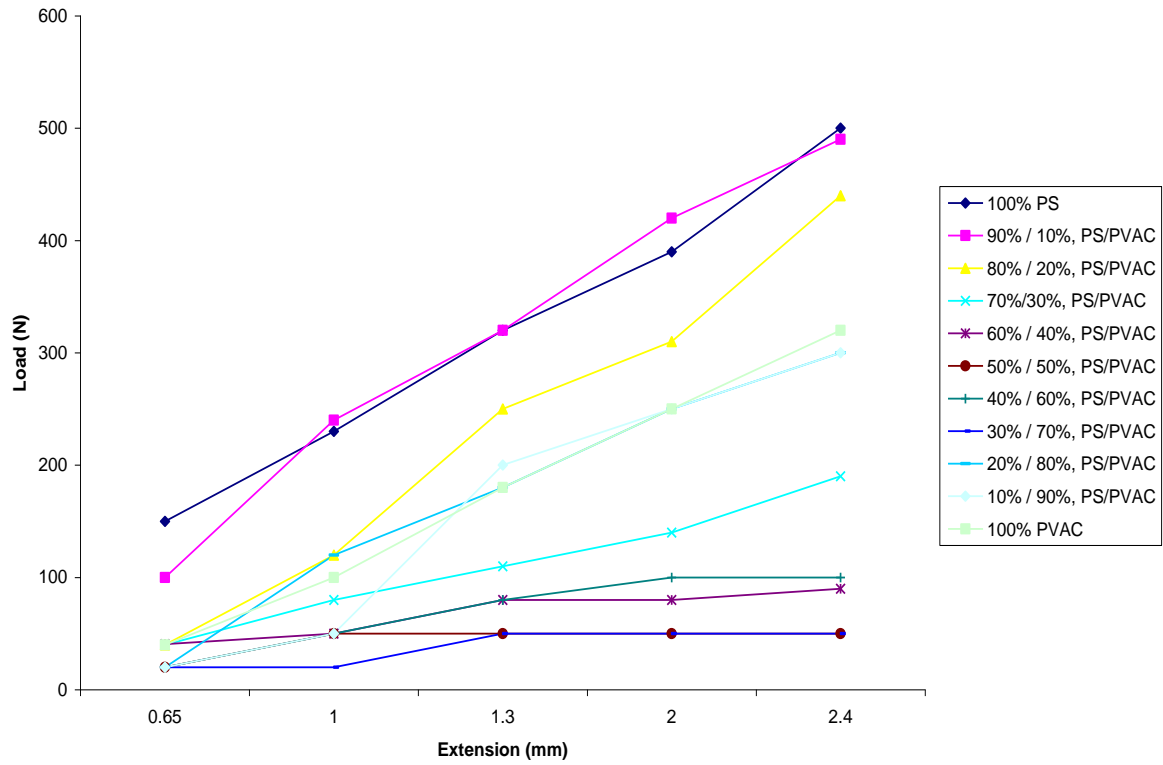


Fig.. 4 Plot of Load Vs Extension for PS/PVAc Blend with 5g Alpha Cellulose Filler Content

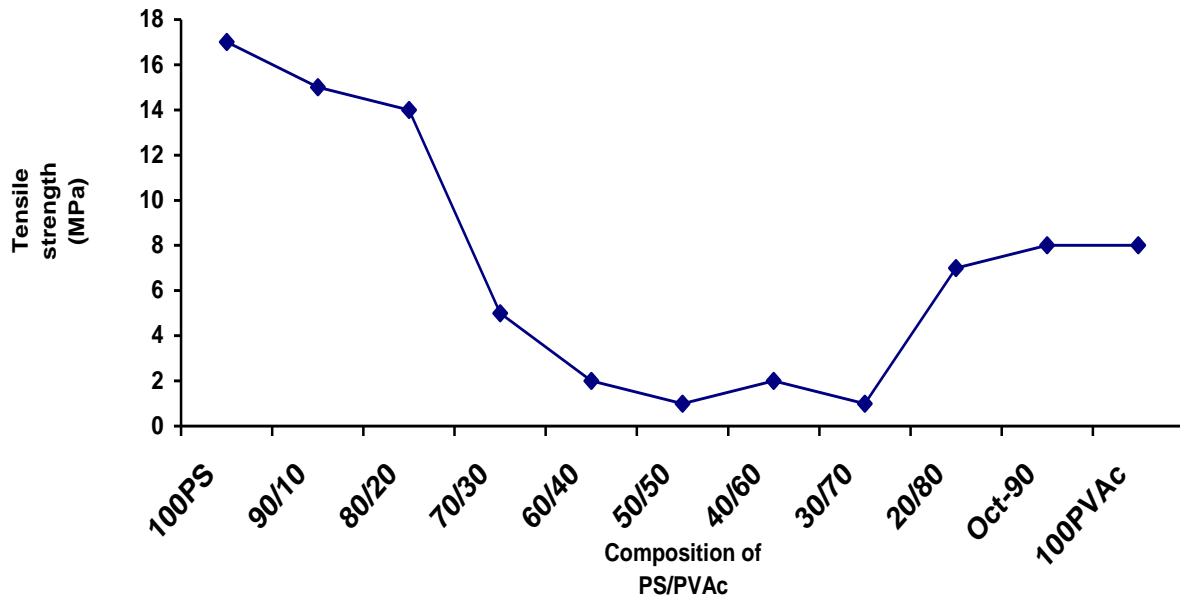


Fig.5 Plot of Tensile strength vs composition for PS/PVAc blend without filler

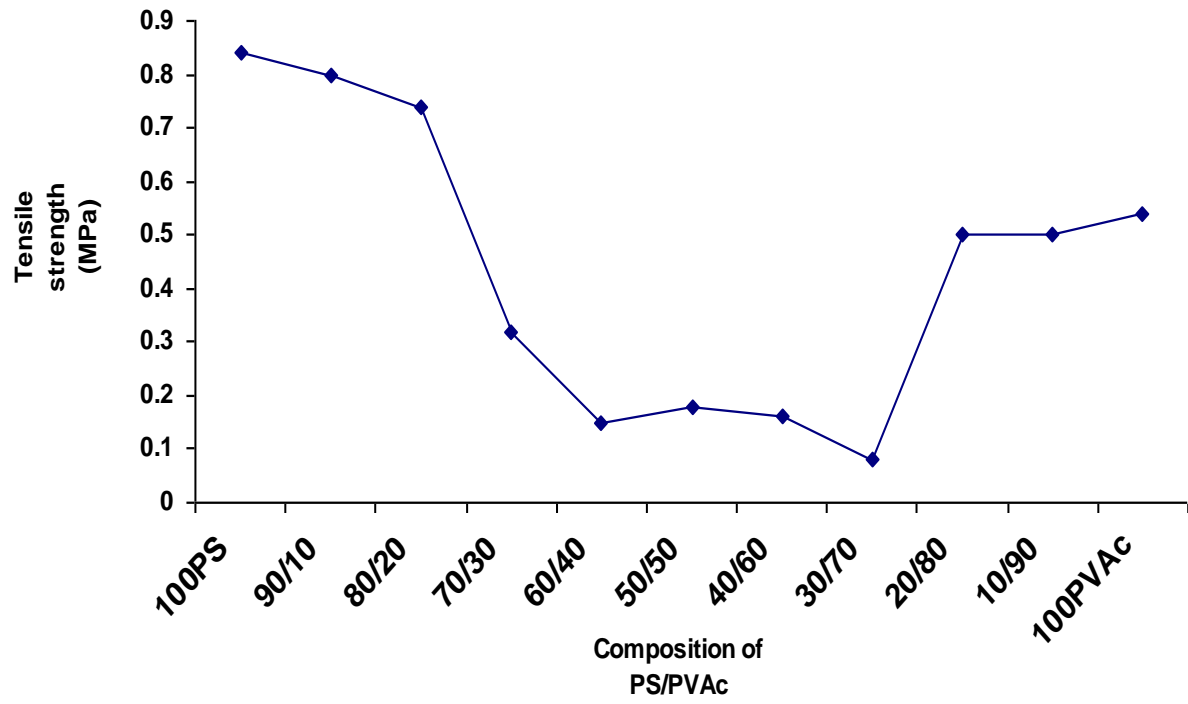


Fig. 6 Plot of Tensile strength vs composition for PS/PVAc blend with filler

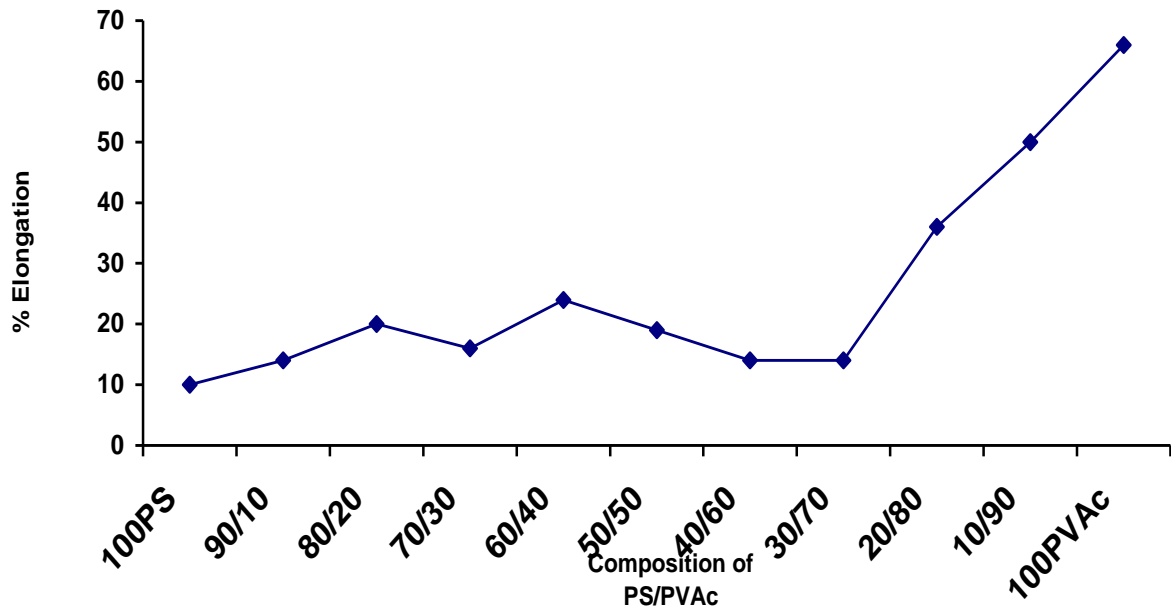


Fig.7 Plot of % elongation vs composition for PS/PVAc blend without filler

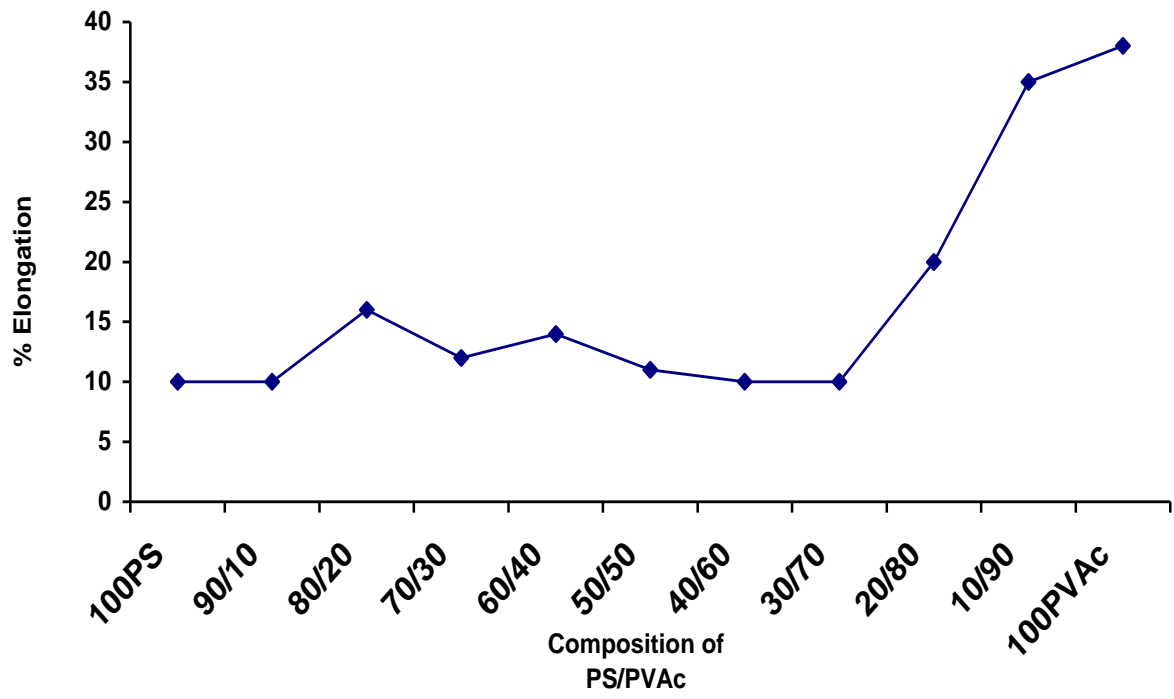


Fig.8 Plot of % elongation vs composition for PS/PVAc blend with filler

Figures 9 and 10 shows the variation in sorption for the different blends in water, 0.05M Hydrochloric acid, 0.05M sodium hydroxide and acetone. While, there's appreciable weight gain in water, HCl and NaOH. The blend showed weight loss when sorption test is carried out in acetone.

Also, density variations in blends (Figure 11) shows that the filler increases its density for virtually all the compositions

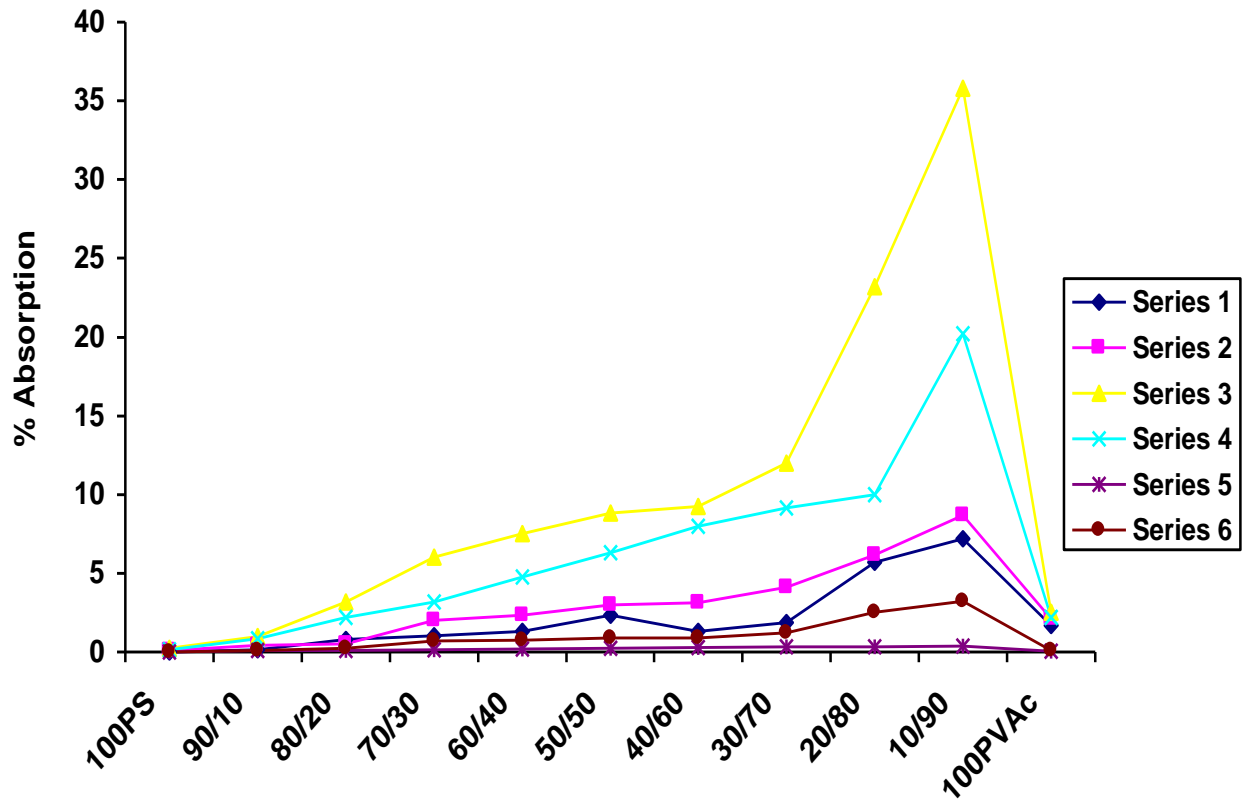


Fig. 9 Sorption test for PS/PVAc Blend in water, 0.05M Hydrochloric Acid, 0.05M Sodium Hydroxide (% weight gain)

Key:

Series 1: Sorption in water for unfilled PS/PVAc blend

Series 2: Sorption in water for filled PS/PVAc blend

Series 3: Sorption in 0.05M HCl for filled PS/PVAc blend

Series 4: Sorption in 0.05M HCl for unfilled PS/PVAc blend

Series 5: Sorption in 0.05M NaOH for unfilled PS/PVAc blend

Series 6: Sorption in 0.05M NaOH for filled PS/PVAc blend

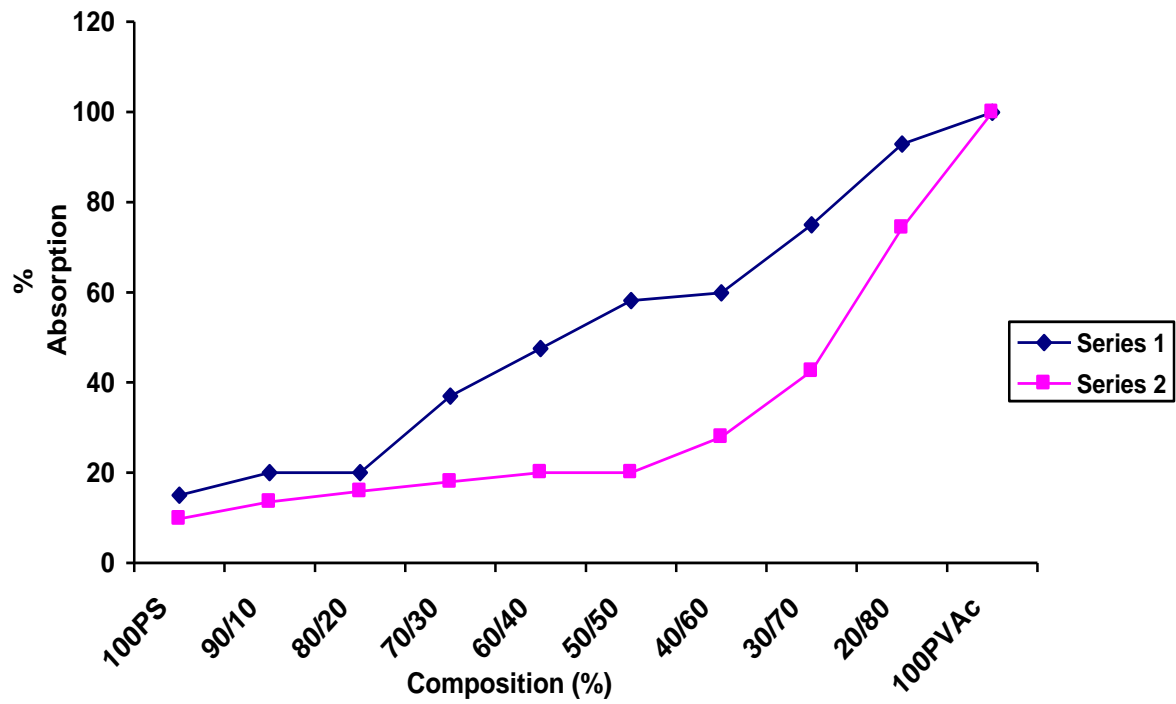


Fig. 10 sorption test for PS/PVAc in Acetone (negative % weight gain)

Key:

Series 1: Sorption in Acetone for unfilled PS/PVAc blend

Series 2: Sorption in Acetone for filled PS/PVAc blend

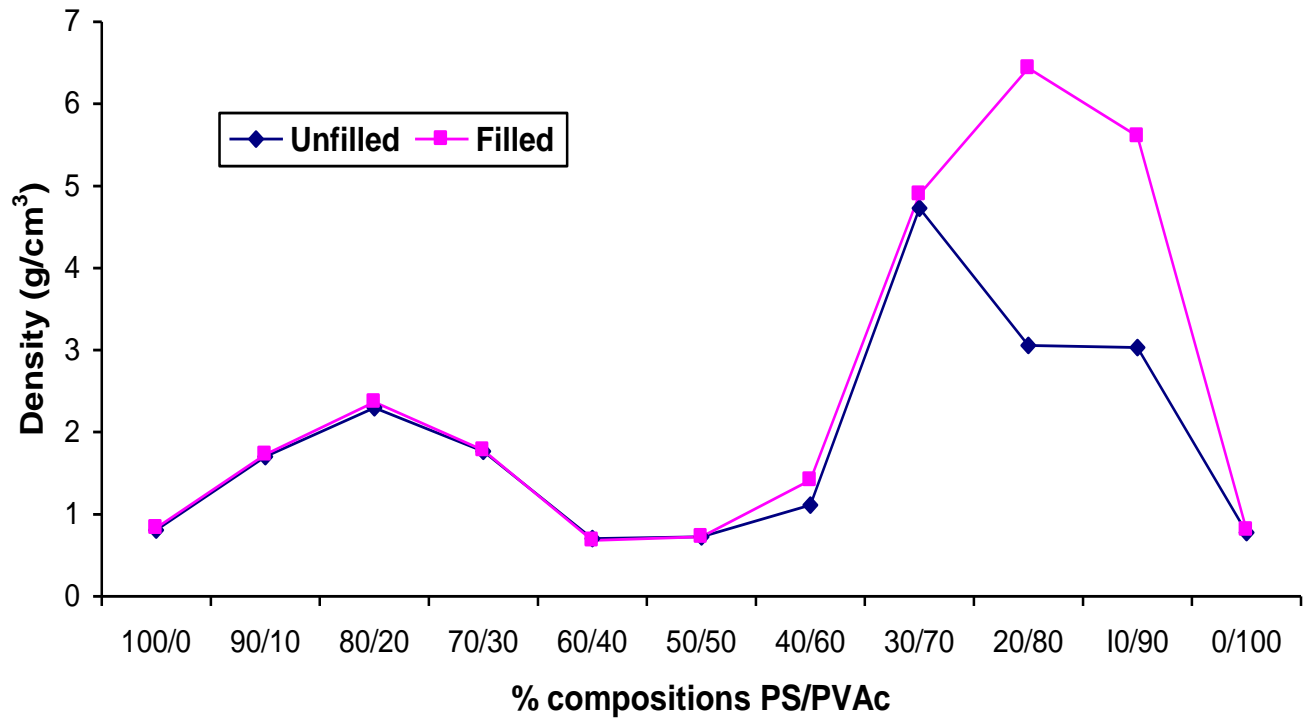


Fig. 11 Variation of Density of Unfilled and Filled PS/PVAc Polymer blends with % blend composition

The photomicrographs of all the PS/PVAc composition with and without filler are shown in Figures 12-31. In a comparative study the microstructure and surface topography of some blends are shown in Figures 32-37, while the Fourier Transform infrared spectra are as shown in Figures 38-43. All these studies have revealed to a large extent the morphological arrangements in the blends and the effect of the filler in altering micro-structural orientations. Also, the swelling kinetics, current voltage characteristics and Arrhenius plots for these blends monitored the effect of temperature on its environmental viability.

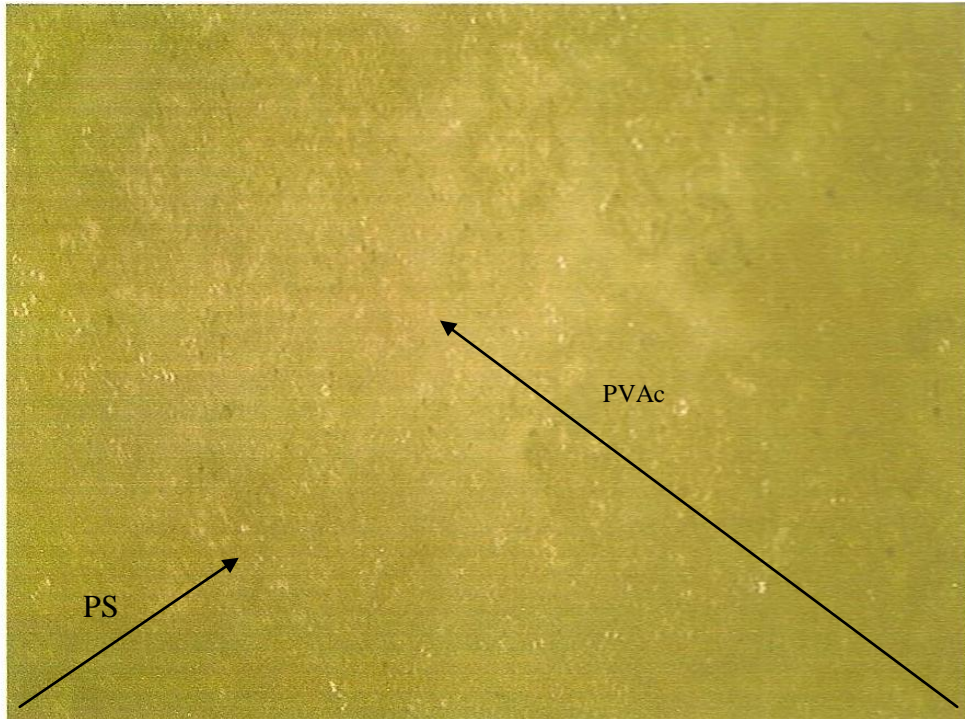


Fig. 12 Photomicrograph of 10% PS/90% PVAc blend without filler

X 1000 Magnification

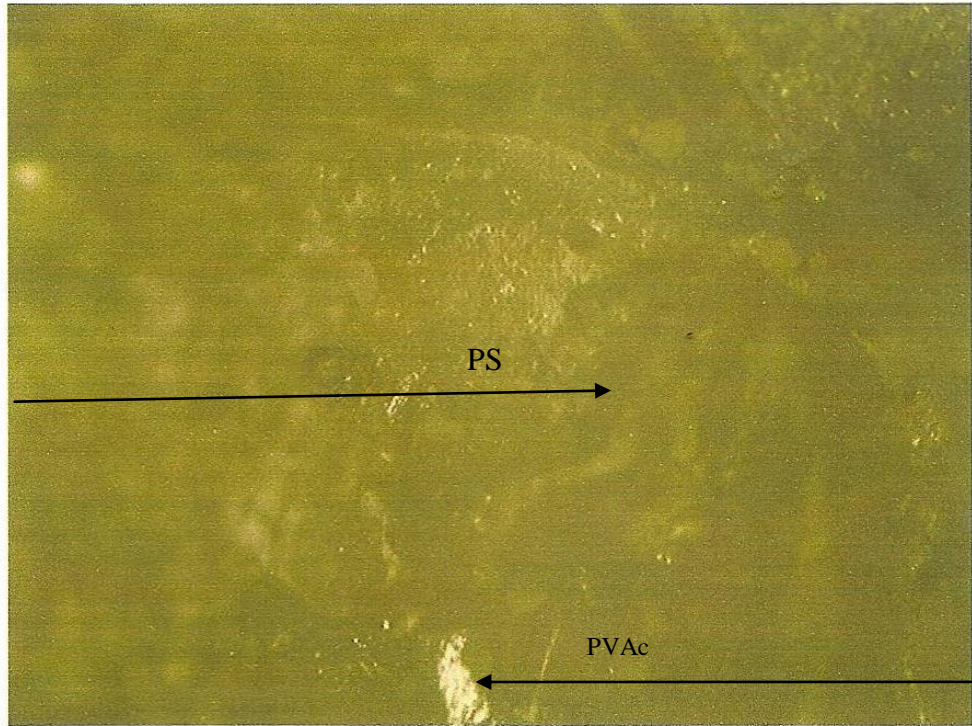


Fig. 13 Photomicrograph of 20% PS/80% PVAc blend without filler

X 1000 Magnification

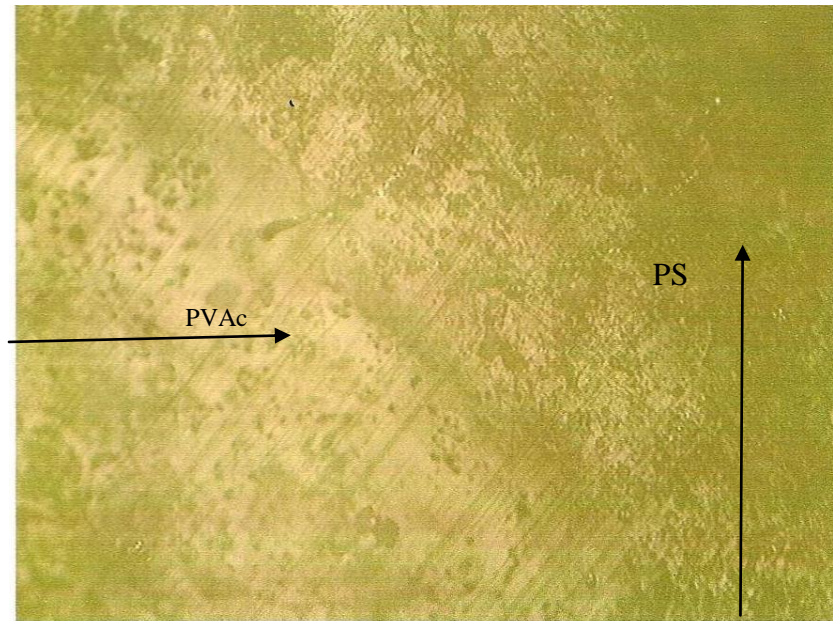


Fig. 14 Photomicrograph of 20% PS/80% PVAc blend with filler

X 1000 Magnification

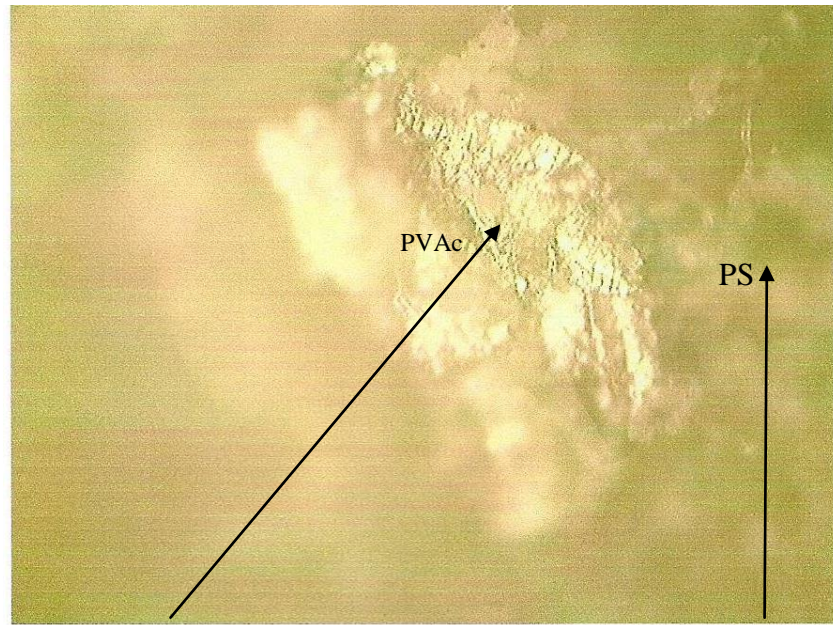


Fig. 15 Photomicrograph of 30% PS/70% PVAc blend without filler

X 1000 Magnification

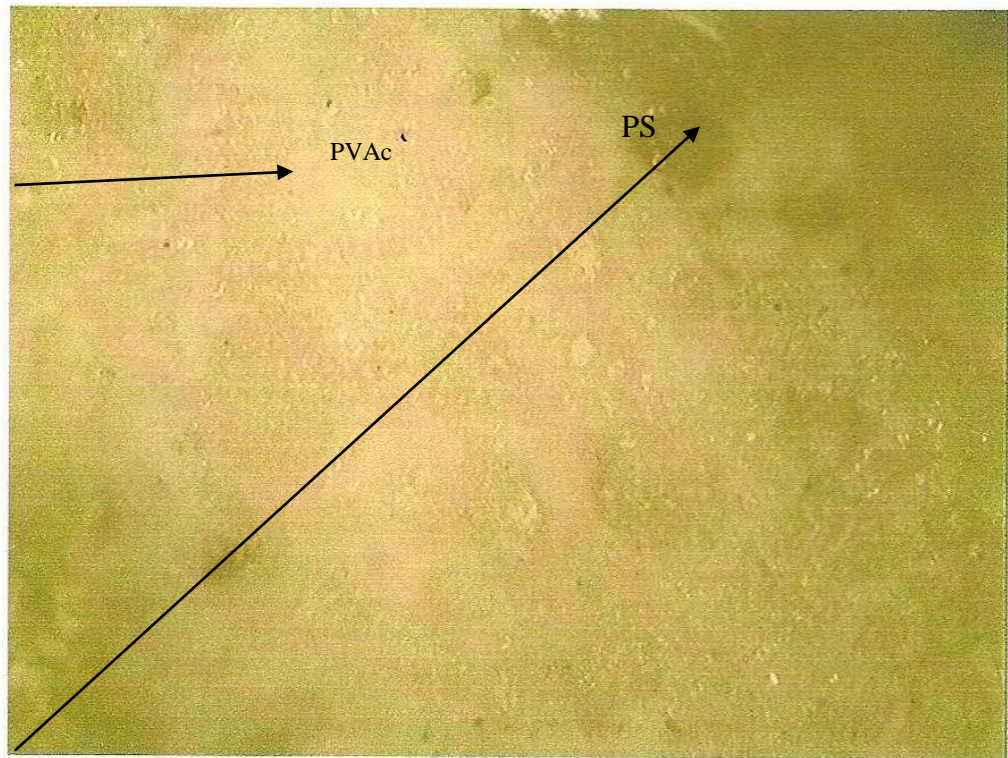


Fig. 16 Photomicrograph of 30% PS/70% PVAc blend with filler

X 1000 Magnification

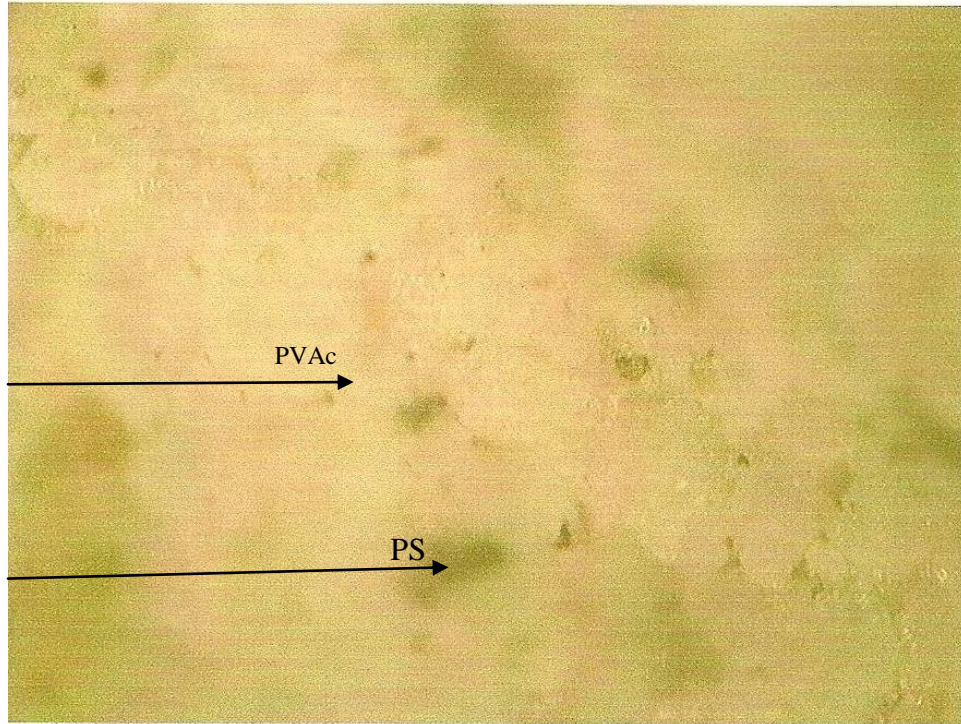


Fig. 17 Photomicrograph of 40% PS/60% PVAc blend without filler

X 1000 Magnification

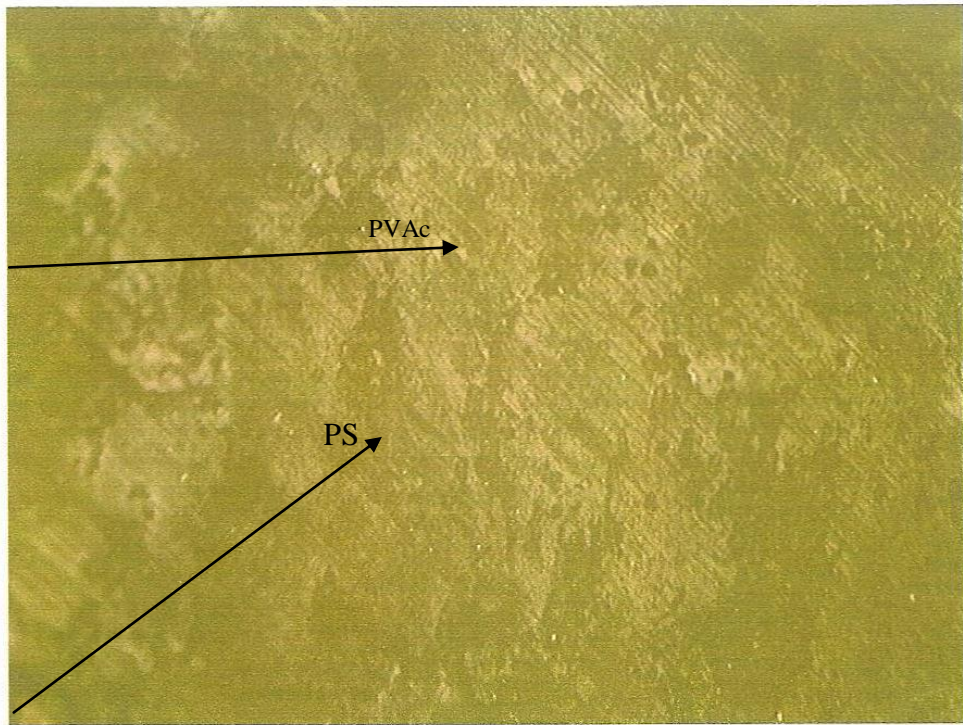


Fig. 18 Photomicrograph of 40% PS/60% PVAc blend with filler

X 1000 Magnification

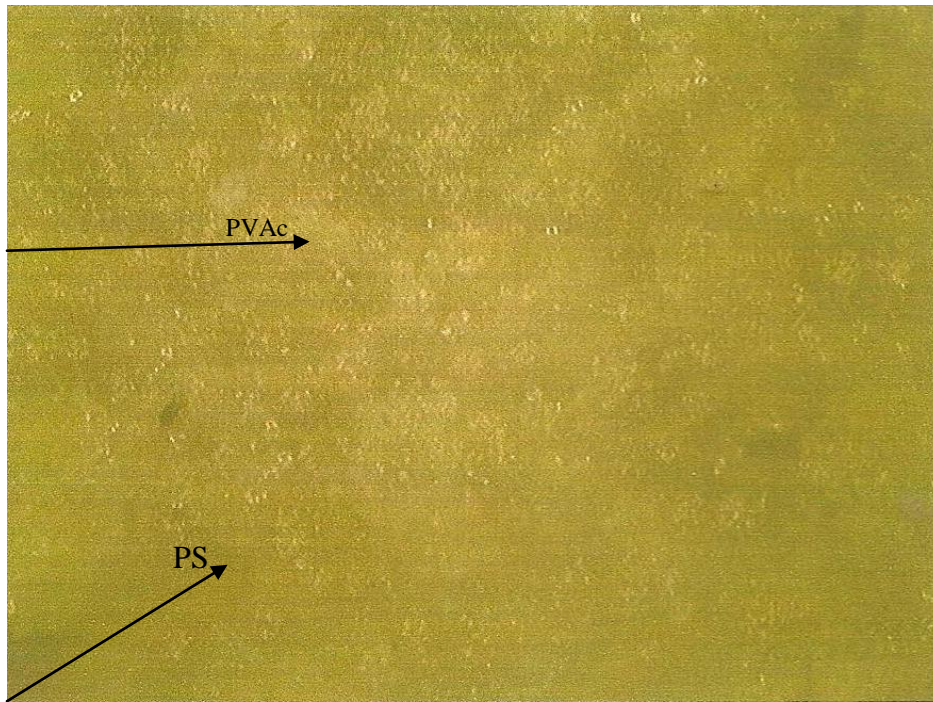


Fig. 19 Photomicrograph of 50% PS/50% PVAc blend without filler

X 1000 Magnification

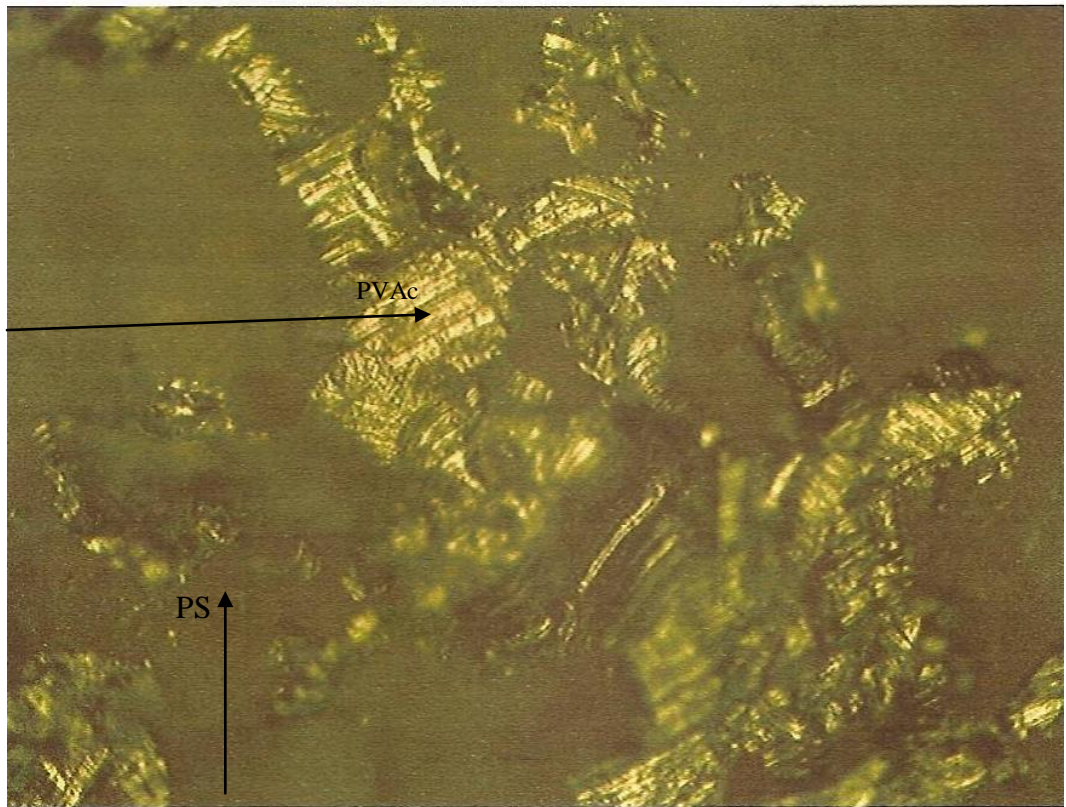


Fig. 20 Photomicrograph of 50% PS/50% PVAc blend with filler

X 1000 Magnification

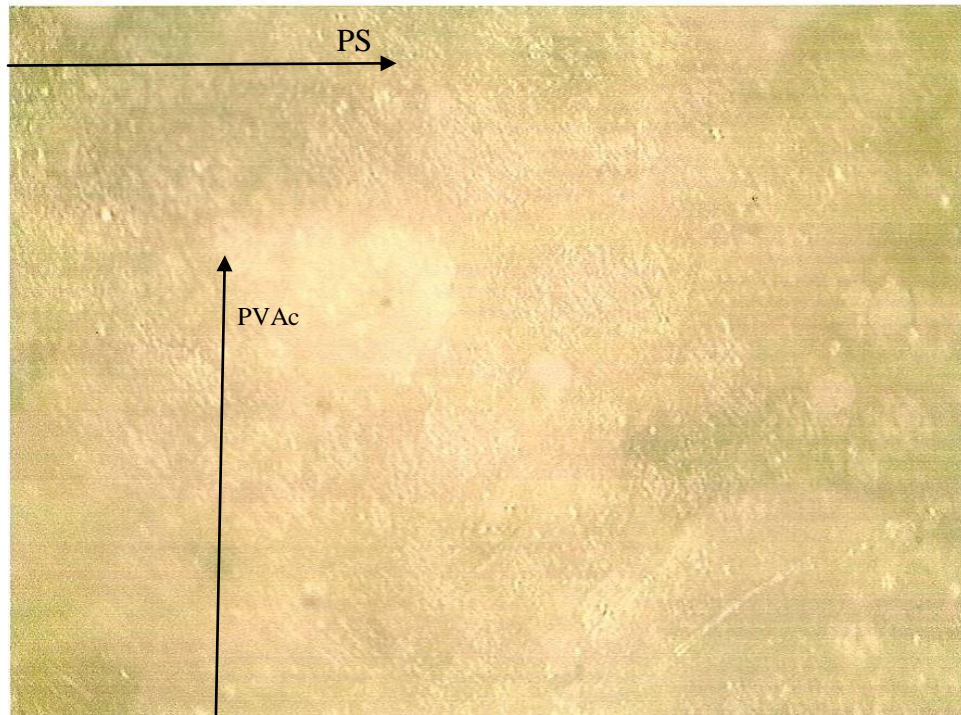


Fig. 21 Photomicrograph of 60% PS/40% PVAc blend without filler

X 1000 Magnification

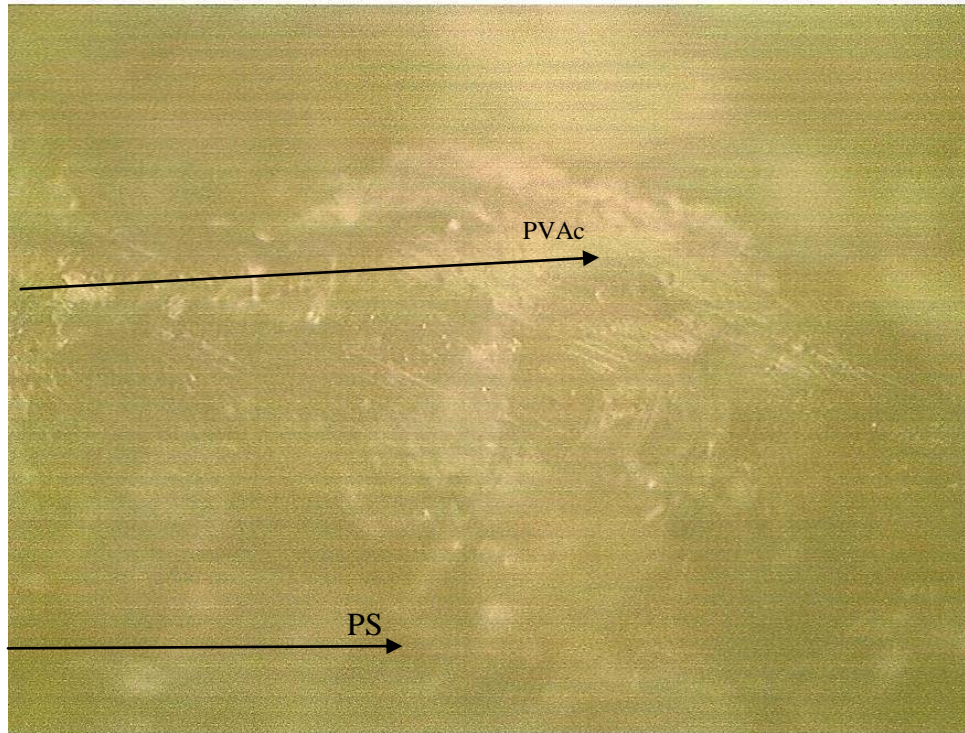


Fig. 22 Photomicrograph of 60% PS/40% PVAc blend with filler

X 1000 Magnification

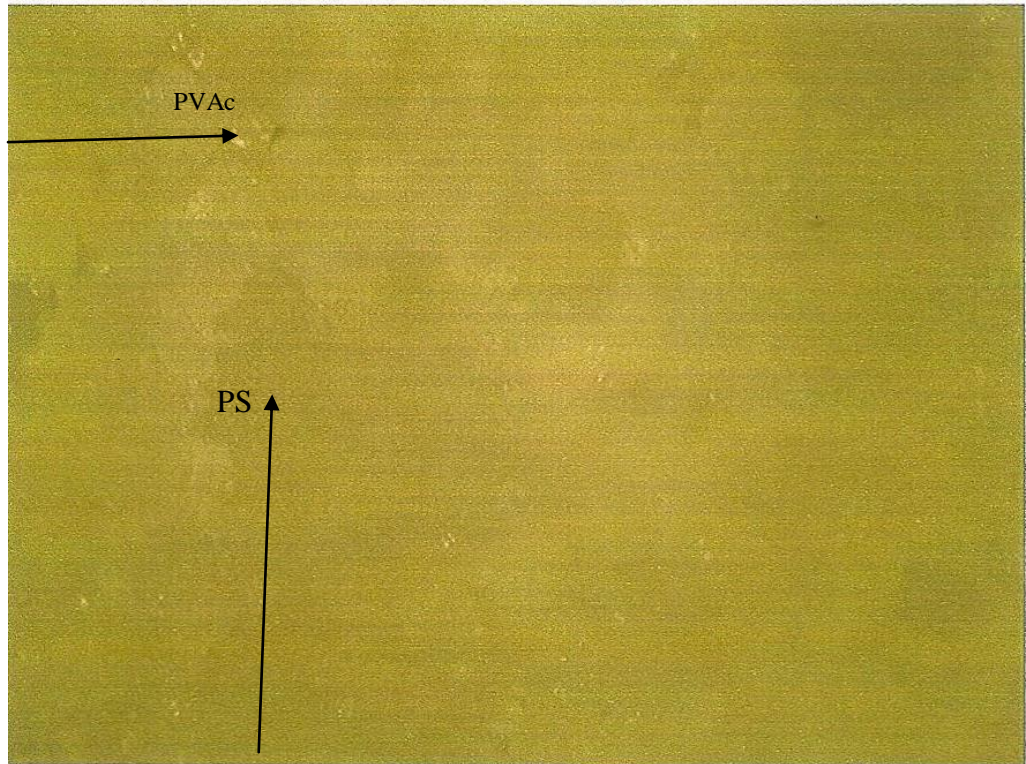


Fig. 23 Photomicrograph of 70% PS/30% PVAc blend without filler

X 1000 Magnification

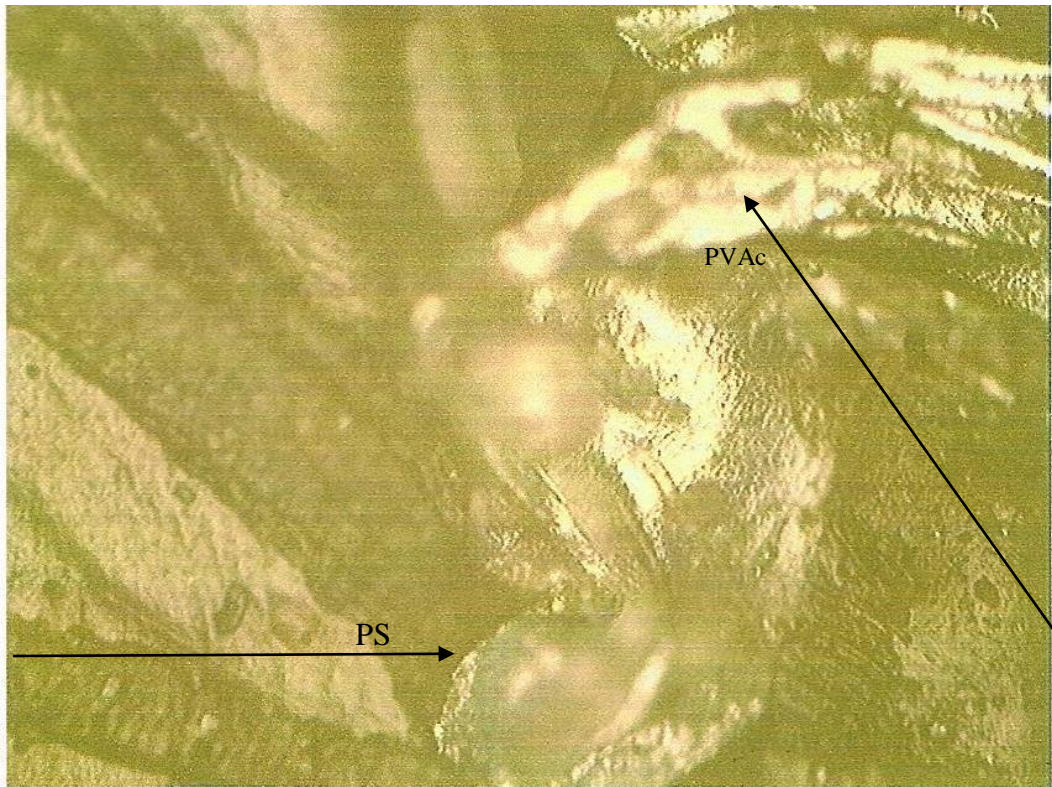


Fig. 24 Photomicrograph of 70% PS/30% PVAc blend with filler

X 1000 Magnification

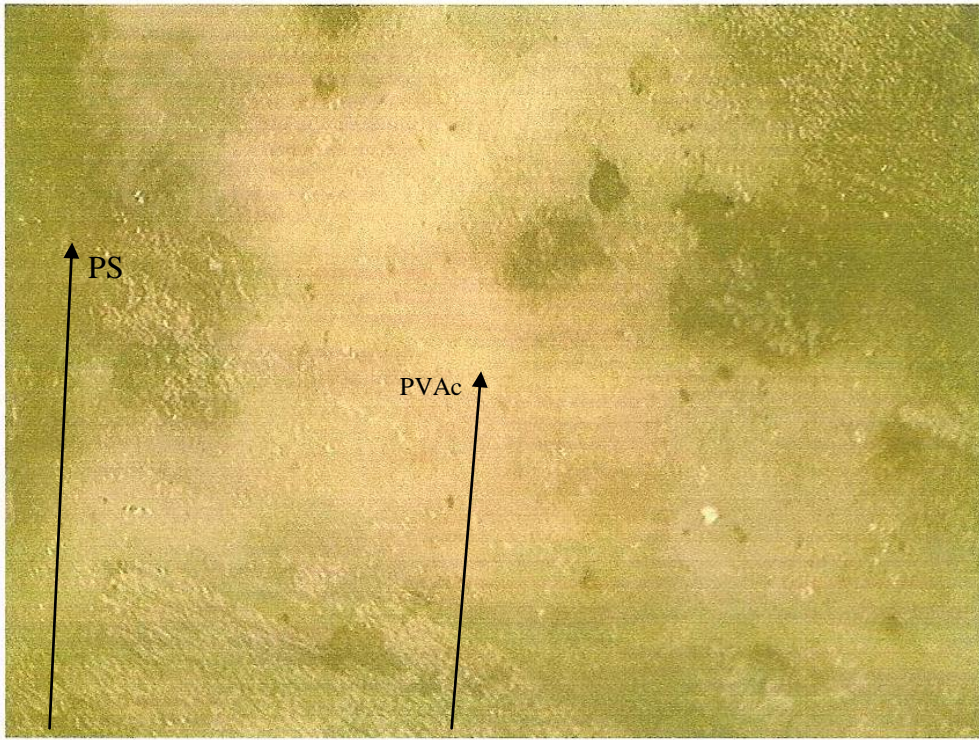


Fig. 25 Photomicrograph of 80% PS/20% PVAc blend without filler

X 1000 Magnification

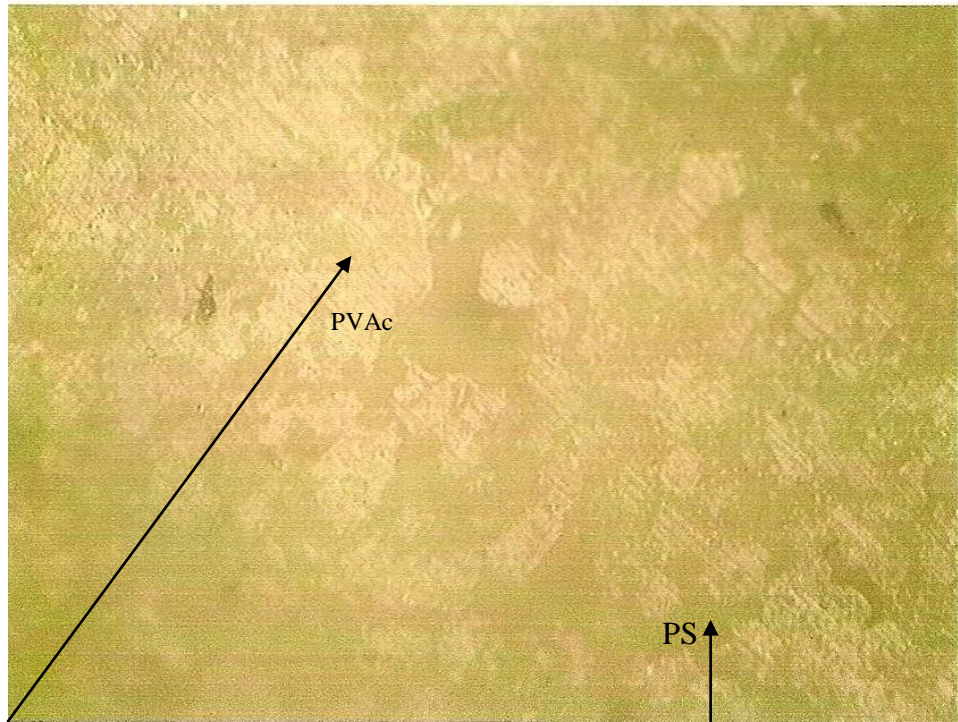


Fig. 26 Photomicrograph of 80% PS/20% PVAc blend with filler

X 1000 Magnification

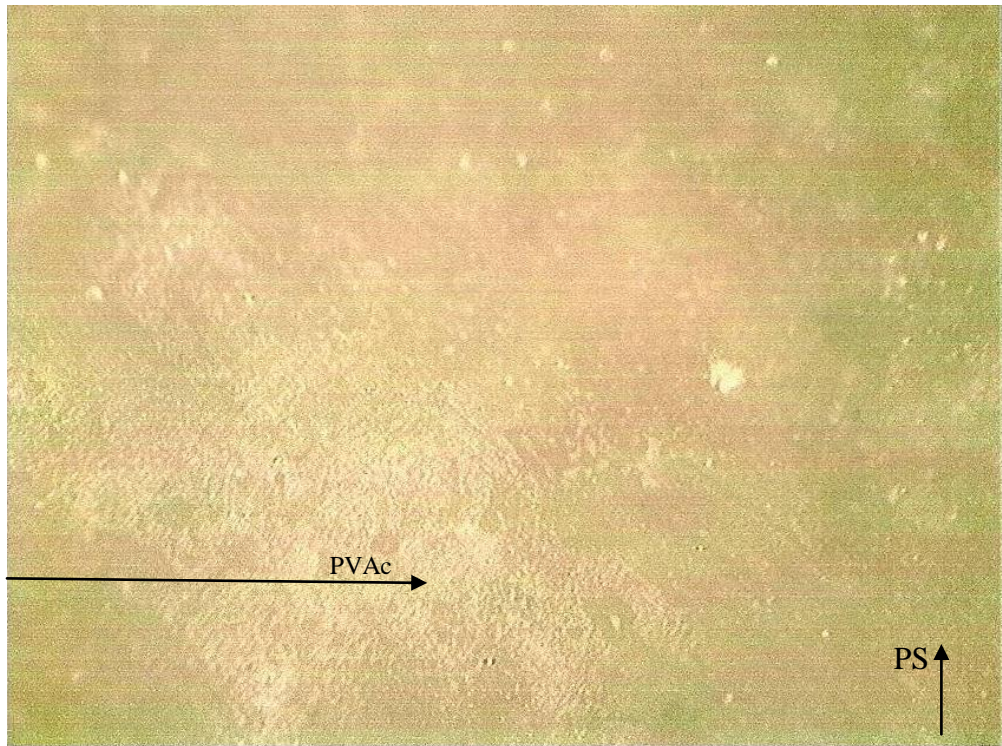


Fig. 27 Photomicrograph of 90% PS/10% PVAc blend without filler

X 1000 Magnification

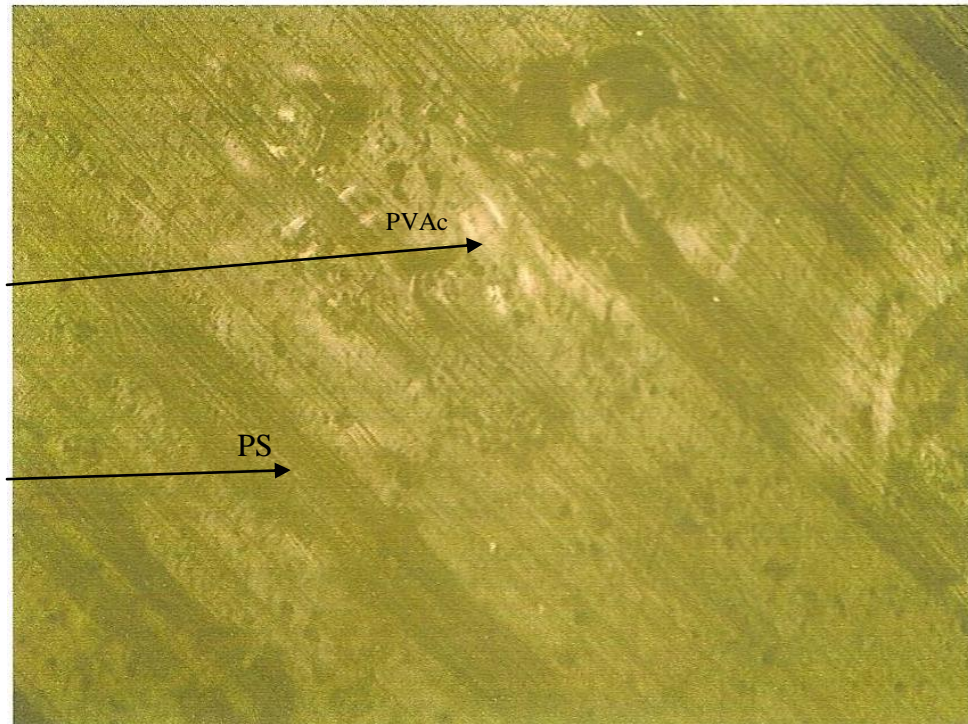


Fig. 28 Photomicrograph of 90% PS/10% PVAc blend with filler

X 1000 Magnification

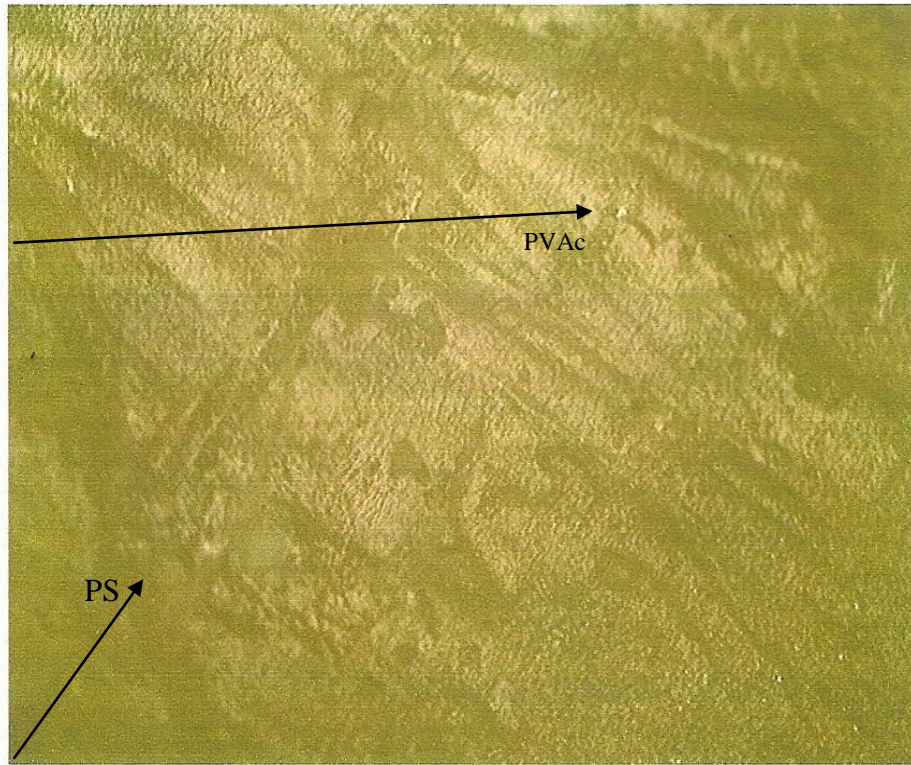


Fig. 29 Photomicrograph of 100% PS without filler

X 1000 Magnification

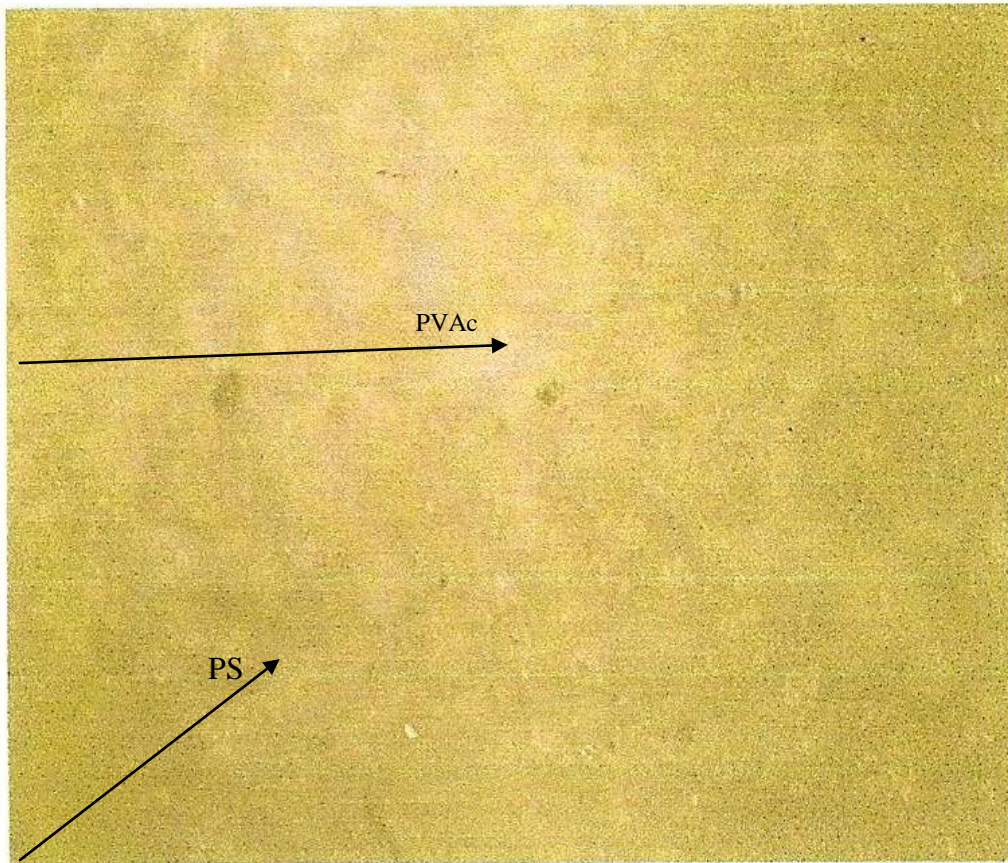


Fig.30 Photomicrograph of 100% PVAc with filler

X 1000 Magnification

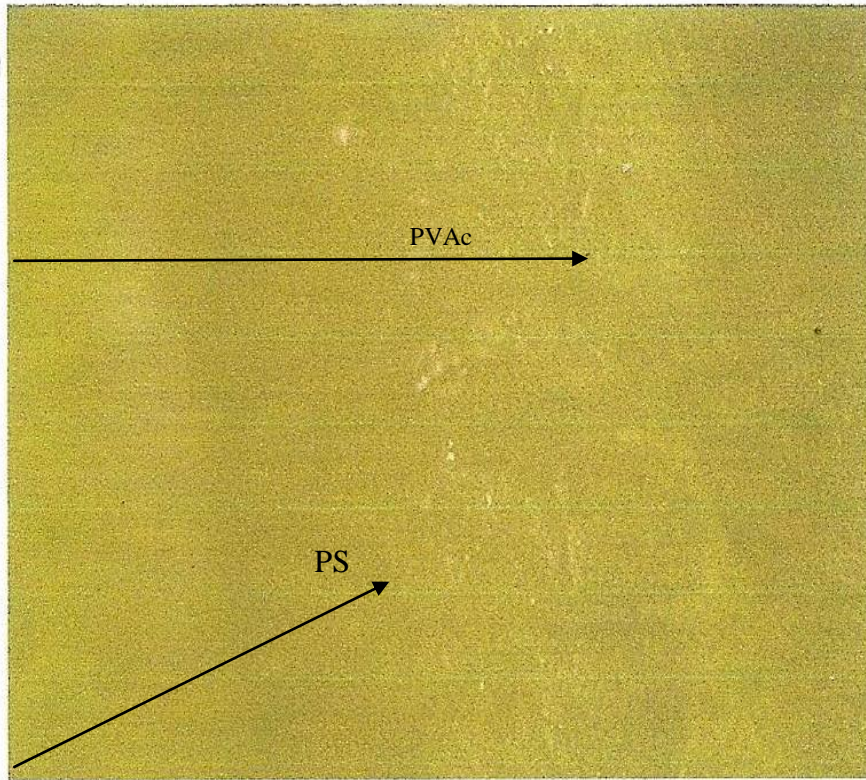


Fig.31 Photomicrograph of 100% PVAc without filler

X 1000 Magnification

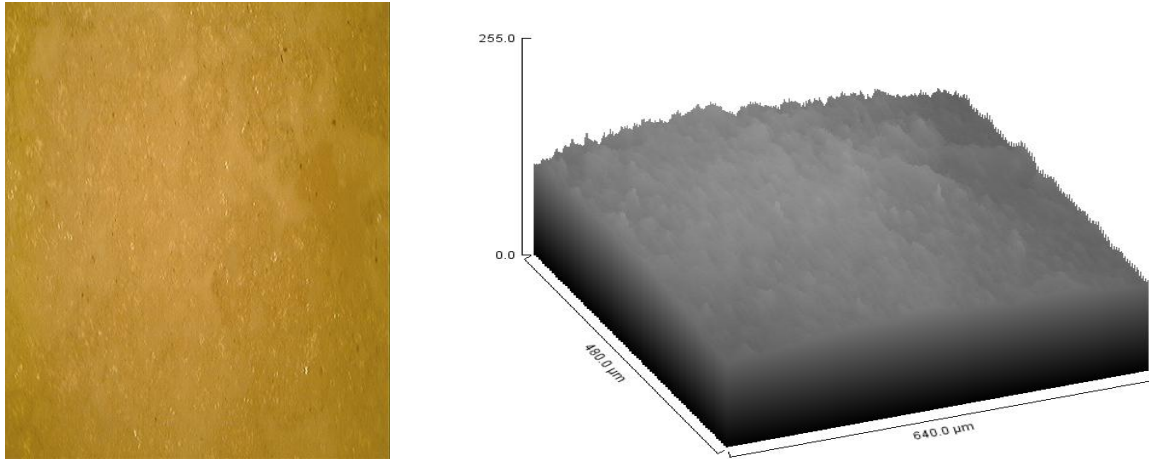


Figure32: Showing the microstructure and surface topography for 10%PS-90PVAc without filler

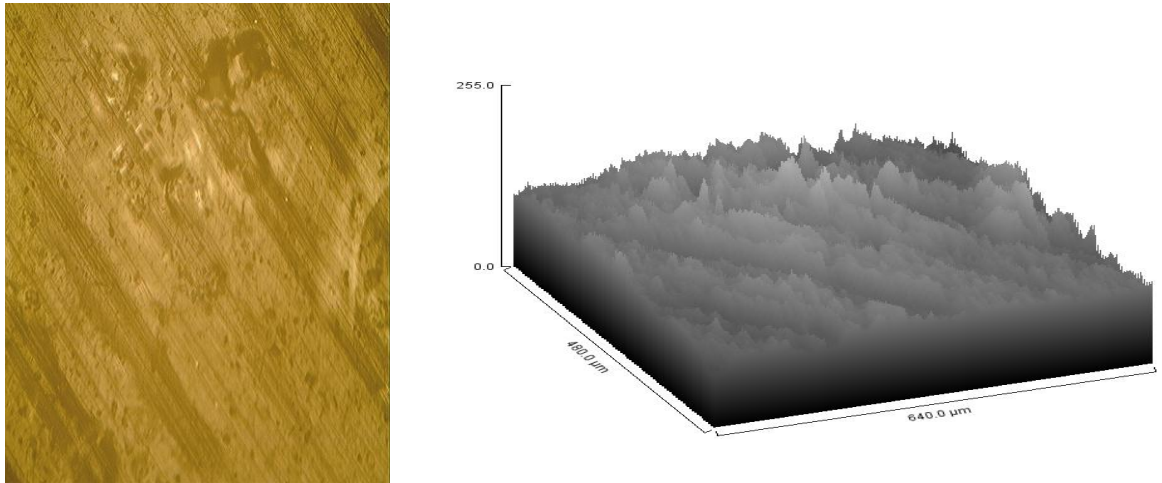


Figure 33: Showing the microstructure and surface topography for 10%PS-90%PVAc with filler

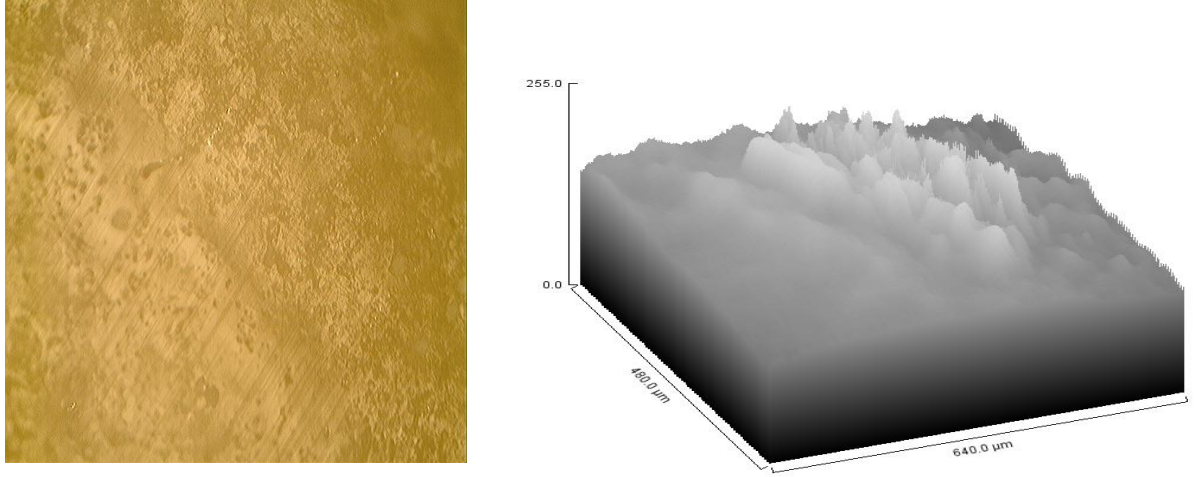


Figure 34: Showing the microstructure and surface topography for 20%PS-80%PVAc without filler

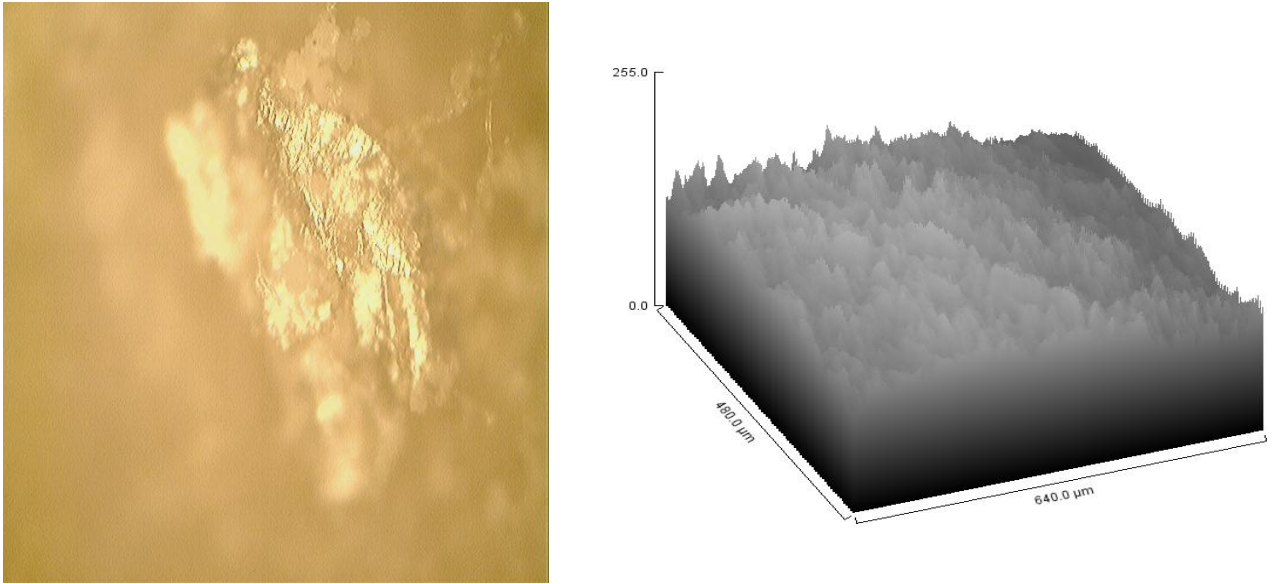


Figure 35: Showing the microstructure and surface topography for 20%PS-80%PVAc with filler

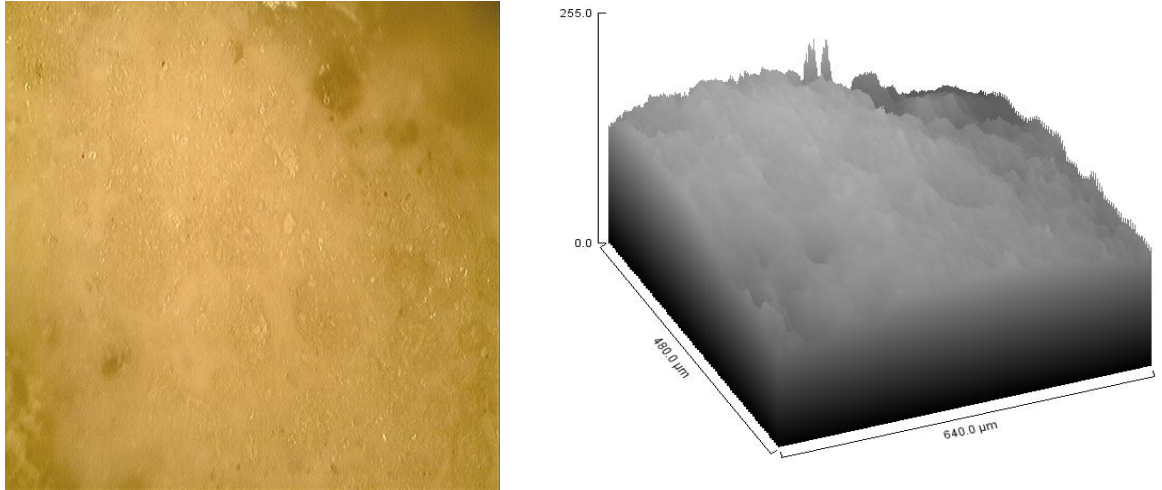


Figure 36: Showing the microstructure and surface topography for 30%PS-70%PVAc without filler

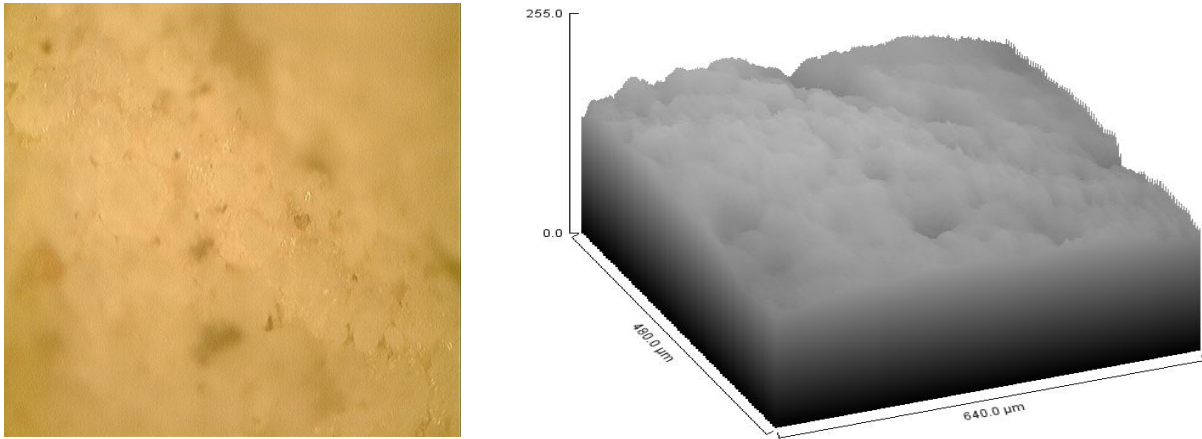


Figure 37: Showing the microstructure and surface topography for 30%PS-70%PVAc with filler

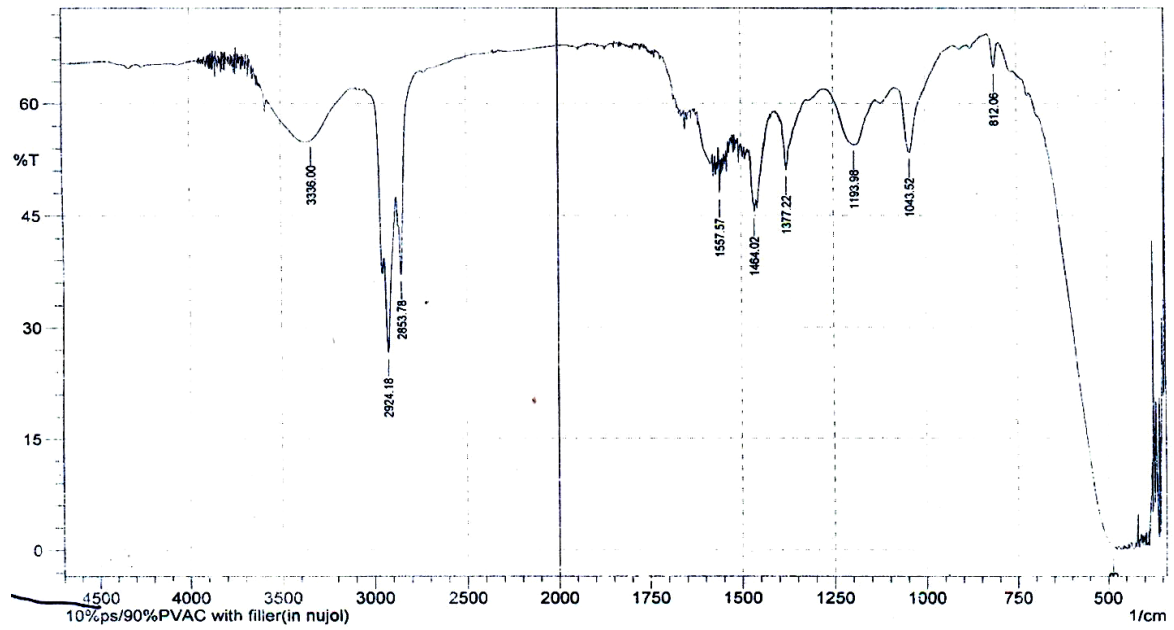


Figure 38: FTIR for 10% PS/90% PVAc with filler

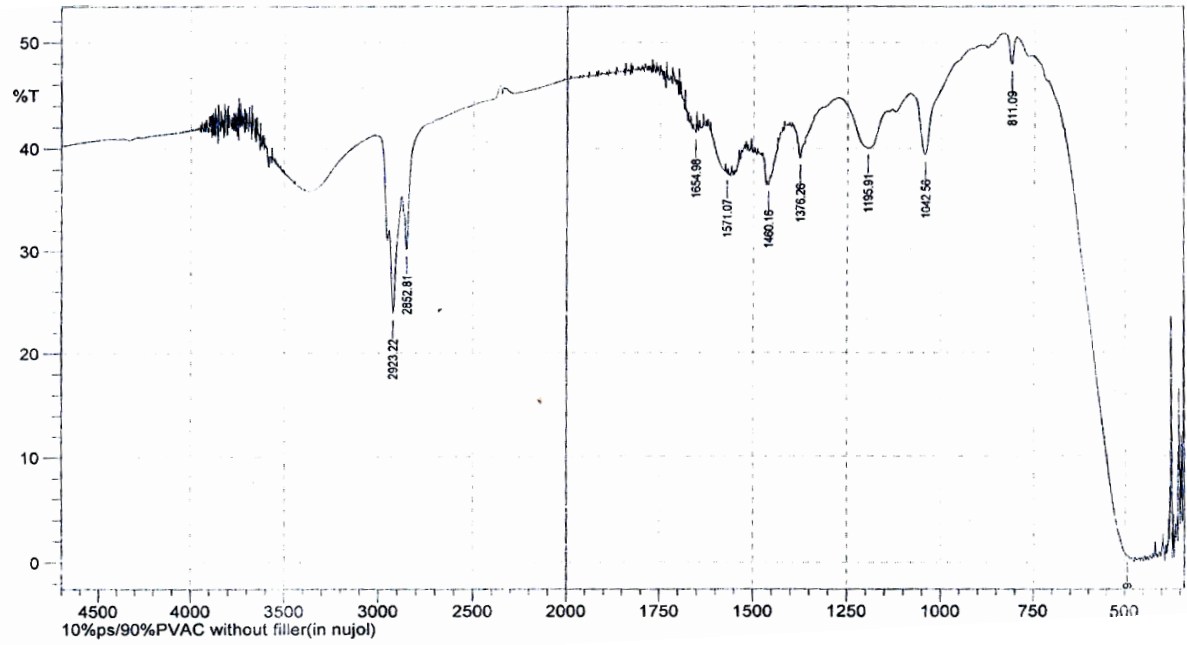


Figure 39: FTIR for 10% PS/90% PVAc without filler

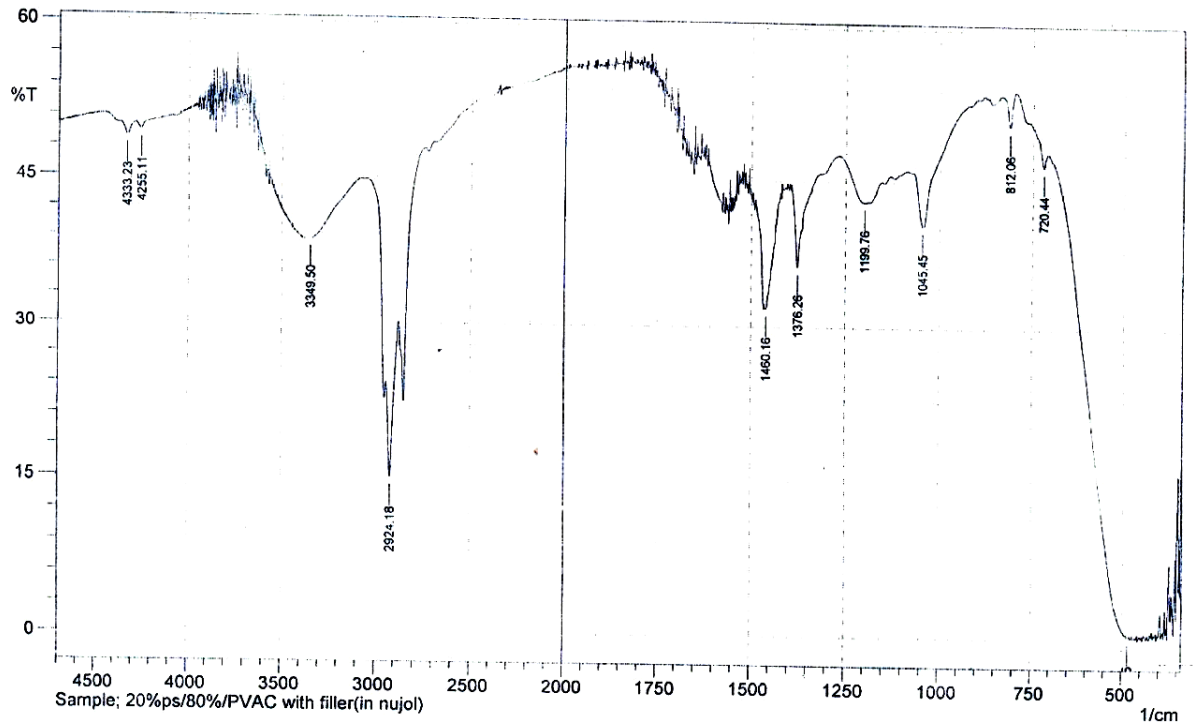


Figure 40: FTIR for 20% PS/80% PVAc without filler

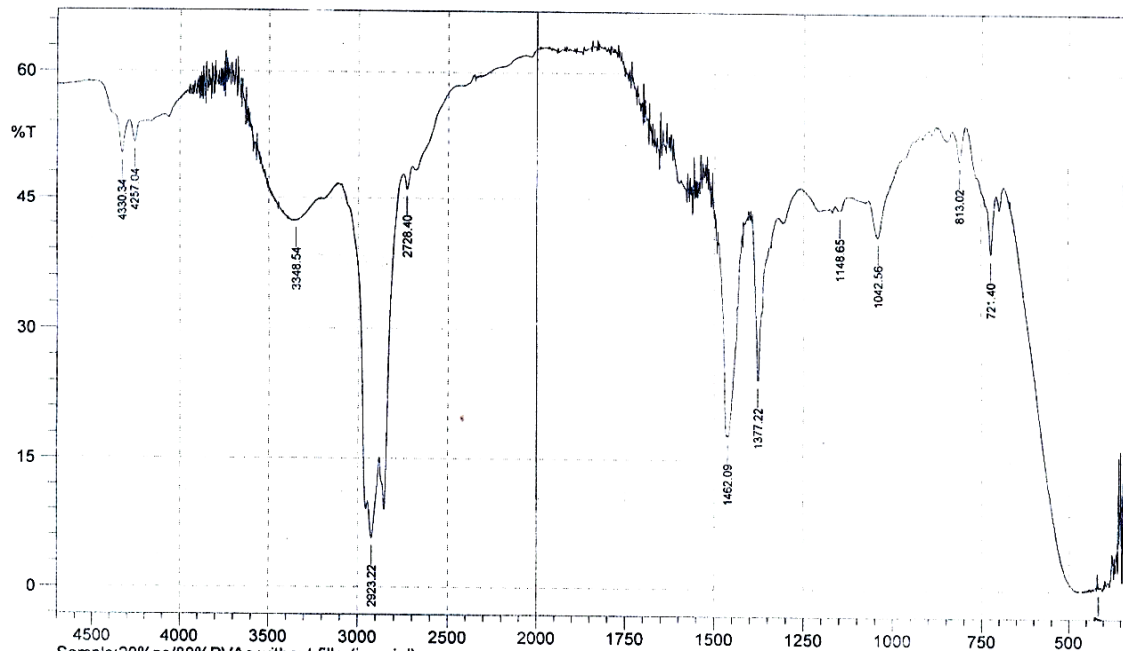


Figure 41: FTIR for 20% PS/80% PVAc with filler

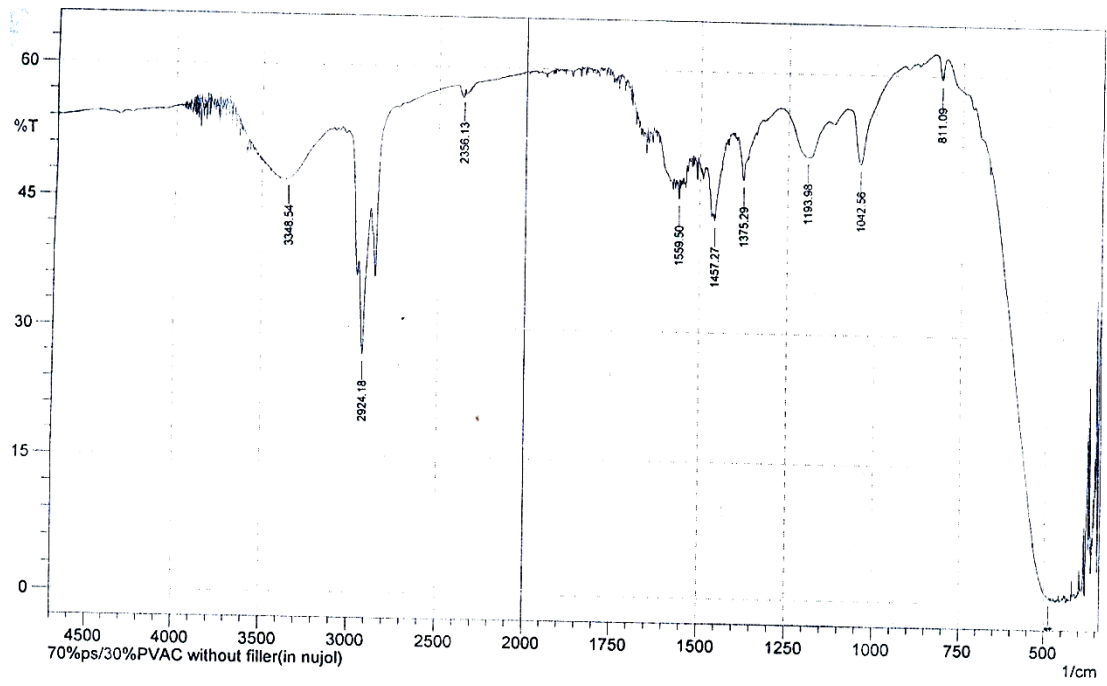


Figure 42: FTIR for 30% PS/70% PVAc without filler

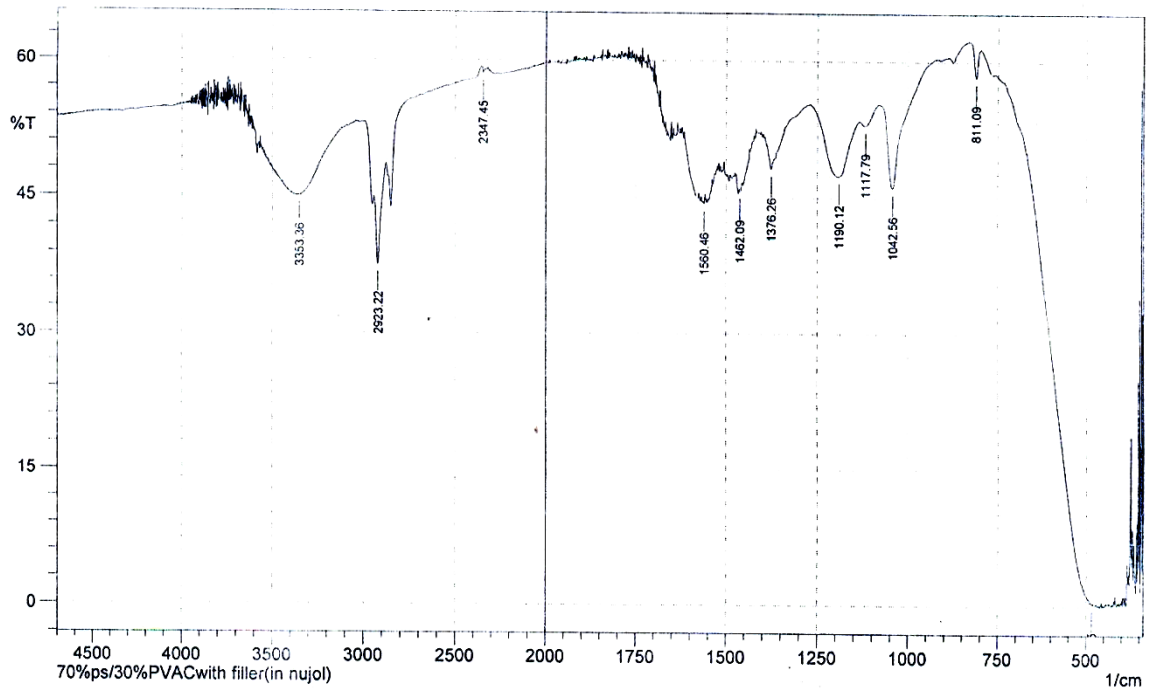


Figure 43: FTIR for 30% PS/70% PVAc with filler

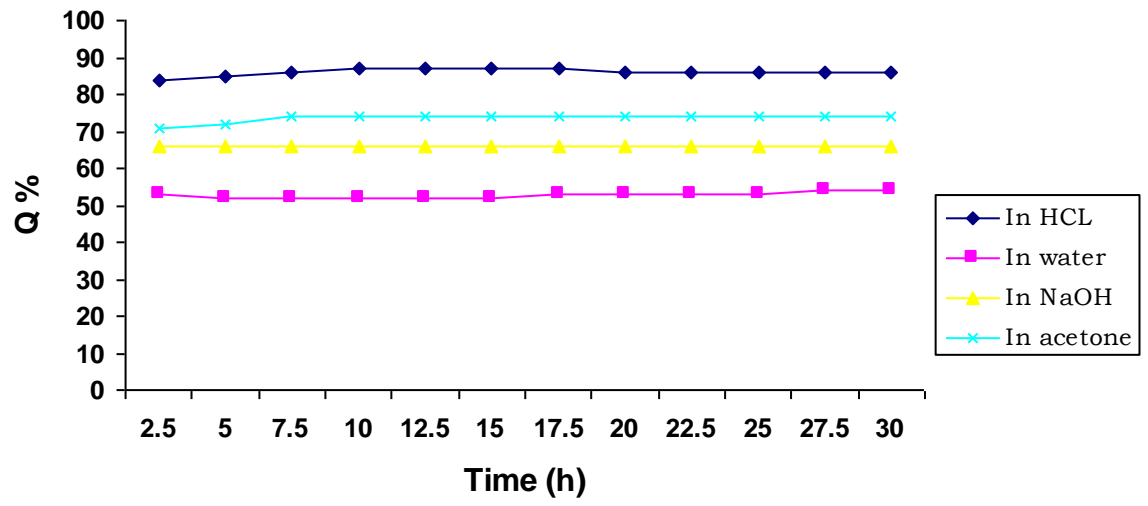


Fig. 44 swelling Kinetics (Q) of 20%/80%, PS/PVAc Blend without filler

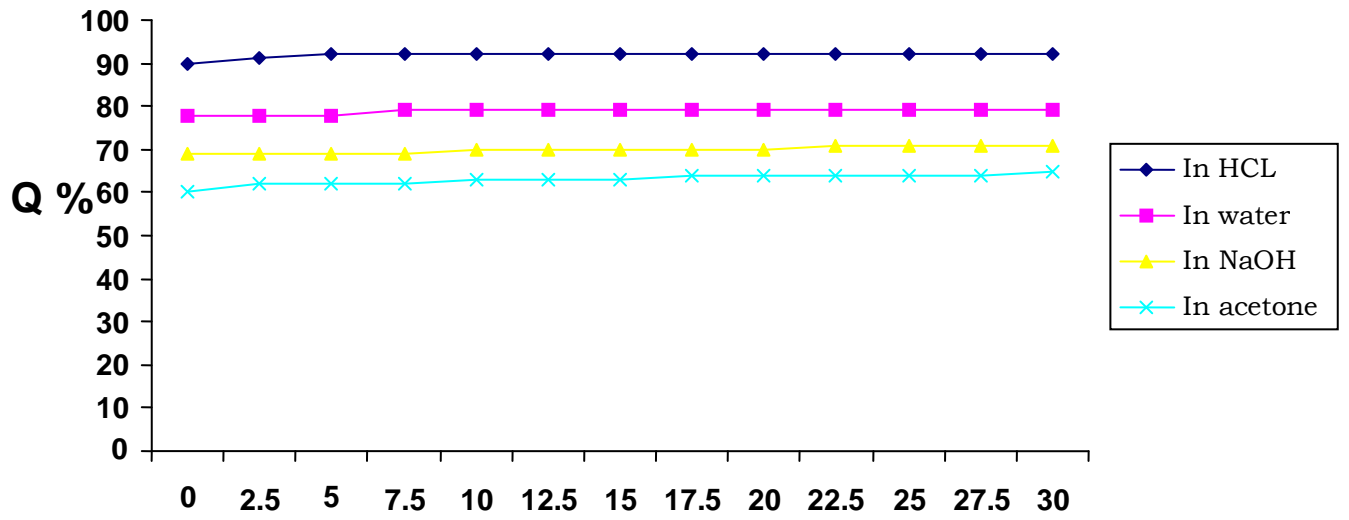


Fig. 45 swelling Kinetics (Q) of 20%/80%, PS/PVAc Blend with α -cellulose filler

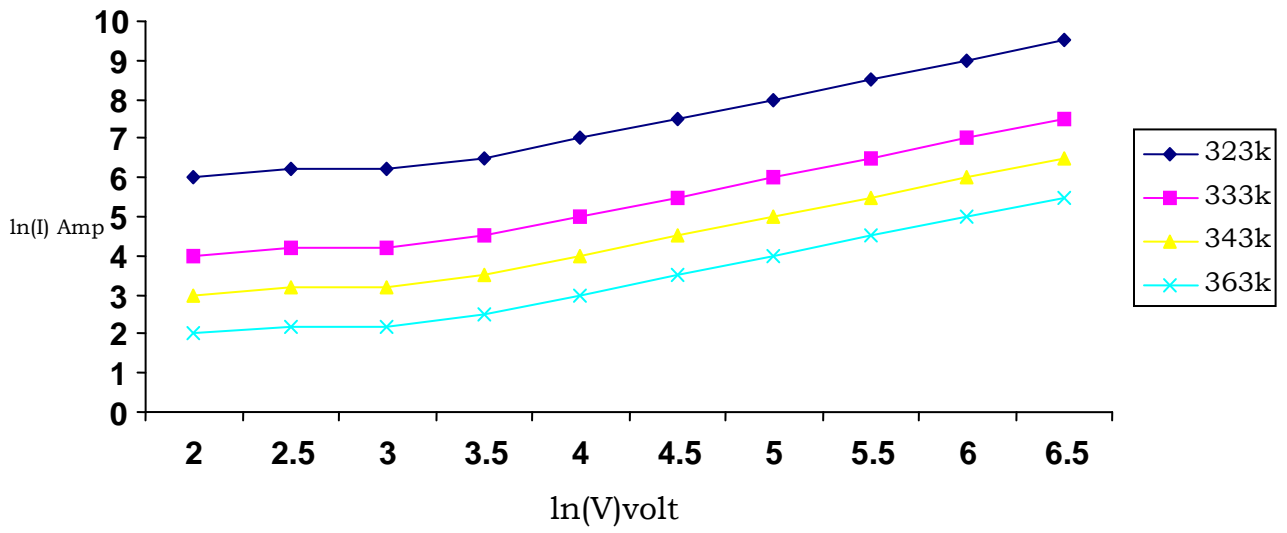


Fig. 46 Current-voltage characteristics for 20%/80%, PS/PVAC blend without filler

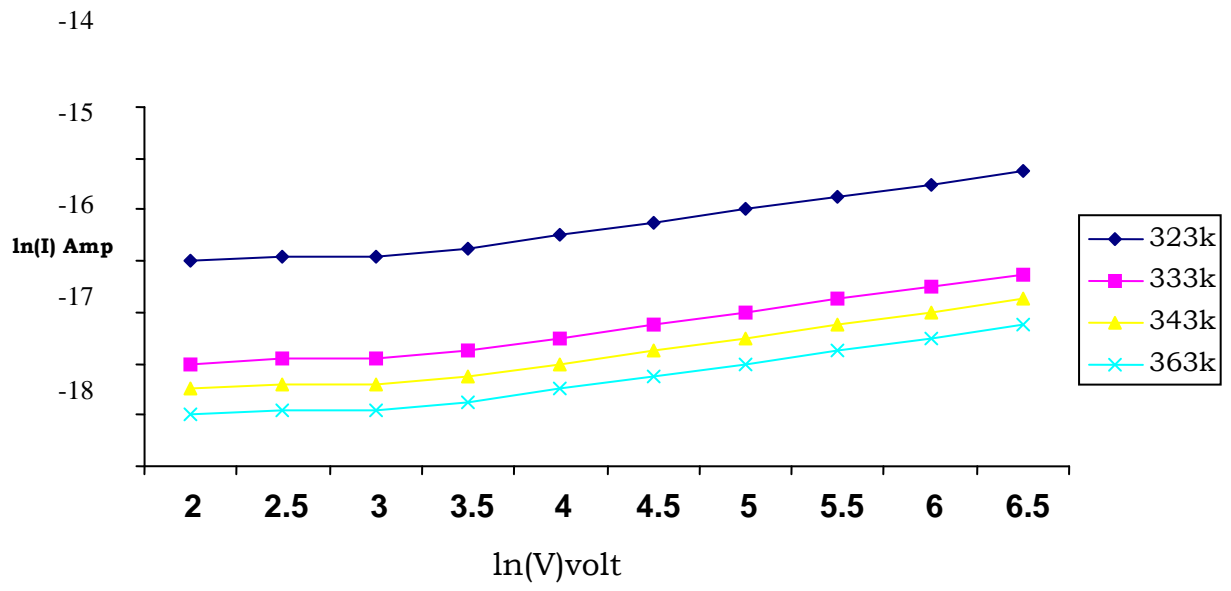


Fig. 47 Current-voltage characteristics for 20%/80%, PS/PVAC blend incorporated with α - cellulose filler

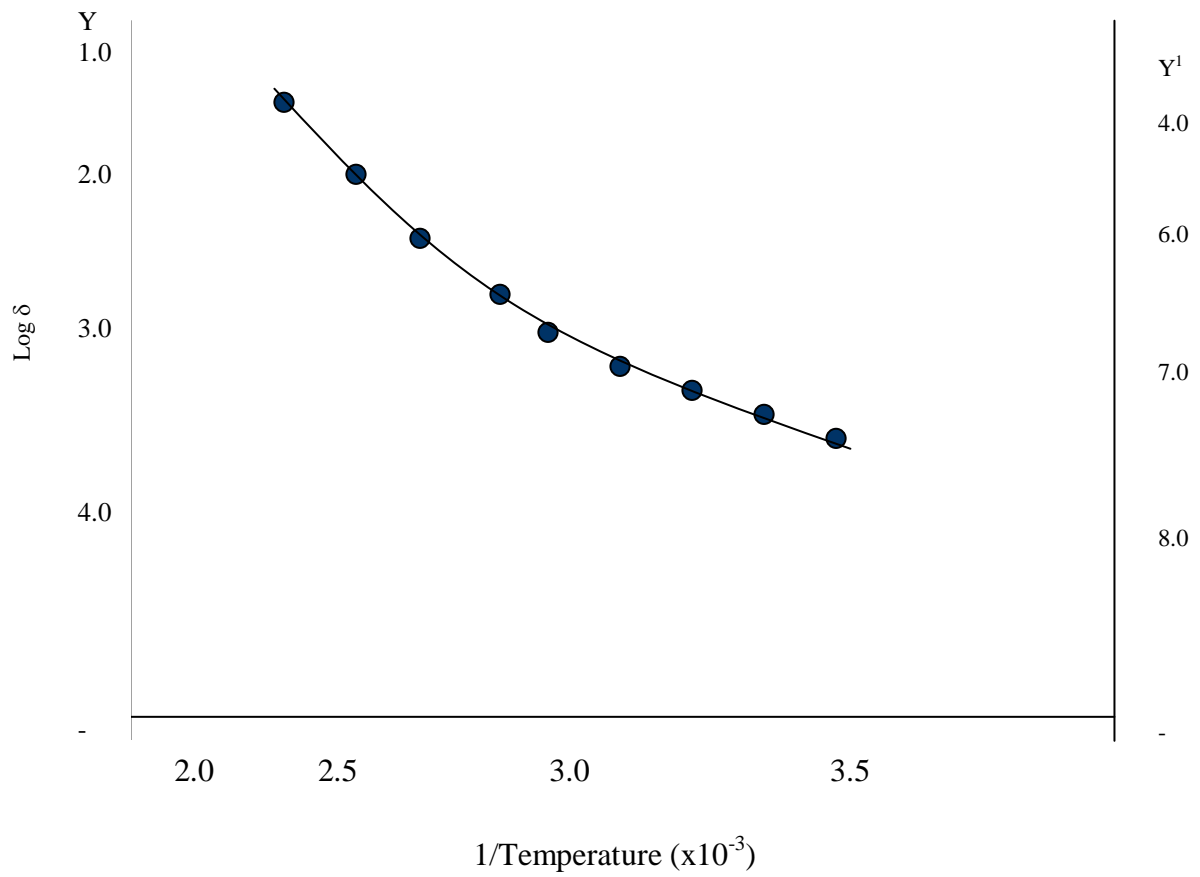


Fig 48 Arrhenius plot for 20%/ 80% PS/PVA_c blend without filler

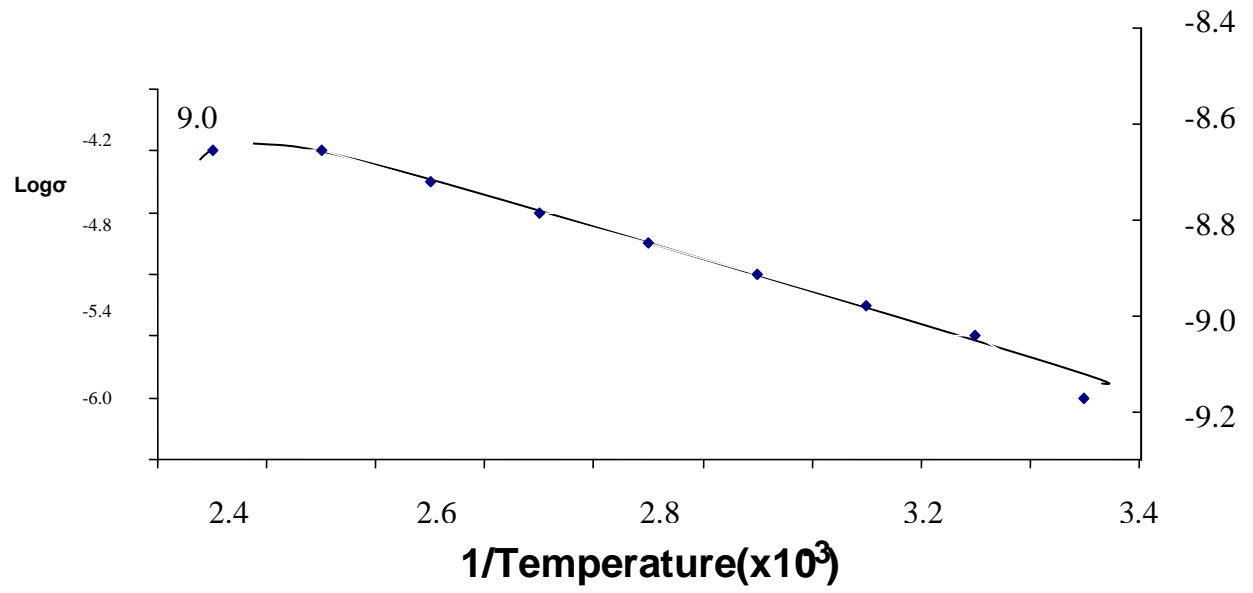


Fig. 49 Arrhenius plot for 20%/80% PS/PVAc blend incorporated with α - cellulose filler

CHAPTER FIVE

DISCUSSION

5.1 TENSILE STRENGTH AND RELATED PROPERTIES

The physico-mechanical properties of PS/PVAc blend with varying compositions for pure and α -cellulose filled blends have been determined. The tensile strength, stress-strain relationship, load vs extension characteristics show a definite confirmation of a phase - matrix that define the parameter (bond strength) which govern its properties. Filler characteristics have a large influence on the physical performance of the blends. The general results show mechanical properties enhancement with filler composition.

Typical stress-strain curves for the different compositions of PS/PVAc are shown in Figures 1 and 2. The modulus decreased and the strength increased as fillers were added. The slopes of the curves showed discontinuities for certain compositions which indicated apparent compatibility domains for 20/80%, PS/PVAc composition as observed in the earlier studies on PS/PVAc blend solutions, Mamza and Folaranmi (1996), where two percent solutions of different blend compositions of PS & PVAc were prepared in toluene, methyl ethyl ketone and tetrahydrofuran. Figures 3 and 4 gives the values of breaking load (KN) Vs. Composition and clearly revealed property improvement in strength appreciation with filler content. It is quite expected because the α -cellulose filler enhances through

reinforcement the polymer blend-filler interactions due to its peculiar nature and structure (very high reinforcing ability and cross-linking sites). The sharp depressions noticed for some compositions in the plot of % elongation/tensile strength against composition (Figures 5, 6, 7 and 8) revealed that the polymer blends were toughened at 90/10%, 40/60% and 30/70%, PS/PVAc compositions without the filler whereas the filled (reinforced) polymer blends showed a wide range of such behaviour except only for 20/80% and 10/90% PS/PVAc blend compositions. These mechanical properties when compared with similar studies on PS/PVAc blends in solution showed a similarity in behavior in terms of effects due to compatibility between the two polymers as a result of the presence of a reinforcing filler i.e. α -cellulose. These results are very important practically in the fact that the addition of α -cellulose filler to the polymer blend led to a new material (composite) with better mechanical properties. The extent of discontinuities observed earlier is expected to decrease with extent of permeation. This principle of using extent of permeation for predicting the extent of discontinuity in polymer blend structure has been applied by other workers, including Huang and Lin (1965), Michaels, (1969) and Paul and Ebra-Lima (1970).

In tensile test, the specimen gradually elongated under tension. The load and the extension curves are shown in Figures 3 and

4. For all the materials, the stress-strain relationship depends on the chemical composition, the heat-treatment and method of processing. Also, it is expected that the strains of neighboring molecules must be evenly distributed for the interactive sites to meet or there would be void in the blend.

Clearly, unless there is strong interaction between α -cellulose particles and PS/PVAc molecules the presence of the former cannot affect molecular rearrangements in the latter. Figures 7 and 8 gives the % elongation versus composition, the value of which varied steadily with the amount of PVAc in the blend. However, a sharp discrepancy is noticed for plot of tensile strength against composition. A medium composition, showed intermediate tensile strength values while compared with extreme compositions, that offers higher value of tensile strength, even then, the compositions incorporated with filler had an appreciably higher values for all the compositions (See Figures 5 and 6). The plot of tensile strength versus composition for the PS/PVAc blends with fillers show that there was a sharp decline of the tensile strength with compositions of 80/20, 90/10 PS/PVAc to 30/70, 40/60 and 50/50 PS/PVAc when compared with the plots without filler (see Figures 5 and 6), however, the percentage elongation versus composition gave a remarkable value for compositions of 20/80 and 10/90 PS/PVAc blend, decreasing to a maximum of between 20% and

34% for 20/80 and 10/90 PS/PVAc blend for blends incorporated with α -cellulose (see Figures 7 and 8). It can now be deduced that α -cellulose filler is a reinforcing filler in the polymer-polymer matrix.

5.2 Effects of modification of unfilled and filled PS/PVAc blends on equilibrium sorption

Tables 3-10 gives the sorption data of the unfilled and filled PS/PVAc blends in four different solvents i.e. dil HCl, NaOH, water and acetone. The % absorption values were plotted against the various compositions (figures 9 and 10). While sorption data in dilute hydrochloric acid (HCl), sodium hydroxide (NaOH) and water (H₂O) gave a weight gain, in acetone, the polymer blends (both unfilled and filled) witnessed a weight loss due to its high polarity. However, solvent absorption increases with filler content in all the four solvents except acetone which showed a dramatic decline in % absorption in the presence of α -cellulose filler. The explanation for this is that the solvent molecules slowly diffused into the polymer blend structure leading to high polymer-polymer and polymer – solvent intermolecular forces as a result of crystallinity or strong hydrogen bonding as earlier observed by Aithal, (1990). Three different mechanism have been proposed for moisture penetration into the composite (two or more physically distinct and mechanically separable materials). The

main process is the diffusion of water molecules into the composite. The main process is the diffusion of water molecules inside the microgaps between the polymer chains. The other two mechanisms are capillary transport of water into the gaps and flaws created at the interface of fibre and polymer matrix because of incomplete wettability and impregnation and also diffusion of water molecules into the microcracks formed in the matrix during the compounding process (Lin, 2002). There is a very sharp increase of percentage absorption for series 3 (Sorption in 0.5M HCl for filled PS/PVAc blend) in which case we observed that for compositions of 10/90, 20/80, 70/30, 60/40, 50/50 and 40/60 PS/PVAc blends the increase was not as much as for compositions 30/70, 20/80, 10/90 PS/PVAc blends, which reached about 37% and dropping sharply to 2% showing that even for the acid solubilized blends certain composition show higher values of absorption (see figure 9). There is a constant variation of percentage absorption versus composition for series 5 (Sorption in 0.05M NaOH for unfilled PS/PVAc blend). The constant values of sorption observed in this series revealed that no interaction has taken place to have altered the molecular order of PS/PVAc blends at that composition compared to the case in series 1(Sorption in water for unfilled PS/PVAc blend) and 2 (Sorption in water for filled PS/PVAc blend) in figures 10, there is a gradual increase in percentage negative absorption for the blends in acetone. The

subsequent rise in sorption values is attributable to the saturation of the gap between PS/PVAc blends matrix and the filler which assist inter-grain friction in the melt, thereby increasing the gelation level, hence the sorption rises (see Figure 9).

The amount of water absorption of the blend increased with the incorporation of filler in the polymer-polymer matrix. The extent of solubilizing the blends is dependent on the nature of solvents used and the filler addition into the poly blend structure (see Figures 9 and 10)

It is evident here to establish from these results that the polymer blend – solvent interactions are more dominant in the presence of the solvents over polymer – polymer interaction. It is also therefore established further for this study that sorption parameters of PS/PVAc blends are largely dependent on solvent types and the dependence are in the order, acid > water > base > acetone. The dil. HCl has the highest % solvent absorption for the virgin polymer blends but a general trend of increase in % solvent absorption is observed for all the α -cellulose-filled polymer blends for all solvents except acetone for the reasons earlier deduced.

Sorption here can be used to detect the structural changes in the PS/PVAc blend, it is observed from Figures 9 and 10 that

equilibrium of absorbed solvents can be attributed to the level of polymer-polymer interactions. In this study, acetone seems to dissolve the crystalline portion of the blends and cannot be used to detect the differences between the polymer blends and their molecular structure, while water, HCl and NaOH which can swell the amorphous regions of the polymer but will not dissolve the blend crystallites, can be used to detect differences between the polymer blends and their molecular structure.

5.3 Effect of filler composition on the density of unfilled and filled PS/PVAc blends

Fig. 11 and Tables 11-12 show the variation of density of the unfilled and filled PS/PVAc blends with blend compositions, the pattern of trend is similar in both the blends except that the filler increases the density of the blends and that in 30/70%, 20/80% and 10/90% PS/PVAc the densities are higher than the other compositions. Matsuaka (1961) reported that density is a measure of order within a polymer, hence it is evident that the level of interaction and compatibility seems to be higher in these three blend compositions. The densities (filled and unfilled) increase slightly for 90/10%, and 80/20%, PS/PVAc and decrease sharply for 70/30%, leveling between 60/40% and 50/50% PS/PVAc blend, increasing, again for 40/60%, at 30/70% for unfilled and 20/80% for filled PS/PVAc blends. The compositions of 20/80 and 90/10 PS/PVAc blends had the highest value of density of between 6.0 to 6.5g/cm³ for the filled

blends when compared with about 3.2 to 3.4g/cm³ for the same compositions without filler. At this point we can attribute this behaviour to the inherent voids in the PS/PVAc blends being filled by the filler particles thereby consolidating the polymer-polymer matrix, hence the rise in the density. The decrease in density is due to the saturation of the gaps between PS/PVAc particles by forming sizeable pockets due to incompatibility capable of separating weakly linked PS/PVAc particles which increases the level of disorder and therefore result to a decrease in density. The rise in density may be attributable to the fillings of the inherent voids within polymer-polymer matrix, which is consolidated by the filler particles. Since it is established that voids are domains of zero density, a high-density polymer will have a low voids content.

5.4 Morphological studies on the unfilled and filled PS/PVAc blends

Figures 12 to 31 show the photomicrographs of the different blends of PS/PVAc with and without the α -cellulose filler loadings. There is always a two-phase system appearing bright (polyvinyl acetate phase) and the other appearing dark (polystyrene phase) in virtually all the micrographs. Large macrodomain of the polyvinyl acetate appear to be dispersed in the dark phase of polystyrene. Likewise polyvinylacetate phase engulfs polystyrene phase. For compositions 70/30, 60/40, 50/50 40/60 and 30/70, PS/PVAc, (with and without filler) i.e.

figures 15, 16, 17, 18, 19, 20, 21, 22, 23 and 24, there's apparent show of heterogeneity of phases which reveals the level of immiscibility of poly(vinyl acetate) with polystyrene at these compositions. This phenomenon is indicative of phase inversions. However, blends of compositions 80/20, 10/90, 20/80 and 90/10 PS/PVAc i.e. Figures 12, 13, 14, 25, 26, 27 and 28 show a considerable miscibility due to a domain distribution in this range of compositions.

This domain distribution is more pronounced in Figures 14, 15, 24, 25 and 26 it is evident from such studies that the compatibility of polymer-polymer structure had an underlying one-phase system. The sharp contrast observed in other extreme compositions is indicative of a level of incompatibility. It is therefore apparent from this study that the level of distribution of the dispersed phase is more pronounced in Figures 22, 23, 30 and 31. In conclusion it can be inferred that the compositions 80/20, 10/90, 20/80 and 90/10 PS/PVAc are compatible pairs.

The structures and the microstructures was confirmed by the comparative FTIR, XRD, and Optical microscopy analyses of the polymer blends with and without filler: PS-10 (wt%)/PVAc-90(wt%)], PS-20 (wt%)/PVAc-80 (wt%) and PS-30 (wt%)/PVAc-70 (wt%). The results of the FTIR spectral analysis of the polymer blends including the characteristic absorption bands and their

assignments are summarized in Table 13. The appearance of the characteristic bands at 2924–2853 cm^{-1} is associated with C-H symmetric bands in the polymer blends with and without filler. The formation of intermolecular hydrogen bonds linkages (H-bonded macro complexes and alcohol groups) can be confirmed by the presence of the following characteristic absorption bands (Fig. 38-43, Table 13): (1) 3336 cm^{-1} (b) and 1043 cm^{-1} (w) for OH stretching and deformation bands, respectively, in alcohol, (2) 2852 cm^{-1} - 2924 cm^{-1} (m) for CH stretching vibrations, (3) 1375 -1464 cm^{-1} (w) for CH bending vibration, (4) 415 cm^{-1} - 487 cm^{-1} for CH ethylenic twisting, (5) 1190 cm^{-1} - 1195 cm^{-1} for COO stretch in esters (6) 811 cm^{-1} - 813 cm^{-1} (w) for CH out plane bending vibration in substituted benzene.

The XRD analysis was employed to confirm the effect of filler on the crystallinity of the polymer blends. The results of the comparative XRD analysis of polymer blends and their individual components were illustrated in Figs. 32-37 and are summarized in Table 14. The following changes in XRD patterns were observed (a) decrease in d-spacings of the polymer blends with filler compared with those without filler, for example 10%PS-90%PVAc without filler has d-spacing value of 4.00616Å at $2\theta=22.19^\circ$ compared with 3.94224Å at $2\theta=22.55^\circ$ for 10%PS-90%PVAc, (b) shift of peak positions to lower positions can be seen in the polymer blends loaded with filler compared with those without filler and (c) visible changes can also

be seen in the XRD parameters as the %PS increases in the polymer blends. The crystallinity index was determined to be higher (84.2%) for the polymer blends containing 10% polystyrene and also the crystallite size for the same composition was small (11.44Å) compared to the remaining compositions (see Table 14).

The surface topography revealed that the surfaces of the polymer samples were not as rough as those loaded with fillers and the morphology of polymer blends is an agglomeration of particles with sizes ranging from 27.44µm to 117.14µm (see Table 14 and Figures 32-37).

5.5 The swelling and electrical conductivity properties of the filled and unfilled PS/PVAc blends

Figures (44 and 45 respectively) show the swelling behaviors of the PS/PVAc, blend films in water, acid, base and acetone. Both plots show a general trend i.e acetone<NaOH <water <HCl, with α -cellulose filled polymer blends exhibiting greater swelling characteristics in all the solvents when compared with the virgin PS/PVAc blend. The explanation is the α -cellulose filler itself, are possible sites for solvent interactions through a solubilizing mechanism. In general, Q is related to the osmotic pressure, cross-linking density and copolymer affinity to absorb water (Higgs, and Joanny, 1991, Flory, 1953). In this particular study the main effect on Q is the affinity to solvents (water, base, acid

and acetone) and filler concentration. The higher Q values obtainable from the Q(%) versus t(h) dependence is in conformity with the results of the earlier studies carried out in the blends (Mamza and Folaranmi, 1996; Mamza and Nwufo, 2008) except that there's sharp discrepancies in the mode of aggregation with filler when films are used instead of moulded articles obtained from a compression press.

The electrical conductivity of the blends were evaluated from the observed behavior of I-V characteristics and the possibility of ohmic conduction as well as space charge limited conduction is ruled out (Figures 46 and 47). The polymers generally falls at low conductivity spectrum and most effects may be due to adventitious ions and hence, the reasons for the observed current-voltage characteristics, with the filler-incorporated blends showing reluctantly an improvement in this regard (Fig. 47). From the Arrhenius plots (Fig 48. and 49), it was observed that the α -cellulose filler enhances its thermal activation energies and falls in the semiconducting behavior of between -0.18 to -0.49eV i.e -0.20 eV from the slope of the plot. It is therefore evident that by a careful consideration of the micro structural arrangement in the polymer matrix a conduction mechanism that would offer considerable impetus for impedance analyses is required especially in the α -cellulose filled PS/PVAC blend.

CHAPTER SIX

CONCLUSION

6.1 SUMMARY OF RESULTS

The present study has revealed that polystyrene and poly (vinyl acetate) blends had improved compatibility in the presence of a filler (α - cellulose) from the values of the mechanical properties like tensile strength, elongation at break and modulus of elasticity and some physical properties like density and morphology. However, studies from sorption measurement show depreciable decrease of resistance to moist environment in virtually all solvents used i.e water, hydrochloric acid, and sodium hydroxide in the presence of the filler except acetone which showed a sharp reduction in % absorption. It can also be inferred that the 20/ 80% PS/ PVAc composition has the best compatibility properties with and without a filler.

6.2 Contribution To Knowledge

No work has been reported on the reinforcement of PS/ PVAc blends by α -cellulose. In this light, this novel approach is useful for the current effort towards research and development aimed at an economic viable and practicably industrial end – use applications. The composition (20/80%, PS/PVAc) can be used for load bearing applications, in humid environment due to its less absorption in solvents and as semi conductors since its

thermal activation energy is within the semi conduction range. Also, the 10/90% PS/PVAc blend have better properties where crystallinity index requirements are needed.

6.3 Conclusion

Whereas the results of this study showed a considerable improvement of some of the mechanical properties of PS/PVAc blends, it was noticed that these properties can be further enhanced by incorporation of filler into the polymer-polymer matrix.

Based on these findings on mechanical properties, the effect on equilibrium sorption was investigated in order to establish its potential applications in different environmental conditions.

This study reveals the effect of α -cellulose filler on the morphological arrangements of crystallites in PS and PVAc. Though the crystallinity index is highest for 10%/90%, PS/ PVAc blend without filler, the compatibility level from surface morphology shows that 20%/80% PS/PVAc blend had better prospects in terms of end-use applications.

The swelling behavior and electrical conductivities of Polystyrene (PS) and Polyvinyl acetate (PVAc) blend showed a corresponding variation in its applicability depending on the choice of solvent and mode of its processing. Reinforced PS/PVAc blends can be utilized as semi conductors.

6.4 Recommendations

However, further studies should be made on the detailed microscopy analysis using sorption kinetic studies and scanning electron microscopy (SEM), so as to reveal more useful microstructural parameters of the polymer blends.

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APPENDIX A

(A) MECHANICAL TESTS WITHOUT FILLER AT CONSTANT STRAIN RATE

Load (N)	Extension (mm)	Area ($\times 10^{-4} \text{m}^2$)	Stress (Mpa) $\times 10^1$	Strain
100,PS				
130.00	0.84	6.0	2.00	0.011
220.00	1.20	6.0	3.50	0.011
300.00	1.56	6.0	5.00	0.011
370.00	2.16	6.0	0.62	0.011
480.00	2.64	6.0	0.80	0.011
90/10PS/PVAc				
100.00	0.72	6.0	1.50	0.011
210.00	1.20	6.0	3.50	0.011
300.00	1.68	6.0	5.00	0.011
390.00	2.40	6.0	0.65	0.011
450.00	3.12	6.0	0.75	0.011
80/20PS/PVAc				
50.00	1.20	1.2	0.50	0.011
100.00	2.40	1.2	1.60	0.011
210.00	3.24	1.2	3.50	0.011
300.00	3.72	1.2	5.00	0.011
420.00	5.04	1.2	7.00	0.011
70/30PS/PVAc				
40.00	2.04	1.2	0.50	0.011
60.00	2.16	1.2	0.10	0.011
90.00	2.40	1.2	1.50	0.011
120.00	3.00	1.2	2.00	0.011
150.00	3.84	1.2	0.25	0.011
60/40PS/PVAc				
40.00	1.20	1.2	0.50	0.011
40.00	2.40	1.2	0.60	0.011
60.00	3.60	1.2	0.10	0.011
60.00	4.80	1.2	1.00	0.011
60.00	5.88	1.2	1.00	0.011
40/60PS/PVAc				
20.00	1.20	1.2	0.20	0.011
40.00	1.92	1.2	0.50	0.011
60.00	2.40	1.2	1.00	0.011
60.00	3.00	1.2	1.00	0.011
60.00	3.36	1.2	1.00	0.011
30/70PSPVAc				
20.50	1.20	1.2	0.02	0.011
20.50	1.68	1.2	0.02	0.011

30.00	2.40	1.2	0.05	0.011
30.00	2.88	1.2	0.05	0.011
30.00	3.36	1.2	0.05	0.011
20/80PS/PVAc				
20.50	1.20	1.2	0.02	0.011
100.00	2.40	1.2	0.15	0.011
150.00	4.32	1.2	0.25	0.011
210.00	6.00	1.2	0.35	0.011
210.00	9.00	1.2	0.35	0.011
10/90PS/PVAc				
20.50	2.40	1.2	0.02	0.011
30.00	4.20	1.2	0.05	0.011
150.00	7.20	1.2	0.25	0.011
240.00	9.60	1.2	0.40	0.011
240.00	12.60	1.2	0.40	0.011
100PVAc				
30.00	5.52	1.2	0.05	0.011
90.00	7.20	1.2	0.15	0.011
150.00	9.60	1.2	0.25	0.011
210.00	12.00	1.2	0.35	0.011
240.00	16.32	1.2	0.40	0.011

(B) THE MECHANICAL PROPERTIES DERIVED WITHOUT FILLER

Composition (PS/PVAc)	TS (Mpa)	Elongation at break	% Elongation	MOE(GPa)
100PS	18.0	3.50	11.0	58.2
90/10	16.0	4.20	13.7	54.5
80/20	15.0	6.17	21.3	26.7
70/30	6.0	4.30	17.2	32.3
60/40	3.0	6.36	25.0	4.1
50/50	2.0	5.00	20.7	11.7
40/60	3.0	4.12	15.7	15.2
30/70	2.0	4.15	15.7	8.3
20/80	8.0	10.00	40.5	10.1
10/90	9.0	13.20	54.3	12.5
100PVAc	10.0	18.20	70.8	11.4

(C) MECHANICAL TEST WITH α - CELLULOSE FILLED AT CONSTANT STRAIN RATE

Load (N)	Extension (mm)	Area(x10-4m2)	Stress (Mpa) x 102	Strain
100PS				
150.00	0.65	1.2	0.25	0.011
230.00	1.00	1.2	0.38	0.011
320.00	1.30	1.2	0.53	0.011
390.00	2.00	1.2	0.65	0.011
500.00	2.40	1.2	0.83	0.011
90/10 PS/PVAc				
100.00	0.60	1.2	0.17	0.011
240.00	1.01	1.2	0.40	0.011
320.00	1.52	1.2	0.53	0.011
420.00	2.00	1.2	0.70	0.011
490.00	2.50	1.2	0.82	0.011
80/20PS/PVAc				
40.00	1.00	1.2	0.07	0.011
120.00	2.00	1.2	0.20	0.011
250.00	2.50	1.2	0.42	0.011
310.00	2.80	1.2	0.52	0.011
440.00	4.00	1.2	0.73	0.011
70/30PS/PVAc				
40.00	1.50	1.2	0.07	0.011
80.00	1.80	1.2	0.13	0.011
110.00	2.00	1.2	0.18	0.011
140.00	2.40	1.2	0.23	0.011
190.00	2.80	1.2	0.317	0.011
60/40PS/PVAc				
40.00	1.00	1.2	0.07	0.011
50.00	1.80	1.2	0.08	0.011
80.00	2.80	1.2	0.13	0.011
80.00	3.50	1.2	0.13	0.011
90.00	3.50	1.2	0.15	0.011
50/50PS/PVAc				
20.00	0.20	1.2	0.03	0.011
50.00	0.50	1.2	0.08	0.011
50.00	1.00	1.2	0.08	0.011
50.00	2.00	1.2	0.08	0.011
50.00	2.50	1.2	0.08	0.011
40/60PS/PVAc				
20.00	1.00	1.2	0.03	0.011
50.00	1.56	1.2	0.08	0.011

80.00	2.00	1.2	0.13	0.011
100.00	2.40	1.2	0.16	0.011
100.00	2.60	1.2	0.16	0.011
30/70PS/PVAc				
20.00	1.00	1.2	0.03	0.011
20.00	1.20	1.2	0.03	0.011
50.00	1.80	1.2	0.08	0.011
50.00	1.80	1.2	0.08	0.011
50.00	2.40	1.2	0.08	0.011
20/80PS/PVAc				
20.00	1.00	1.2	0.03	0.011
120.00	1.20	1.2	0.20	0.011
180.00	1.50	1.2	0.30	0.011
250.00	2.00	1.2	0.42	0.011
300.00	5.00	1.2	0.50	0.011
10/90PS/PVAc				
20.00	1.50	1.2	0.03	0.011
50.00	2.00	1.2	0.08	0.011
200.00	4.00	1.2	0.33	0.011
250.00	7.20	1.2	0.42	0.011
300.00	8.60	1.2	0.50	0.011
100PVAc				
40.00	2.30	1.2	0.06	0.011
100.00	4.52	1.2	0.16	0.011
180.00	8.60	1.2	0.30	0.011
250.00	10.50	1.2	0.42	0.011
320.00	12.00	1.2	0.53	0.011

(D) MECHANICAL TEST WITH PROPERTIES DERIVED WITH FILLER

Composition (PS/PVAC)	TS (Mpa)	MOE(GPa)	Elongation at break	% Elongation
100PS	20.0	54.1	3.00	10.60
90/10	19.0	50.0	4.00	12.50
80/20	17.0	20.7	5.10	20.20
70/30	8.0	31.0	3.41	15.40
60/40	4.0	3.0	5.40	23.50
50/50	3.5	9.9	4.50	19.20
40/60	3.0	13.7	4.00	13.44
30/70	4.7	6.5	4.18	13.44
20/80	10.8	8.7	8.78	36.00
10/90	12.2	10.2	11.50	50.40
100PVAc	10.0	10.0	15.32	65.30

GLOSSARY**Appendix B**

PS	-	Polystyrene
PVAc	-	Poly(vinyl acetate)
ASTM	-	American Society of Testing Materials
μ	-	Micron
ΔG	-	Gibb's Free Energy Change
ΔH	-	Enthalpy change
ΔS	-	Entropy change
MPa	-	Mega pascals
KN	-	Kilo Newtons
N	-	Newton
m^2	-	meter squared
Tg	-	Glass transition temperature
SEM	-	Scanning Electron Microscope
Xr	-	Volume fraction crystallinity
Xw	-	weight fraction crystallinity
BS	-	British Standards
α	-	Alpha
β	-	Beta
γ	-	Gamma
δ	-	delta
Phr	-	Parts per hundred resin
XRD	-	X-ray diffraction
FTIR	-	Fourier Transform infrared

FULL LENGTH RESEARCH PAPER

X-Ray Diffraction and Fourier Transform Infrared Studies of Modified Polystyrene (Ps) and Polyvinyl Acetate (PVAc) Blends

Paul A. P. Mamza¹ and Bathrand T. Nwufor²

¹Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria.

²Department of Chemistry, University of Jos, Nigeria

*Corresponding author: mamzapaul@yahoo.com

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ABSTRACT

The morphology of pure and modified polystyrene (PS) and polyvinyl acetate (PVAc) blends were studied using X-ray diffraction (XRD) and Fourier transform infrared (FTIR). The heterogeneity of the blend composition distribution manner revealed apparent compatibility domains with 100/0% PS/PVAc having the highest crystallinity index. Observed morphological changes showed that 20%/80% PS/PVAc with filler has highest compatibility level.

Keywords: Polystyrene, polyvinyl acetate, morphology and adsorption studies

INTRODUCTION

Polymers can be modified by a variety of physical or chemical methods. The physical modification of polymers can be carried out by mixing of polymers with special additives. For surface modification various kinds of irradiation are employed such as x-ray, γ -irradiation, ultraviolet radiation, plasma action, ion or electron beams etc (Sarmiska et al. 2002). Also, Mamza and Folaremi (1998), carried out studies on the compatibility of PS and PVAc blend in solution using density and viscometric methods and found that the polymers are compatible at 20%/80% PS/PVAc composition. Studies on the effect of α -cellulose filler on the surface morphological modification of the blend of PS and PVAc had not been reported in literature, except that Mamza and Nwufor (2008) reported the swelling parameters of the

same blend. The aim of this work is to study the surface morphology of PS and PVAc blends reinforced with cellulose filler compounded with the pure blends and monitoring the changes caused in these samples using the Fourier transform infrared spectroscopy.

A statement of Problem

Polystyrene is a highly brittle polymer, while Polyvinylacetate is essentially elastic. The blends of the two polymers is expected to have a moderate properties required for some household applications. The present study is to establish the most convenient blend composition that is desirable for such applications through the morphological studies of these blends.

METHODOLOGY

Sample Preparation

Different blends of PS and PVAc with a total solid content of 6.0g were prepared in the following compositions- 10%PS-90%PVA, 20%PS- 80%PVA and 30%PS- 70%PVA

Material Characterization

Fourier transform infrared (FTIR) spectra of the polymer blends with and without filler (in nujol) were recorded with an FTIR Shimadzu spectrometer in the 4500–500 cm^{-1} range, taking 10 scans at 2-cm $^{-1}$ resolution. The indices of absorption for the polymer blends with and without filler were calculated using the formula (Cross, 1964):

$$K = \frac{\alpha\lambda}{4\pi}$$

where K is the index of absorption, α is the absorption and λ is the wavelength of the scanned region of the infrared spectrum.

The surface topography and morphology of the polymer blends with and without filler were observed using optical microscope (model NJF-120A) with a resolution of 400X and in conjunction with Image J; surface topography software, the surface topography and the particle sizes were determined. The ratio of crystalline/amorphous phase contents in the polymer blends with and without filler was determined by X-ray powder diffraction (XRD) analysis using MD-10 automated Diffractometer employing Cu K α ($\lambda=1.5402\text{\AA}$) radiation over the range $15^\circ \leq 2\theta \leq 75^\circ$. The crystallinity of the polymer blends with and without filler was calculated using the following equation (Rabek, 1980):

$$X_c = \frac{\int_0^\pi S^2 I_c(s) ds}{\int_0^\pi S^2 I(s) ds}$$

where S is the magnitude of the reciprocal-lattice vector which is given by $S = (2 \sin \theta) / \lambda$, θ is one-half the angle of derivation of the

diffracted rays from the incident X-rays, and λ is the wavelength; $I(s)$ and $I_c(s)$ are intensities of coherent X-ray scattering from both crystalline and amorphous regions and from only crystalline region of polymer sample, respectively, and d is the interlayer spacing. The average crystallite sizes D of the synthesized powders were estimated from the peak broadening effect using Scherrer formula (Cullity *et al.*, 2001):

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

RESULTS AND DISCUSSION

The structures and the microstructures was confirmed by the comparative FTIR, XRD, and Optical microscopy analyses of the polymer blends with and without filler: PS-10 (wt%)/PVAc-90(wt%), PS-20 (wt%)/PVAc-80 (wt%) and PS-30 (wt%)/PVAc-70 (wt%). The results of the FTIR spectral analysis of the polymer blends including the characteristic absorption bands and their assignments are summarized in Table 1. The appearance of the characteristic bands at 2924–2853 cm^{-1} is associated with C-H symmetric bands in the polymer blends with and without filler. The formation of intermolecular hydrogen bonds linkages (H-bonded macro complexes and alcohol groups) can be confirmed by the presence of the following characteristic absorption bands (Fig. 1, Table 1): (1) 3336 cm^{-1} (b) and 1043 cm^{-1} (w) for OH stretching and deformation bands, respectively, in alcohol, (2) 2852 cm^{-1} - 2924 cm^{-1} (m) for CH stretching vibrations, (3) 1375 -1464 cm^{-1} (w) for CH bending vibration, (4) 415 cm^{-1} - 487 cm^{-1} for CH ethylenic twisting, (5) 1190 cm^{-1} - 1195 cm^{-1} for COO stretch in esters (6) 811 cm^{-1} - 813 cm^{-1} (w) for CH out plane bending vibration in substituted benzene.

The XRD analysis was employed to confirm the effect of filler on the crystallinity of the polymer blends. The results of the comparative XRD analysis of polymer blends and their individual components are illustrated in Figs. 1- 12 and are summarized in Table 2. The following changes in XRD patterns were observed (a) decrease in d-

spacings of the polymer blends with filler compared with those without filler, for example 10%PS-90%PVA without filler has d-spacing value of 4.00816Å at $2\theta=22.19^\circ$ compared with 3.94224Å at $2\theta=22.55^\circ$ for 10%PS-90%PVA, (b) shift of peak positions to lower positions can be seen in the polymer blends loaded with filler compared with those without filler and (c) visible changes can also be seen in the XRD parameters as the %PS increases in the polymer blends. The crystallinity index was determined to be higher (84.2%) for the polymer blends

containing 10% polystyrene and also the crystallite size for the same composition was small (11.44Å) compared to the remaining compositions (see Table 2).

The surface topography revealed that the surfaces of the polymer samples were not as rough as those loaded with fillers and the morphology of polymer blends is an agglomeration of particles with sizes ranging from 27.44µm to 117.14µm (see Table 2 and figures 1-6).

Table 1: Characteristics FTIR Absorption band and their assignments for 10%PS-90%PVA, 20%PS-80%PVA and 30%PS-70%PVA Polymer blends with and without filler (The maximum peak is at 20%PS-80%PVA)

S/NO	Band Assignment	Absorption band (cm ⁻¹)					
		10%PS-90%PVA		20%PS-80%PVA		30%PS-70%PVA	
		WITH FILLER	WITHOUT FILLER	WITH FILLER	WITHOUT FILLER	WITHOUT FILLER	WITH FILLER
1	O-H _{int} , Intermolecular H bonding (b)	3336	-	3349.50	3348.54	3353.36	3348.54
2	C-Hstr (m) (aliphatic)	2924.18	2923.22	2924.18	2923.22	2923.22	2924.18
3	C-Hstr vib (m)	2853.78	2852.81	-	-	-	-
4	C-Hstr (w) in aldehydes	-	-	-	2728.40	-	-
5	P-H _{ar} (w)	-	-	-	-	2347.45	2356.13
6	COO _{as} vib (non-conjugated) in amides	-	1654.98	-	-	-	-
7	C-NO ₂ (w) (asymmetric)	1557.57	1571.07	-	-	-	-
8	NOOstr (w)	-	-	-	-	1560.46	1559.50
9	C-H _{asnd} vibration (w) in CH ₂	1464.02	1460.16	1460.16	1462.09	1462.09	1457.27
10	C-H _{asnd} vib (w) in CH ₃	1377.22	1376.26	1376.26	1377.22	1376.26	1375.29
11	C-O-C _{as} (w) vib. in ester	1193.98	1195.91	1199.76	1148.65	1190.12	1193.98
12	C-OHstr (w) in alcohol	-	-	-	-	1117.79	-
13	C-OHstr (w) in alcohol	1043.52	1042.56	1045.45	1042.56	1042.56	1042.56
14	C-H out plane bending vibration in substituted benzene	812.06	811.09	812.06	813.02	811.09	811.09
15	C-H out of plane deformation in substituted benzene	-	-	720.44	721.40	-	-
16	C-H twisting in ethylene	486.08	493.79	484.15	415.67	484.15	487.04

Table 2: Showing comparative XRD, microscopic and FTIR Analyses

Sample	2 θ (degree)	D (Å)	I _{max}	XRD		Particle size (μ m) microscopy	Absorption Index (%) FTIR
				%	D (Å)		
10%PS- 90%PVA WITHOUT FILLER	22.19 32.97 45.93	4.00616 2.71626 1.97581	134.0 337.9 70.1	84.2	11.44	55.77	52.0
10%PS- 90%PVA WITH FILLER	22.55 34.5 40.5 47.0 54.5 64.5	3.94224 2.28367 2.66545 3.07077 3.52809 4.10937	330.7 25 40 25 20 30	38.4	24.96	69.56	48.0
20%PS- 80%PVA WITHOUT FILLER	26.21 28.81 29.69 30.86 33.33 34.02 40.82 47.11 58.03 64.74	3.39937 3.09864 3.00906 2.89741 2.68809 2.63493 2.2107 1.92882 1.58941 1.4398	71.7 29.9 25.7 5.6 36.8 69.4 7.0 34.9 7.3 14.2	64.6	20.5	47.39	56.0
20%PS- 80%PVA WITH FILLER	33.5 34.21 41.26 47.09 58 63.86	2.67478 2.62097 2.18787 1.92997 1.59006 1.4576	68.5 46.5 5.8 24.8 5.5 1.8	34.8	33.01	117.14	51.0
30%PS- 70%PVA WITHOUT FILLER	22.57 31.47 40.15 46.17 63.87	3.94 2.84259 2.24565 1.96806 1.45731	229.5 19.9 22.6 12.1 20.4	48.0	34.7	35.72	46.0
30%PS- 70%PVA WITH FILLER	22.77 64.33	3.90515 1.44797	189.9 32.2	31.37	12.42	27.44	49.00

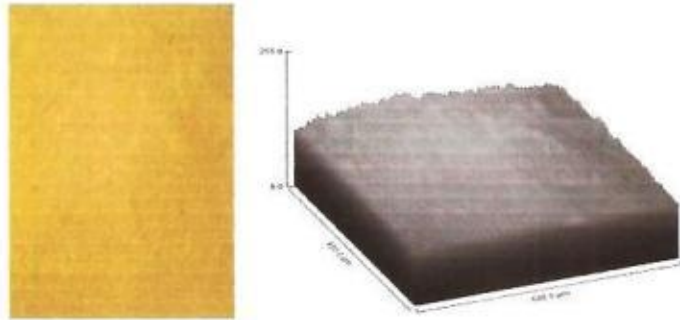


Figure1: Showing the microstructure and surface topography for 10%PS-90%PVAC without filler

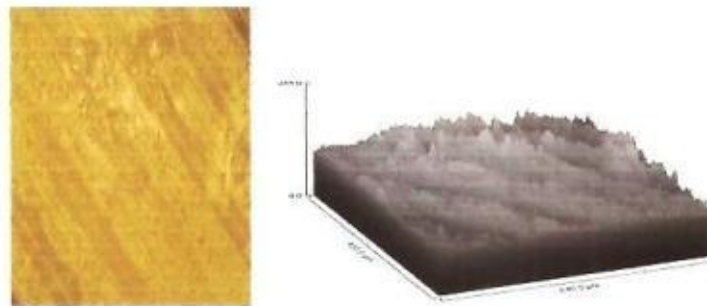


Figure 2: Showing the microstructure and surface topography for 10%PS-90%PVAC with filler

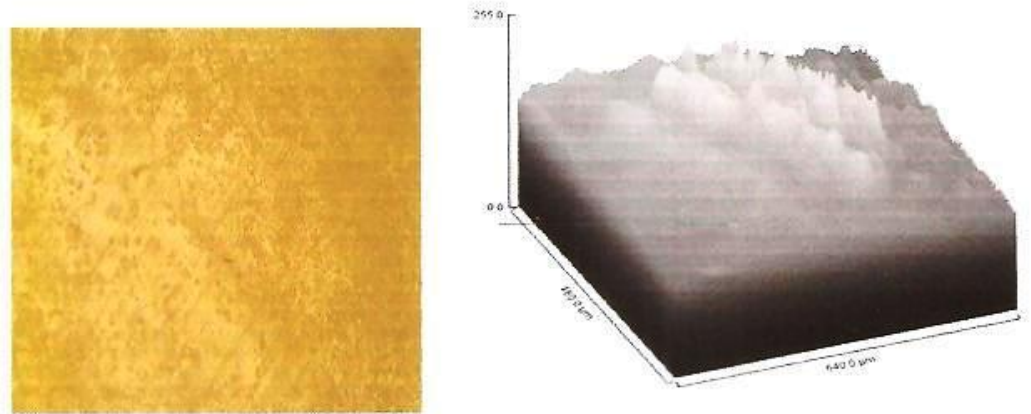


Figure 3: Showing the microstructure and surface topography for 20%PS-80%PVAC without filler

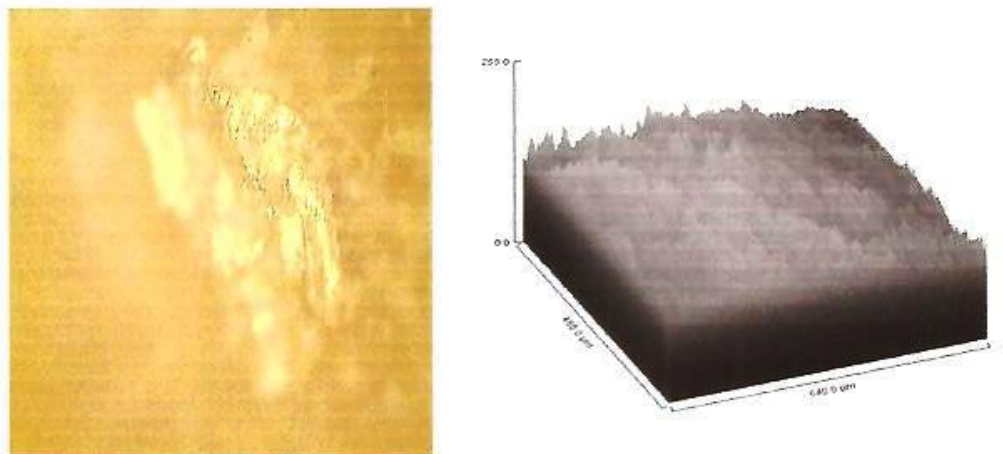


Figure 4: Showing the microstructure and surface topography for 20%PS-80%PVAC with filler

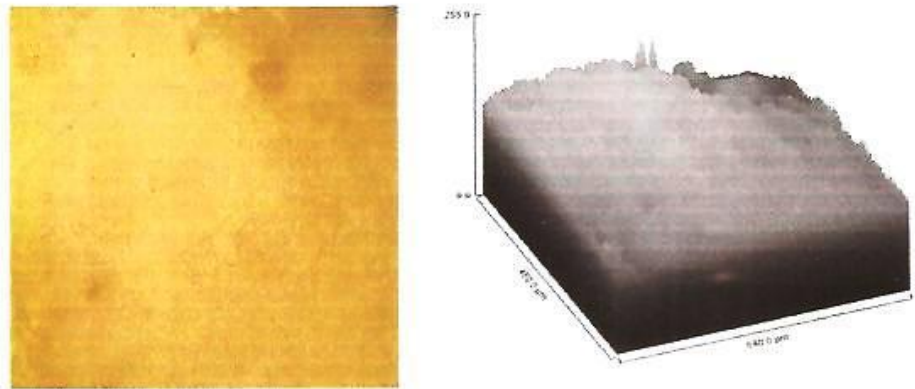


Figure 5: Showing the microstructure and surface topography for 30%PS-70%PVAC without filler

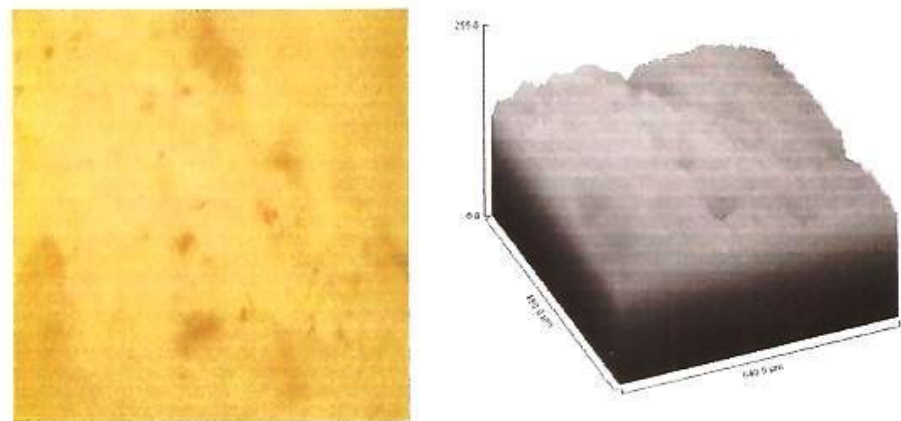


Figure 6: Showing the microstructure and surface topography for 30%PS-70%PVAC with filler

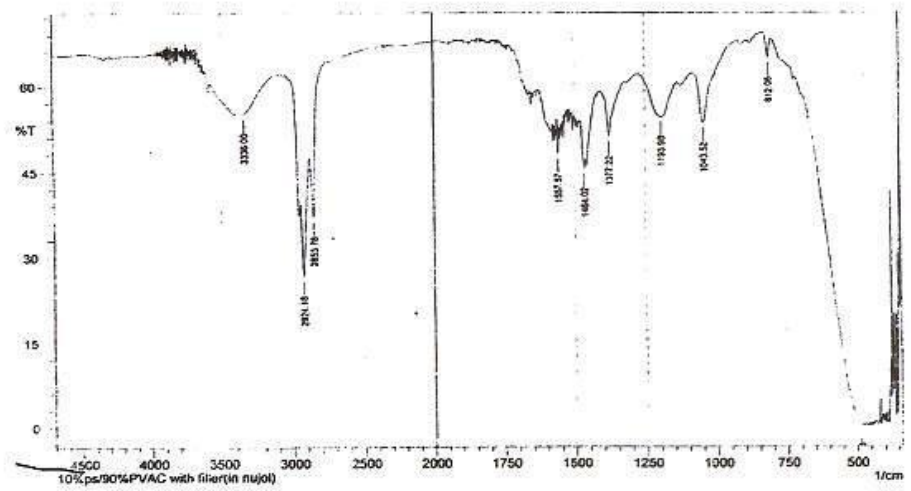


Figure 7: FTIR spectrum for 10% PS/90% PVAc with filler

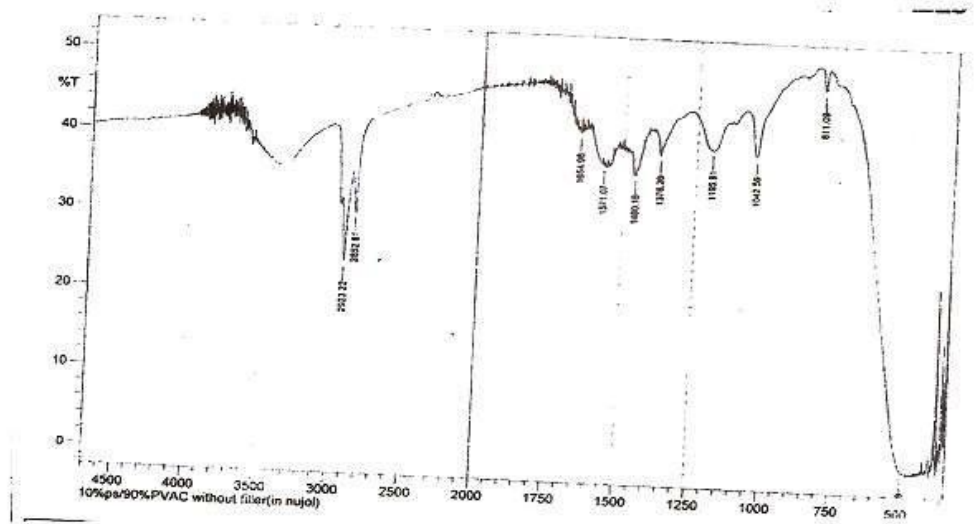


Figure 8: FTIR spectrum for 10% PS/90% PVAc without filler

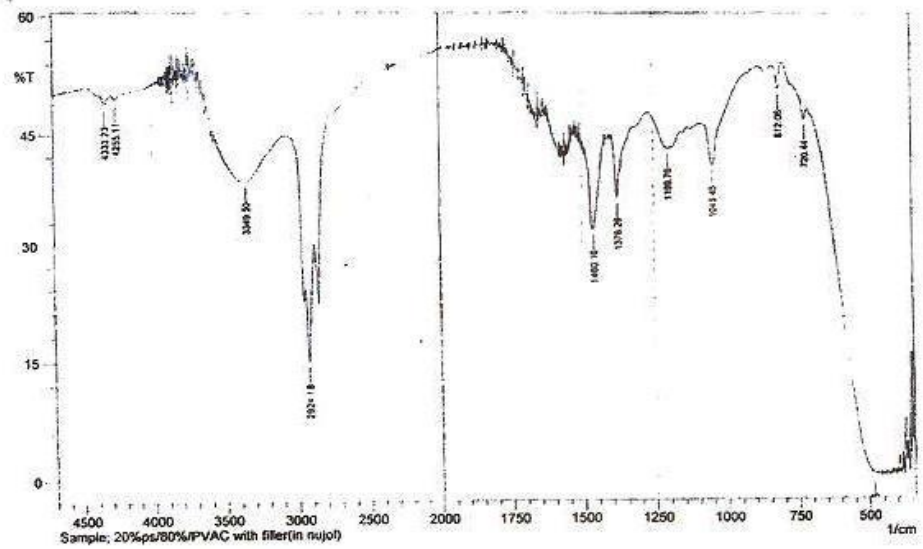


Figure 9: FTIR spectrum for 20% PS/80% PVAc without filler

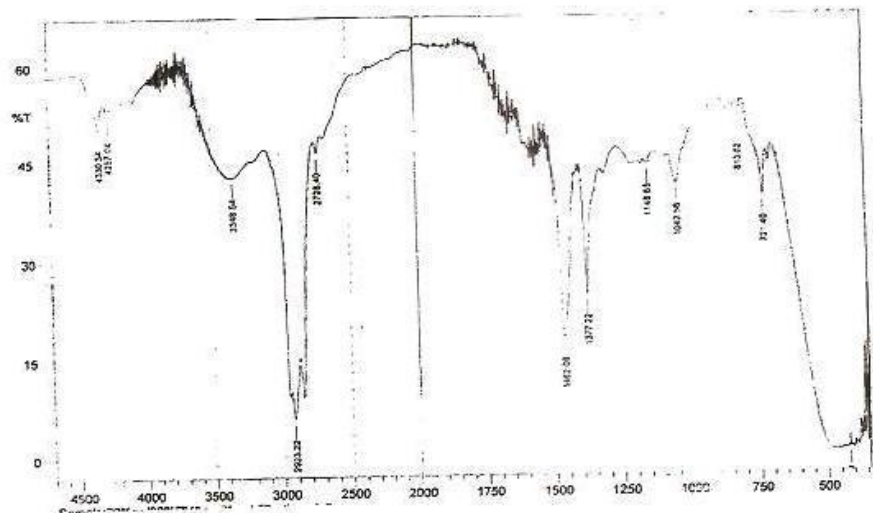


Figure 10: FTIR spectrum for 20% PS/80% PVAc with filler

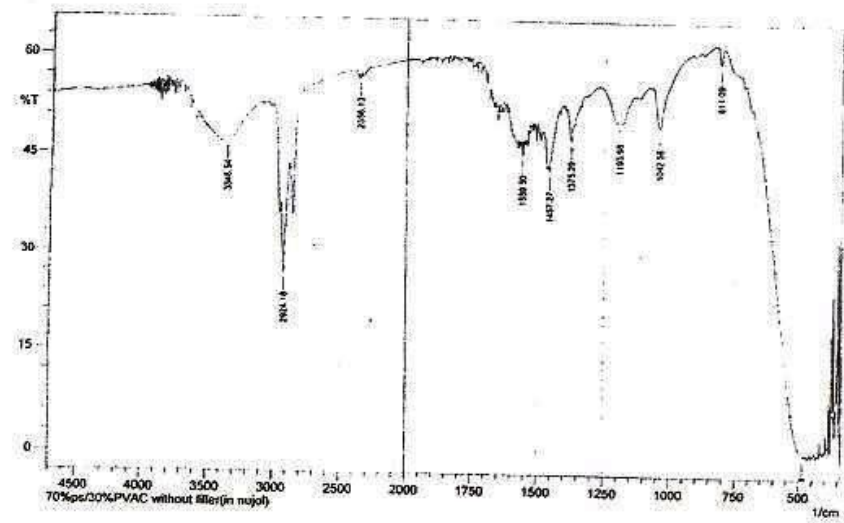


Figure 11: FTIR spectrum for 30% PS/70% PVAc without filler

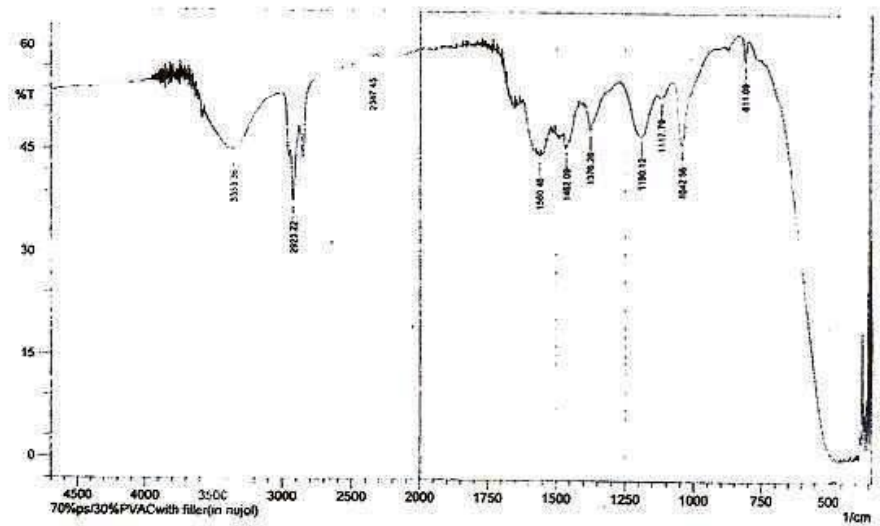


Figure 12: FTIR spectrum for 30% PS/70% PVAc with filler

CONCLUSION

This study reveals the effect of α -cellulose filler on the morphological arrangements of crystallite in PS and PVAc. Though the crystallinity index is highest for 10%/90%, PS/PVAc blend without filler, the compatibility level from surface morphology shows that 20%/80%, PS/PVAc blend had better prospects in terms of end-use applications.

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The Swelling Behaviour of Polystyrene (PS)/ Polyvinylacetate (PVA) Blends in Different Solvents and the Effects of α -Cellulose used as Filler on the Electrical Conductivity.

*P. A. P. Mamza and †B.T. Nwufe

¹Polymer Testing Laboratory, Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria

²Department of Chemistry, University of Jos, Nigeria

(*Corresponding Author: royalcomputersz@yahoo.com)

ABSTRACT: The effect of the variation of the type of solvent responsible for the differences in the swelling kinetics of Polystyrene (PS) and Polyvinyl acetate (PVAc) blends was studied. The results showed that the nature of solvent control or affects the degree of swelling. Also, I-V characteristics at temperature range of 323-363K shows promising semi conducting ability which appreciated with amount of filler in the polymer-polymer matrix.

Keywords: Swelling behavior, Polystyrene (PS) - Polyvinyl acetate (PVA) blends, electrical conductivity, filler composition.

INTRODUCTION

When using polymeric materials, environmental factors play significant role in determining their operational characteristics. Chemical interaction of a polymer with solvents is one such factor that can limit the service life of polymeric materials, other important delimitating factor is electric field.

In this study the swelling behaviours of pure PS-PVA₂ blends are compared with α -cellulose-filled PS- PVAc blends under the influence of different solvents i.e water, 0.05M HCl, 0.05M NaOH and acetone. Also, the variation in its electrical conductivity due to the filler-composition was assessed by their I-V plot characteristics.

The water sorption kinetics in light-cured PolyHEMA and Poly (HEMAco-TEGDMA) by assessing the selfdiffusion coefficient through a new Iterative method was reported earlier (Sideridon *et al.*, 2007). The electrical conduction in iodine doped Polystyrene (PS) and Poly (MethylMethacrylate) (PMMA) has already been reported (Chakraborty *et al.*, 1991; Sangawar, 1995). Keller *et al.*(1991) reported the thermally simulated discharge current (TSDC) study of polyblends of PS and PMMA. Belsare and Deogaonkar (1998) measured the electrical conductivity of iodine doped polyblend films of PS and PMMA. Electrical conduction of succinic acid doped glycine pellet was reported by Burghate *et al.* (2004). Khare

(1994) studied the current-voltage characteristics of malachite green doped cellulose acetate films. Deshmukh *et al* (2005) reported electrical conduction in semi conducting PVC-PMMA thin film. Microhardness and X-ray diffraction studies on Polymer blends of Polyethylene Methacrylate (PEMA) and Polyethylene oxide (PEO) have been reported by Awasthi and Bajpai (2001). Also, Deshmukh *et al* (2007) reported the electrical conductivity of Polyaniline doped PVC-PMMA polymer blends.

Theoretical section

Swelling behavior

According to Liao *et al* (1997), the swelling ratio (S.R) of a polymer can be calculated assuming additivity of volume by

$$S.R = \frac{\frac{W_d}{\rho_{polymer}} + \frac{W_s - W_d}{\rho_{solvent}}}{\frac{W_d}{\rho_{polymer}}} \dots\dots\dots(1)$$

Where W_d and W_s are the weight of dry and swollen polymers respectively and P is density.

The weight of the swollen blends was measured at certain time intervals. The Quotient, Q of the blends was calculated using the equation.

$$Q(\%) = \frac{W_s - W_d}{W_d} \times 100 \dots\dots\dots(2)$$

Where W_s and W_d are the weights of the swollen blends for each time period and the dried one, respectively

Electrical conductivity

There are four possible mechanisms/models of electrical conduction as reported by Deshmukh *et al.*, (2007), however the fifth which is the Arrhenius plots reveals greater details. In this work the Arrhenius plots (\ln vs. $1000/T$) at all values of applied voltage was adopted.

MATERIALS AND METHODS

Materials

Polystyrene (PS) was supplied by Philip Marris Limited, England, Polyvinylacetate (PVA), σ -cellulose filler, hydrochloric acid and acetone were purchased from BDH, Poole, England. Digital Metler Balance AT400, Ammeter, Voltmeter, Platinum electrodes were some instruments used.

Film casting and measurement

Different compositions of PS/PVA_c blend solutions were prepared in Toluene. 20cm³ of the 2% solution of PVA_c were poured carefully into a clean dry Petri dish placed on a flat surface in a fume cupboard and left for 24hours for the solvent to evaporate. 10cm³ of distilled water were then poured on the dry film in the dish. The dish with the content was left for 20minutes to allow the water penetrate the sides of the dish to release the films from the base of the dish. The procedure was repeated in turn for PS, and all the blend solutions. A micrometer screw gauge was used to measure the thickness of the films. Films of thickness of 70 μ m were used in this study.

Swelling properties measurement

The specimens were placed in a dessicator and transferred to a preconditioning oven at 50°C. After 24hours they were removed, stored in the desiccator for 1hour and weighed to an accuracy of ± 0.0001 g using a Mettler balance. This cycle was repeated until a constant mass (m_s) was obtained. The films were in turn immersed in water, HCl, NaOH and acetone at 50°C. At fixed time intervals they were removed, blotted dry to remove excess liquid, weighed and returned to the solvent. The uptake of the liquid was recorded for time intervals up to 30hours.

Electrical conductivity measurements

A thermostatically controlled oven was used for heating purpose. The sample films with silver electrodes were sandwiched between two platinum electrodes (diameter, 2.5cm) and currents measured using an ammeter while the voltage was assessed using a voltmeter.

RESULTS AND DISCUSSION

Previous studies (Mamza and Folaranmi, 1996, Mamza and Nwifo, 2008) showed that the PS/PVA_c ratio corresponding to 20%/80% composition has some considerable degree of compatibility. This was concluded from the plots of reduced viscosity versus concentration, which revealed higher value of observed intrinsic viscosity over the calculated one using Krigbaum - Wall equations. The mechanical properties observed from the StressStrain measurements also supported this. It is based on this, that a further study of the swelling and electrical properties are needed in order to investigate any correlation between the two, it will also give insight into the micro structural arrangements of the composite. Figures (1 & 2) show the swelling behaviors of the PS/PVA_c blend films in water, acid, base and acetone. Both plots show the following general trend; acetone < NaOH < water < HCl, with -cellulose filled polymer blends exhibiting greater swelling characteristics in all the solvents when compared with the virgin PS/PVA_c blend. The explanation is that the -cellulose filler itself, possesses sites for solvent interactions through solubilizing mechanism. In general, Q is related to the osmotic pressure, cross-linking density and copolymer affinity to absorb water (Higgs, and Joanny, 1991; Flory, 1953). In this particular study the main effect on Q is the affinity to solvents (water, base, acid and acetone) and filler concentration. The higher Q values obtainable from the $Q(\%)$ versus $t(h)$ dependence is in conformity with the results of the earlier studies carried out on the blends (Mamza and Folaranmi, 1996; Mamza and Nwifo, 2008). However, the sharp discrepancies observed is attributable to the mode of aggregation with filler in solvent cast-films as compared with articles obtained from a compression press.

The electrical conductivity of the blends were evaluated from the observed behaviour of I-V characteristics and the possibility of ohmic

conduction as well as space charge, limited conduction is ruled out (Figures 3 and 4). The polymers generally falls at low conductivity spectrum and most effects may be due to adventitious ions and hence, the reasons for the observed current-voltage characteristics, with the filler-incorporated blends showing reluctantly an improvement in this regard (Fig. 4). From the Arrhenius plots (Fig 5. and 6), it was observed that the -cellulose filler enhanced the thermal activation energies and decreased the semiconducting behavior of between -0.18 to -0.49eV i.e -0.20 eV from the slope of the plot. It is therefore evident that by a careful consideration of the micro structural

arrangement in the polymer matrix a conduction mechanism that would offer considerable impetus for impedance analyses is required especially in the -cellulose filled PS/PVAC blend.

CONCLUSION

The results of the swelling behaviour and electrical conductivities of Polystyrene (PS) and Polyvinyl acetate (PVA_c) blend showed that the choice of solvent, filler content and mode of processing appreciably determines a possibility for specific applications according to standard methods. The reinforced PS/PVA_c blends can be utilized as semi conductors.

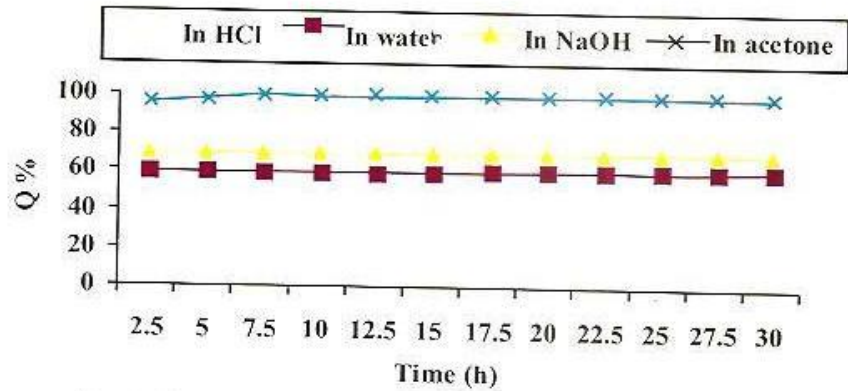


Fig. 1: Swelling Kinetics (Q) of 20%/80%, PSPVAc Blend without filler

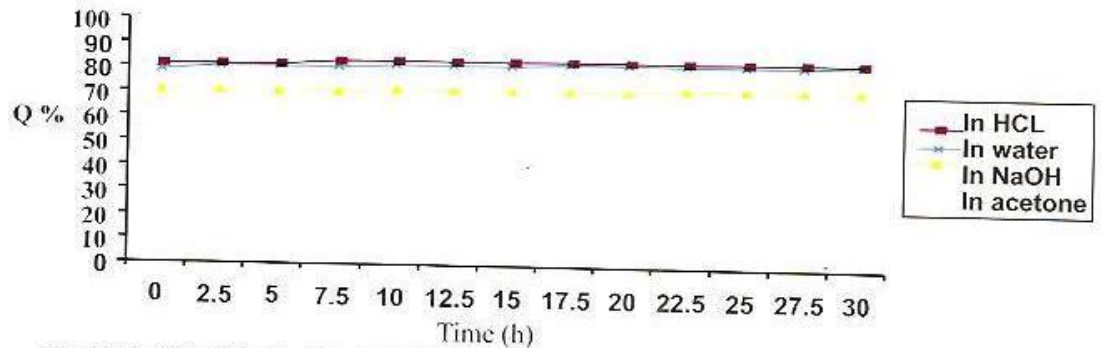


Fig. 2: Swelling Kinetics (Q) of 20%/80%, PS/PVAc Blend with α-cellulose filler

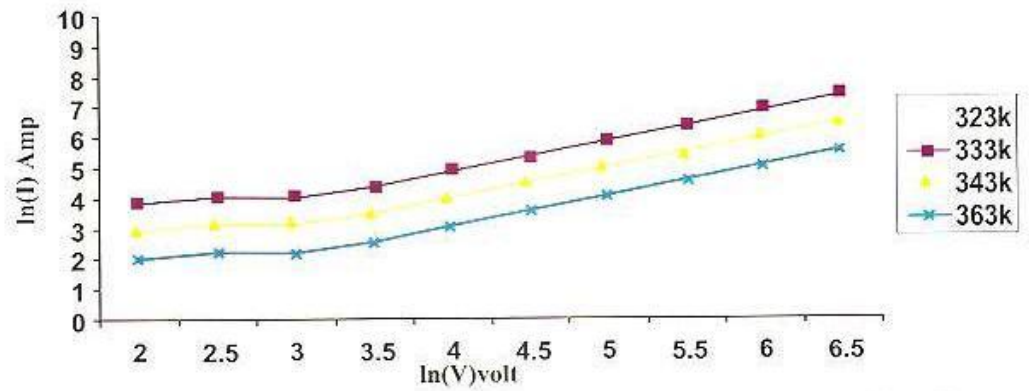


Fig. 3: Current-voltage characteristics for 20%/80%, PS/PVAc blend without filler

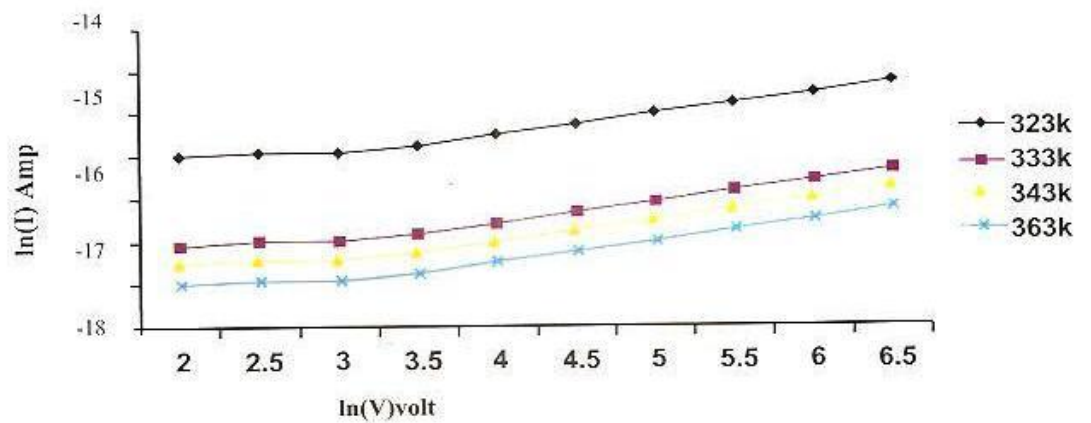


Fig. 4: Current-voltage characteristics for 20%/80%, PS/PVAc blend incorporated with α -cellulose filler

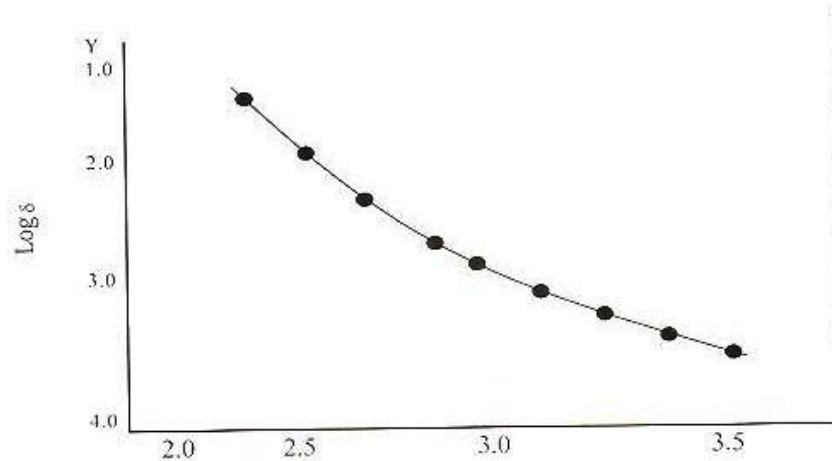


Fig 5: Arrhenius plot for 20%/80% PS/PVAc blend without filler

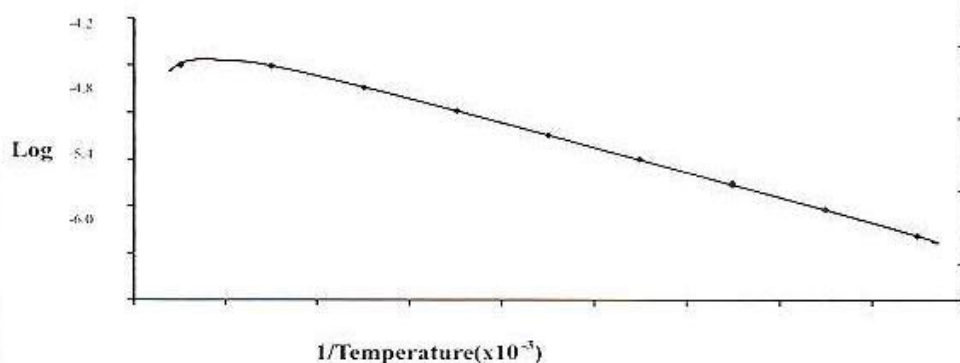


Fig. 6: Arrhenius plot for 20%/80% PS/PVAc blend incorporated with α - cellulose filler

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Density and Morphological Properties of Some Reinforced Polymers

¹P.A.P. Mamza* and ²B.T. Nwufu

¹Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria.

² Department of Chemistry, University of Jos, Nigeria.

[* Corresponding Author's email: mamzapaul@yahoo.com]

ABSTRACT: The morphology of some reinforced blends of Polystyrene (PS) and Polyvinyl Acetate (PVAc) were estimated by density measurements, showing a definite pattern except that the filler composition increases the densities of the blends with 30/70, 20/80 and 10/90, PS/PVAc having highest values than other compositions. Also, photomicrographs of the different blends show a two phase system appearing bright (PVAc phase) and the other appearing black (PS phase) in virtually all the micrographs, even though the heterogeneity due to phase inversions is relevant for some compositions. For some composition a domain distribution shows considerable miscibility within the range of compositions.

KEYWORDS: Phase inversions, domain distribution, miscibility, phase system.

INTRODUCTION

Mechanical and viscometric studies on blends of polystyrene {PS} and Polyvinyl acetate {PVAc} had been reported earlier (Mamza and Folaranmi, 1996; Mamza and Nwufu, 2008) revealing compatibility domains along composition ranges. Also, the swelling behaviour of these blends in different solvents and the effects of filler on the electrical conductivity was reported earlier (Mamza and Nwufu, 2008). Three techniques are widely used to measure densities of polymer sample, these include density gradient column, dilatometry and pycnometry (Tager, 1978). Densities of melted crystallized polymers of semi-crystallized polymers are based on two phase systems (crystalline and amorphous) and each phase may be characterized by a unique density (Sheldon, 1963; Wunderlich 1973). It can be shown that, the weight fraction crystallinity can be expressed as a function of density. In this work the BS 2782 part 6 method is used, while the morphological arrangements of the blends were studied by Scanning Electron Microscopy.

EXPERIMENTAL METHODS

Density Measurement of the PS/PVAc Blends

The density of the blends (both virgin and reinforced) was measured as mass per unit volume, according to BS 2782 part 6. Graphs were plotted of density of unfilled and filled PS/PVAc blend versus blend compositions.

Establishment of Blend Morphologies of the Ps/Pva_c Blends

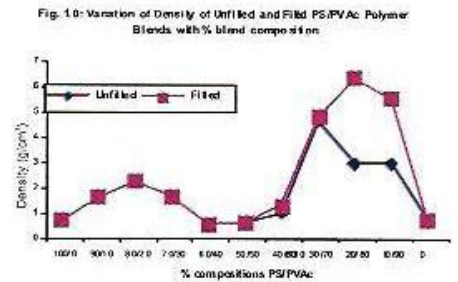
The morphologies of the cross-section of the blend of different compositions with or without the filler incorporated in the polymer-polymer matrix were examined by Scanning Electron Microscope N.J.F (SEM, Jeol, JSM-840 SEM) at magnification of 1000 X (at the Department of Metallurgical Engineering, Ahmadu Bello University, Zaria).

RESULTS AND DISCUSSION

Effect of Filler Composition on the Density of the PS/PVAc Blends

Figure 1.0 show the variation of density of the virgin and reinforced PS/PVAc blends with blend compositions. The trend is similar in both the blends except that the filler increase the density of the blends and that in 30/70%, 20/80% and 10/90% PS/PVAc the densities are higher than the other compositions. Matsuaka (1961) reported that density is a measure of order within a polymer and hence it is evident that the level of interaction and compatibility seem to be higher in these three blend compositions. The densities increase slightly for 90/10% and 80/20%, PS/PVAc and decreases sharply for 70/30%, 60/40% 50/50% PS/PVAc blends increasing, again for 40/60% PS/PVAc and more pronounced in the case of 30/70%,

20/80% and 10/90% PS/PVAc blends. The rise in density is attributable to the fillings of the inherent voids within polymer-polymer matrix by the filler particles. Since it is established that voids are domains of zero density and hence, a high density polymer will have low voids content.



Morphological Studies on the PS/PVAc Blends

Figure 2.0 to 2.19 show the photomicrographs of the different blends of PS/PVAc with and without the B-cellulose filler loadings. They all show two phase systems, bright poly(vinylacetate) phase and black Polystyrene phase. Large macrodomain of the polyvinyl acetate appear to be dispersed in the dark phase of the Polystyrene. Likewise, Polyvinylacetate phase engulfs polystyrene phase. For compositions 70/30, 60/40, 50/50 40/60 and 30/70, PS/PVAc, (with and without filler) i.e.

Figures 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 2.13, 2.14, 2.15, and 2.16 there's apparent show of heterogeneity of phases which reveals the level of immiscibility of Poly(vinyl Acetate) with Polystyrene at these compositions. This phenomenon is indicative of phase inversions. However, blends of compositions 80/20, 10/90, 20/80 and 90/10 PS/PVAc i.e. Figures 2.0, 2.1, 2.2, 2.16, 2.17, 2.18 and 2.19 show a considerable miscibility due to a domain distribution in these ranges of compositions.



Fig. 2.0 Photomicrograph of 10%PS/90% PVAc blend without filler



Fig. 2.2 Photomicrograph of 20%PS/80% PVAc blend with filler



Fig. 2.1 Photomicrograph of 20%PS/20% PVAc blend without filler



Fig. 2.3 Photomicrograph of 20%PS/80% PVAc blend without filler



Fig. 2.4 Photomicrograph of 30%PS/70% PVAC blend without filler



Fig. 2.8 Photomicrograph of 30%PS/50% PVAC blend without filler



Fig. 2.5 Photomicrograph of 30%PS/50% PVAC blend without filler



Fig. 2.9 Photomicrograph of 30%PS/50% PVAC blend without filler



Fig. 2.6 Photomicrograph of 40%PS/60% PVAC blend without filler



Fig. 2.10 Photomicrograph of 60%PS/40% PVAC blend without filler



Fig. 2.7 Photomicrograph of 30%PS/30% PVAC blend without filler



Fig. 2.11 Photomicrograph of 30%PS/30% PVAC blend without filler



Photomicrograph of 70%PS/30%PVAC blend with filler



Photomicrograph of 70%PS/30%PVAC blend without filler



Photomicrograph of 50%PS/50%PVAC blend without filler



Photomicrograph of 50%PS/50%PVAC blend with filler



Fig. 2.14

Photomicrograph of 50%PS/50%PVAC blend with filler



Photomicrograph of 100%PVAC blend with filler



Fig. 2.15

Photomicrograph of 100%PS/0%PVAC blend without filler



Photomicrograph of 100%PS/0%PVAC blend without filler

CONCLUSION

The Density and Morphological studies carried out on the blends had established the level of micro-structural arrangements in the polymer-polymer matrixes, under the effect of α -cellulose filler and had shown that structure-property relationships are essential aspect of Polymer blend Technology through proper end -use applications in the industries.

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