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Monitoring and Evalution of Exotherms as Trouble-Shooting Processes in Polyurethane Foam Manufacture

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Authors' contributions

This work was carried out in collaboration between all authors. Author MBD designed the study, performed the physical analysis, wrote the protocol, and wrote the final draft of the manuscript. Authors AQI and HMA managed the literature searches and proof read the first draft of manuscript. All authors read and approved the final manuscript.

Original Research Article

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ABSTRACT

Monitoring and evalution of exotherms as temperature rises were investigated using various foam formulations from two types of polyols with variations in blow indices as volume of water added. It was observed that exotherms increase linearly with blow index. The results also showed that density variations are in inverse relationship with the exotherms, foam heights and compression sets. Furthermore, it was similarly observed that as the blow index increases, ΔT_1 and ΔT_2 increase for both conventional (CPO) and polymer (PPO) polyols far above the acceptable temperature range of 22-26ºC for foam manufacture with consequences on physical properties.

Keywords: Conventional polyols; polymeric polyol; exotherms; density; compression set.

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1. INTRODUCTION

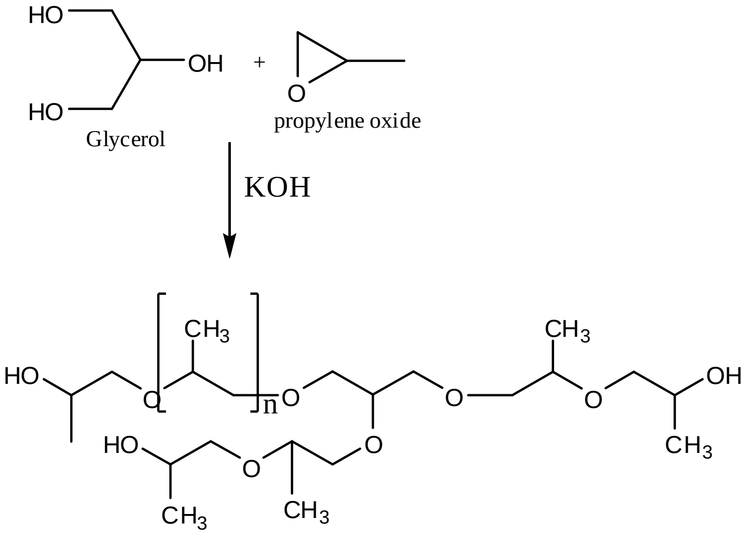
Polvinylchloride (PVC), polystyrene (PS), polyurethane (PU), acrylonitrile butadiene-styrene (ABS), and cellulose acetate are some of the plastics that can be commercially produced in cellular or expanded forms as foams [1]. Foamed plastics comprise a versatile new family of low density, cellular materials which are made in a variety of processes resembling the making of bread whereby a cake rises with the decomposition of the baking powder [2]. Foams, generally have low densities with high modulus to density and high strength to weight ratios and are good heat insulators due to the low conductivity of a gas (air) contained in the matrix [3-4].

Expanded plastics (plastics foams or cellular plastics) have been reported in several literature materials. If a gas is introduced chemically or mechanically during polymerization, a cell-like structure is left of the polymer material, giving it the characteristic foam or cellular appearance [2].

Foamed plastics can be classified based on several schemes, one of which is the nature of the foam cells [4-5]. A closed cell foam has each individual cell, more or less spherical in shape, and is completely closed in a wall of plastics. Closed cell foams are usually produced in processes where some pressure is maintained and the gas is entrapped during cell formation stage, for instance, in the reaction of isocyanate with water in the manufacture of urethane foams [6]. On the other hand, open cell foams have individual cells cross –linked as sponges as a result of free expansion during cell formation. Open cell foams are more suitable for cushioning application because they allow for compression and consequently air flow between cells [7].

Polyurethane foams are formed by reacting a monomer containing at least two isocyanate functional groups R–(N=C=O) with another monomer containing at least two or more hydroxyl groups in the presence of a catalyst system and other additives. These may be aliphatic or aromatic isocyanates and polyols (polyether or polyester resins) [7-8]. Flexible polyurethane foams are produced from linear or high molecular weight polyols that contain few hydroxyl groups per molecule, which on reaction with a isocyanate, give structures with low degree of cross-links [9]. On the other hand, polyols of high functionalities react with isocyanates to produce rigid foams with high degree of cross linking. These foams may be of semi – rigid or rigid grades consisting of closed cells with characteristic low compression set and heat transmission [9]. Several types of conventional polyols are available in the market today mostly formulated from patented works of several investigators [11]. Their backbones are based mainly on ethylene oxide or propylene oxide or their derivatives or blends of the two (equation1). Various percentage compositions of these oxides have been reported ranging from molecular weight averages (450 – 30,000) depending on the end-use requirements of the final product. The primary hydroxyl groups for these polyols have been reported to range from 2 – 6, depending on the type of glycols (glycerol, pentaerithritol, sorbitol etc) incorporated in the formulation of the prepolymer [8,10,11].

Polymer polyols are essentially the conventional polyols or their blends incorporated with a co-polymer mainly styrene-acrylonitrile copolymer or styrene-acrylonitrile-vinylidene chloride terpolymer dispersed or dissolved within the conventional polyols to produce high density, high resilient, higher load bearing, non-shrinking, free rise foams compared to those from unmodified polyols. The compositions of these polymer polyols are dependant on the copolymerization of one or two ethylenically unsaturated monomers dissolved or dispersed in a conventional polyol to form a stable dispersion of polymer particles in the polyols [10-12].



........................(1)

Molecular weight ca 3000

Much have been reported and several patents are available on the development of polyurethane foam Chemistry and Technology since the end of World War II (1945). The concern here is that polyurethane foam formation is extremely an exothermic process, producing large amount of heat during the reaction process leading to trouble-shooting [13-14] Makanjuola, and Ikeh, et al. in their separate reports indicated that manufacturers of polyurethane foams must understand the chemistry of the process, so that trouble-shooting is easily carried out with necessary formulation adjustment to compensate for local prevailing conditions. If the chemicals are too hot or cold, problems will be encountered as viscosity, density and chemical reactivity of polyols and TDI vary with temperature. Consequently, the monitoring and correlation of temperature rises with extent of reaction and physical properties are essential at optimal heat level. The first and chain propagating reaction is the basic reaction for the formation of urethane, that is polymerization reaction between polyol and TDI [15-16].

$$R'\text{–}OH + R\text{–}NCO \longrightarrow R – NH – CO – OR' \ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

$$\text{Urethane} \qquad \Delta H = -90 KJ/mol$$

The second reaction is the gas –forming reaction, which liberates CO_2 and simultaneous formation of urea. This is the reaction between TDI and water. The first step in this reaction is the formation of an unstable carbamic acid, which decomposes to form a primary amine and carbon dioxide which serves as the primary blowing agent, with evolution of large amount of heat (equation 2). Therefore the overall reactions are extremely exothermic with temperature rises between 160-180ºC [3]

$$R\text{–}N{=}C{=}O + H_2O \longrightarrow R\text{–}NH\text{–}CO\text{–}OH \longrightarrow RNH_2 + CO_2(g) \ldots\ldots\text{(3)}$$

$$\text{Carbamic acid} \qquad \Delta H = -170 KJ/mol$$

Water serves as a primary blowing agent for polyurethane systems. Several researchers have reported the effect of water as a blowing agent in polyurethane foam manufacture and have `observed that the large amount of heat liberated during this process has great effects on the physical and mechanical properties of foams manufactured and the causes of factory fire outbreaks [17]. Monitoring the effects of exotherms (equations 2 & 3) on foam densities, heights and compressions with variations in the amount of water added as blowing agent using conventional and polymer polyols is necessary as this has consequences on the comfort and mechanical properties during service life [18].

The aim of this research is to monitor and evaluate the effects of exotherms on some foam physical properties with variations in the amount of water added as blowing agent using conventional and polymer polyols.

2. MATERIALS AND METHODS

2.1 Samples/Industrial Chemicals

Conventional polyols (CPO) - polyether based,
Polymer polyol (PPO) - polyether based with dispersed (grafted) copolymers such as ABS, Acrylonitrile, Styrene etc.
Toluene diisocyanate (TDI 80:20) Bpt 250ºC.
De-ionised water (blowing agent)
Stannous Octanoate - catalyst.
Dimethyl ethanolamine - catalyst.
Poly silicone fluid (polydimethyl siloxane) - surfactant.
Methylene dichloride- Flame retardant and auxiliary blowing agent
Calcium carbonate ($CaCO_3$) - Filler (bulk and reinforcing filler).
All the chemicals, except water were graciously obtained from Vitafoam Nig. Plc. JOS factory.

2.2 Equipment/Apparatus

Transparent cylindrical plastic moulds (14cm- diameter by 20cm height) were locally assembled Glasswares/vernier calipers, micrometer screw gauge, micro-syringes, thermometers, balances etc were obtained in our laboratory.

2.3 Determination of Some Physical Properties of the Polyols

The refractive indices, specific densities and pH values of the polyols were determined by conventional methods [19].

2.4 Determination of Some Chemical Parameters of the Polyols

2.4.1 Determination of acid value [20]

2.4.1.1 Method

Three grams (3g) of the polyol was weighed into a 250cm^3 conical flask and 40cm^3 of mixed solvent (2 parts benzene and 1 part ethanol (v/v) was added. This was dissolved by rotating the flask and warming on a water bath. It was cooled and titrated rapidly with 0.1M ethanolic

KOH until change of colour occurred. Similarly, a blank titration (without polyol sample) was concurrently run.

The acid values were calculated from the expression: Acid value = $\frac{56.1 \times M(a - b)}{w}$ --------(4)

a = Volume of KOH (in cm^3) for blank
b = Volume of KOH (in cm^3) for polyol
M = molarity of KOH
w = weight of polyol sample (g)

2.4.2 Determination of hydroxyl value of the polyols [11]

2.4.2.1 Acetylating agent

This was prepared by addition of sufficient amount of distilled pyridine to 25g of dry acetic anhydride in a $100cm^3$ volumetric flask and diluted to volume. The entire content was mixed by swirling the flask gently, and the mixture stored in a brown glass container, stoppered and placed in the fume cupboard.

2.4.2.2. Method

1.5g of polyol was weighed into a $250cm^3$ flask and $5cm^3$ acetylating agent was added using a pipette. The mixture was shakened gently to ensure uniformity. A blank was also prepared by measuring an equal amount of the acetylating agent ($5cm^3$) into a second $250cm^3$ flask. The two flasks were place in a steam bath and heated for one hour under reflux. They were allowed to cool and water was added through the condenser. The mixtures were shakened to ensure turbidity was absent. The mixtures were allowed to cool and the flasks and condenser washed down with $5cm^3$ ethanol to neutralize. Each mixture was then titrated with 0.5M ethanolic potassium hydroxide solution and 3drops of 1% ethanolic phenolphthalein indicator added until a faint pink colour was reached. The hydroxyl value was calculated from the expression: Hydroxyl value $= \frac{56.1 \times M(v_2 - v_1)}{w} + A$ -------------------------------(5)

Where: A = Acid value as calculated above, M = Molarity of KOH solution, v_2 = Volume of KOH solution used for blank, v_1 = Volume of KOH solution used for oil, w = weight of Polyol.

2.5 Monitoring of Exotherms in Foam Formulation [16]

Standard formulations were prepared from recipes as shown on Tables 1a and 1b for CPO and PPO. Transparent air-tight cylindrical plastic moulds (flasks) of 14cm-diameter and 20cm heights were assembled. With a motorized screw, two holes were drilled through the lid of each mould to insert a thermometer and a flighted glass stirrer to fit. The thermometer was inserted in such a way that the lower bulb goes three-quarters into the mould to enable easy contact with rising foam mix. The one-shot technique was employed whereby all the “ingredients” were added stepwisely using syringes and mixed thoroughly for 10mins before the Toluene Diisocyanate (TDI) was added and stirred to cream. The room temperature and the temperature at cream, and final temperature at rise were taken and recorded. Furthermore, the difference between room temperature and rise temperature is taken as ΔT_1 and between cream and rise as ΔT_2. Various formulations were then carried out with water at 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, $1.0cm^3$ in that order and temperatures recorded, with some formulations carried out in the presence or absence $CaCO_3$ and MC as shown on

Table 1b. The densities and the blow indices of the foams from the formulations are calculated as:

$$\text{Density} = \frac{\text{weight of foam (g)}}{\pi r^2 h} \quad \text{----- (6a)}$$

Volume of foam = $\pi r^2 h$: r = radius of cylinder (cm), h =foam height (cm), π = 22/7

$$\text{Blow index} = \frac{\text{weight of water (g) + weight of MC (g)}}{10} \quad \text{--- (6b)}$$

Where MC = Dichloromethane (auxiliary blowing agent)

Table 1a. Standard formulations for preparing CPO and PPO based foams for monitoring of exotherms

	Pbv (cm^3)	Pbw(g)
CPO or PPO	10.00	10.40
TDI	4.50	5.54
Water	0.10	0.10
D.M.E.A	0.02	0.02
Silicone	0.10	0.10
Stannous Octonoate	0.04	0.05
Methylene Chloride	1	1.5
Calcium Carbonate	--	2.10

Where Pbv and Pbw = Part by volume and part by weight respectively

Table 1b. Summary of formulations for exotherm studies

Sample Identity for CPO	Formulations	Sample Identity for PPO
A_1 ---A_{10}	In the presence of $CaCO_3$ and MC	X_1 ---X_{10}
B_1 ---B_{10}	In the presence of $CaCO_3$ only	Y_1 ---Y_{10}
C_1 ---C_{10}	In the presence of MC only	W_1 ---W_{10}
D_1 ---D_{10}	In the absence of $CaCO_3$ and MC	Z_1 ---Z_{10}

2.6 Determination of % Compression Set [21-22]

The test pieces were cut into dimensions. The samples were placed in the compression device which consisted of two flat plates with parallel to each other was ensured and the space between plates was adjusted to the required deflected height. The test piece was compressed by 50%, maintained at ambient temperature of 27°C for 22 hours. At the end of the 22 hours, the test piece was removed from the device and placed on a wooden surface since wood is of low thermal conductivity. The test piece was allowed to recover for 30minutes after which its thickness was measured as

$$\text{(Tr)}\textbf{;}\ \%\ \text{Compression Set} = \frac{T_o - Tr}{T_o} \times 100 \quad \text{------- (7)}$$

Where T_o = initial thickness, Tr = thickness after removal of load after 30 mins.

3. RESULTS AND DISCUSSION

The results of some physical and chemical properties of the polyols are presented on Table 2 while the results of the exotherms for the various foam formulations are shown on Tables 3-10.

Table 2 gives some physical and chemical properties of the polyols. It indicates that the Polymer polyol (PPO) is more viscous, acidic, with higher boiling point, density and invariably higher molecular weight than conventional polyol (CPO). However CPO has a higher hydroxyl number than PPO because it has more free primary OH-groups than PPO. The reason is that PPO as grafted co-polymer has a higher molecular weight with less primary hydroxyl groups than CPO. This implies that PPO would form more rigid and denser foams than CPO [8,10,23,24].

Table 2. Some physical and chemical properties of the conventional and polymer polyols

Properties	Conventional polyol(CPO)	Polymeric polyol (PPO)
Colour (visual)	Clear	milk white
State	Liquid	Liquid
Relative viscosity at 25^{0}C	10.25	11.66
Solubility in alcohol	Complete	Complete
Boiling point (^{0}C)	145	182
Refractive index	1.47	---
Density (g/cm^3)	1.01	1.04
pH	10.25	5.52
Hydroxyl value (mgKOH/g)	187.20	169.20
Acid value (mg KOH/g)	1.16	2.23

Tables 3-10 present the results of co-relations of exotherms and blow indices with physical properties in the presence or absence of $CaCO_3$ filler or methylene dichloride (MC), an auxiliary blowing agent and fire retardant. The results show the effects of variations of volume of water (a primary blowing agent) as blow indices in the presence or absence of MC (a prohibited volatile organic compound (VOC) and one of the CFCs banned by EU and the Federal Government of Nigeria [25-28], yet the foam industry in Nigeria still uses) or $CaCO_3$ a conventional filler, on exotherms, foam densities, heights and % compression. The results generally show that % compression and height increase with increase in blow index as exotherm also increases while density decreases. Generally it was observed that CPO foam formulations generate more heat (exotherms) compared to the ones formulated with PPO. This can be explained on the fact that CPO system has higher concentration of free primary OH-groups making it more reactive than PPO which has higher concentration of secondary OH-groups making less reactive comparatively [16,24]. Furthermore, because of viscosity build up at gelation, the dissipation of heat at gelation stage for the CPO system is easily achieved since it is less viscous than PPO, leading to higher exotherms compared to PPO which does it slowly. Again, PPO cross-link density is higher than that of CPO leading to a corresponding gradual increase in temperature with increase in volume of water as blowing agent. Consequently, PPO foams have higher densities than CPO foams at increasing volume of water and also % compression [8]

Comparing and contrasting parameters on Tables 3 and 4, exotherms A_1-A_{10} CPO versus X_1-X_{10} PPO formulations respectively in presence of $CaCO_3$ and methylene chloride (MC) show, ΔT_1 (38-50ºC); ΔT_2 (37-39.5ºC) and ΔT_1 (32-42ºC); ΔT_2 (29-36ºC) in that order. These gradual increases are expected with increasing volume of water from 0.1-1.0 cm^3 as more heat is liberated. This is expected as the volume of water increases, more CO_2 is generated leading to inflation of the foams, with increase in exotherms (equation 2 and 3). Furthermore ΔT_1 and ΔT_2 values for CPO formulations are correspondingly higher than ΔT_1 and ΔT_2 for PPO. However, X_1-X_{10} PPO foam densities are higher than those of A_1-A_{10}, CPO due to composition differentials earlier mentioned and the same reason goes for % compression which increases linearly with blow index and height for both CPO and PPO [21].

Comparing and contrasting parameters on Tables 5 and 6, exotherms for B_1-B_{10} CPO versus Y_1-Y_{10} PPO formulations respectively in the presence of $CaCO_3$ only, shows; ΔT_1 (33-52ºC); ΔT_2 (32-42.5ºC) and ΔT_1 (17-28ºC); ΔT_2 (14-18.8ºC) in that order. Again, the same trend is observed as indicated on Tables 3 and 4. However, it was observed that the absence of MC has little or no effects on the exotherms ΔT_1 and ΔT_2 CPO formulations on Table 5 compared to the corresponding ΔT_1 and ΔT_2 CPO exotherms displayed on Table 3. On the other hand, the absence of MC has drastic effects on the exotherms, ΔT_1 and ΔT_2 PPO formulations on Table 6 compared to ΔT_1 and ΔT_2 PPO shown on Table 4 with ΔT_1 and ΔT_2 on Table 6 displaying much lower values than the corresponding ΔT_1 and ΔT_2 on Table 4. However, the corresponding densities are in reverse order. The reason for this phenomenon may be explained by the fact that the heat generated in the process is absorbed more or less by $CaCO_3$ present [15,29]. Again compression (%) increases linearly with increases in blow indices and heights for both CPO and PPO samples.

Comparing and contrasting parameters on Tables 7 and 8, exotherms for C_1-C_{10} CPO versus W_1-W_{10} PPO formulations respectively in the presence of MC only, show, ΔT_1 (35-50ºC); ΔT_2 (33-41.3ºC) and ΔT_1 (22-38.8ºC); ΔT_2 (20-27ºC) in that order. Again it was observed that the presence of MC has little or no effects on CPO formulations compared to the results on Table 3. However, the presence of MC only, has a drastic effect on the exotherms on PPO formulations; as ΔT_1 and ΔT_2 PPO exotherms on Table 8 are much lower than the corresponding ΔT_1 and ΔT_2 on Table 4. This means that MC suppresses heat evolved easily in PPO formulations than in CPO which is more reactive [11]. Compression (%) increases linearly with increases in blow indices and heights for both CPO and PPO samples.

Comparing and contrasting parameters on Tables 9 and 10 exotherms for D_1-D_{10} CPO versus Z_1-Z_{10} PPO formulations respectively in the absence of $CaCO_3$ and MC indicates that ΔT_1 (34-49.2ºC); ΔT_2 (33-41.2ºC) and ΔT_1 (36-54ºC); ΔT_2 (35-47.1ºC) in that order. It was observed again that both $CaCO_3$ and MC has no effects on exotherms of CPO formulations compared to CPO exotherms on Table 3 with added $CaCO_3$ and MC, even though corresponding densities are higher compared to those on Table 9 because $CaCO_3$ as a filler increases density. On the other hand, the absence of $CaCO_3$ and MC have tremendous effect on the PPO exotherms as ΔT_1 and ΔT_2 PPO exotherms on Table 10 in the absence of $CaCO_3$ and MC are higher than the corresponding exotherms on Table 4 in the presence of $CaCO_3$ and MC. Similarly, PPO formulation exotherms on Tables 4, 6 and 8 in the presence of MC only, have much lower values compared to the corresponding exotherms on Table 10. This suggests that the effects of MC as a fire (flame) retardant on PPO formulations are more pronounced, but its effects are overshadowed by the high reactivity of the free-primary OH-groups in CPO. In any case, it blends (interacts) favorably with PPO [14]. Compression (%) increases linearly with increases in blow indices and heights for both CPO and PPO samples while density shows an inverse relationship with these parameters.

Table 3. Results of variations of exotherms and physical properties with blow index for conventional Polyol (CPO) foam formulations in the presence of MC and $CaCO_3$

Foam identity	**Blow index**	**Temperatures (^{o}C)**					**Physical properties**		
Sample code		**Room (t_o)**	**Cream (t_c)**	**Rise (t_f)**	**ΔT_1**	**ΔT_2**	**Density (g/cm^3)**	**Height (cm)**	**Compression (%)**
A_1	0.16	26.00	27.00	64.00	38.00	37.00	22.90	8.00	2.90
A_2	0.17	26.00	27.50	65.50	39.50	38.00	22.50	8.50	3.23
A_3	0.18	26.00	28.00	69.00	41.00	39.00	21.90	8.90	3.27
A_4	0.19	26.00	29.00	70.50	43.00	40.00	21.70	9.90	3.74
A_5	0.20	26.00	31.00	71.80	44.50	39.50	21.43	9.95	4.09
A_6	0.21	26.00	31.50	72.00	45.80	40.30	21.05	10.00	4.27
A_7	0.22	26.00	32.50	73.50	46.00	39.50	20.85	10.48	4.65
A_8	0.23	26.00	33.00	75.00	47.50	40.30	20.60	10.85	5.09
A_9	0.24	26.00	36.50	75.00	49.00	40.00	20.30	10.90	5.73
A_{10}	0.25	26.00	36.50	76.00	50.00	39.50	19.70	11.05	6.18

Where $\Delta T_1 = t_f - t_o$; $\Delta T_2 = t_f - t_c$

Table 4. Results of variations of exotherms and physical properties with blow index for Polymer Polyol (PPO) foam formulations in the presence of MC and $CaCO_3$

Foam identity	**Blow index**	**Temperatures (^{o}C)**					**Physical properties**		
Sample code		**Room (t_o)**	**Cream (t_c)**	**Rise (t_f)**	**ΔT_1**	**ΔT_2**	**Density (g/cm^3)**	**Height (cm)**	**Compression (%)**
X_1	0.16	26.00	29.00	58.00	32.00	29.00	23.60	7.20	2.50
X_2	0.17	26.00	29.50	59.00	33.00	29.50	23.20	7.35	2.72
X_3	0.18	26.00	30.00	62.50	36.00	32.00	23.00	8.40	3.00
X_4	0.19	26.00	30.50	62.50	36.50	32.50	22.96	8.58	3.28
X_5	0.20	26.00	31.00	63.80	37.50	32.80	22.95	8.60	3.94
X_6	0.21	26.00	32.00	63.50	38.80	32.50	22.90	8.61	4.70
X_7	0.22	26.00	33.00	64.00	38.00	31.50	22.50	9.65	5.63
X_8	0.23	26.00	33.50	65.00	39.50	31.50	22.42	9.70	5.77
X_9	0.24	26.00	33.50	67.00	41.50	32.00	22.35	10.72	6.01
X_{10}	0.25	26.00	36.00	68.50	42.50	36.50	22.30	10.80	6.07

Where ΔT1 = tf - to; ΔT2 = tf – tc

Table 5. Results of variations of exotherms and physical properties with blow index for CPO foam formulations in the presence of $CaCO_3$ only

Foam identity	Blow index	Temperatures (ºC)					Physical properties		
Sample code		Room (t_o)	Cream (t_c)	Rise (t_f)	ΔT_1	ΔT_2	Density (g/cm^3)	Height (cm)	Compression (%)
B_1	0.16	26.00	26.90	59.00	33.00	32.10	23.40	7.20	2.24
B_2	0.17	26.00	27.00	62.00	36.00	35.00	23.00	7.40	2.26
B_3	0.18	26.00	28.00	64.00	38.00	36.00	22.80	7.80	3.10
B_4	0.19	26.00	30.00	65.50	39.50	35.50	22.45	7.89	3.43
B_5	0.20	26.00	31.00	67.00	41.00	36.20	22.01	8.80	3.86
B_6	0.21	26.00	32.80	69.00	43.00	36.50	21.90	8.85	3.91
B_7	0.22	26.00	34.00	70.50	44.50	36.50	21.70	8.90	4.72
B_8	0.23	26.00	34.50	71.00	45.00	36.50	21.30	9.07	4.98
B_9	0.24	26.00	35.00	73.50	47.50	38.50	21.00	9.50	5.59
B_{10}	0.25	26.00	36.00	78.50	52.50	42.50	20.85	10.20	6.13

Where $\Delta T_1 = t_f - t_o$; $\Delta T_2 = t_f - t_c$

Table 6. Results of variations of exotherms and physical properties with blow index for PPO foam formulations in the presence of $CaCO_3$ only

Foam identity	Blow index	Temperatures (ºC)					Physical properties		
Sample code		Room t_o	Cream t_c	Rise (t_f)	ΔT_1	ΔT_2	Density (g/cm^3)	Height (cm)	Compression (%)
Y_1	0.16	26.00	29.00	43.00	17.00	14.00	25.80	5.50	1.11
Y_2	0.17	26.00	30.00	43.50	17.50	13.50	25.75	6.00	1.18
Y_3	0.18	26.00	30.50	45.00	19.00	14.50	25.00	7.20	2.01
Y_4	0.19	26.00	31.00	47.50	21.00	16.00	24.95	8.00	2.45
Y_5	0.20	26.00	31.00	47.50	21.50	16.50	24.70	8.50	2.87
Y_6	0.21	26.00	33.00	48.00	22.00	16.00	24.40	8.90	3.11
Y_7	0.22	26.00	34.00	49.00	23.00	17.00	24.10	9.00	3.75
Y_8	0.23	26.00	34.50	51.00	25.00	16.50	24.00	9.50	4.55
Y_9	0.24	26.00	35.00	53.00	27.00	18.00	23.80	10.00	4.98
Y_{10}	0.25	26.00	36.00	54.80	28.80	18.80	23.45	10.10	5.07

Where $\Delta T_1 = t_f - t_o$; $\Delta T_2 = t_f - t_c$

Table 7. Results of variation of exotherms and physical properties with blow index for CPO foam formulations in the presence of MC only

Foam identity		**Temperatures (ºC)**					**Physical properties**		
ample code	**Blow index**	**Room t_o**	**Cream t_c**	**Rise (t_f)**	**ΔT_1**	**ΔT_2**	**Density (g/cm^3)**	**Height (cm)**	**Compression (%)**
C_1	0.16	26.00	28.00	61.00	35.00	33.00	19.80	8.70	3.17
C_2	0.17	26.00	28.50	62.50	36.50	34.00	19.45	8.80	3.20
C_3	0.18	26.00	29.00	63.00	37.00	34.00	18.00	8.94	4.03
C_4	0.19	26.00	30.00	65.00	39.00	35.00	18.90	9.00	4.29
C_5	0.20	26.00	31.50	67.20	41.20	35.70	18.71	9.90	4.67
C_6	0.21	26.00	31.90	68.90	42.90	37.00	18.46	9.58	4.98
C_7	0.22	26.00	32.50	69.00	43.00	36.50	17.13	9.95	5.15
C_8	0.23	26.00	33.00	72.00	46.00	39.00	17.01	10.20	6.79
C_9	0.24	26.00	34.50	73.00	47.00	38.50	18.82	10.82	7.77
C_{10}	0.25	26.00	35.20	76.50	50.00	41.30	18.51	11.00	8.53

Where $\Delta T_1 = t_f - t_o$; $\Delta T_2 = t_f - t_c$

Table 8. Results of variations of exotherms and physical properties with blow index for PPO foam formulations in the presence of MC only

Foam identity		**Temperatures (ºC)**					**Physical properties**		
Sample code	**Blow index**	**Room t_o**	**Cream t_c**	**Rise (t_f)**	**ΔT_1**	**ΔT_2**	**Density (g/cm^3)**	**Height (cm)**	**Compression (%)**
W_1	0.16	26.00	28.00	48.00	22.00	20.00	15.50	9.90	3.01
W_2	0.17	26.00	28.00	48.50	22.50	20.50	15.00	10.50	3.17
W_3	0.18	26.00	28.00	50.00	24.00	22.00	14.90	10.90	3.39
W_4	0.19	26.00	28.00	52.00	26.00	24.00	14.24	11.20	3.72
W_5	0.20	26.00	30.00	55.50	29.50	25.50	14.00	11.80	4.12
W_6	0.21	26.00	31.50	57.00	31.00	25.50	13.80	11.80	5.16
W_7	0.22	26.00	33.00	58.50	32.50	25.00	13.40	12.10	5.56
W_8	0.23	26.00	34.00	61.00	35.00	27.00	13.00	12.50	6.78
W_9	0.24	26.00	34..50	63.00	37.00	28.50	12.50	12.60	7.46
W_{10}	0.25	26.00	37.00	64.80	38.80	27.80	12.00	12.80	8.20

Where $\Delta T_1 = t_f - t_o$; $\Delta T_2 = t_f - t_c$

Table 9. Results of variations of exotherms and physical properties with blow index for CPO foam formulations in the absence of MC and $CaCO_3$

Foam identity	Blow index	Temperatures (ºC)					Physical properties		
Sample code		**Room t_o**	**Cream t_c**	**Rise (t_f)**	**ΔT_1**	**ΔT_2**	**Density (g/cm^3)**	**Height (cm)**	**Compression (%)**
D_1	0.16	26.00	27.00	60.00	34.00	33.00	23.40	5.50	2.63
D_2	0.17	26.00	28.00	61.50	35.50	33.50	23.01	6.10	2.91
D_3	0.18	26.00	29.00	63.00	37.00	34.00	22.50	6.70	3.24
D_4	0.19	26.00	29.50	63.50	37.50	34.00	22.04	6.95	3.97
D_5	0.20	26.00	30.00	64.00	38.00	34.00	22.00	7.60	4.11
D_6	0.21	26.00	30.20	66.00	40.00	35.80	21.35	7.51	4.97
D_7	0.22	26.00	31.50	68.00	42.00	36.50	21.35	7.75	5.73
D_8	0.23	26.00	31.00	69.80	43.80	37.80	21.08	8.00	5.97
D_9	0.24	26.00	33.00	72.00	46.00	39.00	20.90	8.70	6.29
D_{10}	0.25	26.00	34.00	75.20	49.20	41.20	20.75	8.85	7.61

Where $\Delta T_1 = t_f - t_o$; $\Delta T_2 = t_f - t_c$

Table 10. Results of variations of exotherms and physical properties with blow index for PPO foam formulations in the absence of MC and $CaCO_3$

Foam identity	Blow index	Temperatures (ºC)					Physical properties		
Sample code		**Room t_o**	**Cream t_c**	**Rise (t_f)**	**ΔT_1**	**ΔT_2**	**Density (g/cm^3)**	**Height (cm)**	**Compression (%)**
Z_1	0.16	26.00	27.00	62.00	36.00	35.00	21.00	4.90	2.97
Z_2	0.17	26.00	27.50	63.70	37.70	36.20	20.90	5.50	3.03
Z_3	0.18	26.00	28.50	66.00	40.00	37.50	20.50	5.90	3.18
Z_4	0.19	26.00	28.50	68.50	42.50	39.50	20.00	6.20	3.47
Z_5	0.20	26.00	29.00	70.00	44.00	41.00	19.80	6.80	4.01
Z_6	0.21	26.00	30.50	71.00	45.00	40.50	19.20	7.00	4.22
Z_7	0.22	26.00	31.00	73.50	47.50	42.50	19.00	7.10	4.67
Z_8	0.23	26.00	32.00	74.00	48.00	42.00	18.70	7.50	5.99
Z_9	0.24	26.00	32.50	78.00	52.00	45.50	18.50	8.00	6.38
Z_{10}	0.25	26.00	32.90	80.00	54.00	47.10	18.10	8.80	7.88

Where $\Delta T_1 = t_f - t_o$; $\Delta T_2 = t_f - t_c$

4. CONCLUSION

From this study, it has been demonstrated that the concentration of blowing agent invariably, relates to the physico-mechanical properties of foams hence monitoring of exotherms is very critical [30-35] . The production of polyurethane foams is an exothermic process, liberating large amount of heat which depends on the following factors; type and functionality of the polyol, and type and amount of blowing agent. The temperature-amount of water profile reveals the extent of heat liberated using CPO and PPO. The relative importance of both the blowing and the gelling steps can be assessed by their individual contribution to the overall exotherms. The CPO based formulations liberate more heat than the corresponding polymer polyol based formulations which relate to their compositions as earlier mentioned [10-12]. Based on foam densities and compositions, the polymer polyol is more suitable for both high and low density rigid and flexible polyurethane foams while the conventional polyol on the other hand is suitable for very low density flexible polyurethane foams [36-39].

5. RECOMMENDATION

It is recommended that more research should be carried out to find ways of reducing exotherms in polyurethane foam manufacture. Appropriate mold design should be employed to minimized the adverse effect of high exotherms on the end products. Furthermore, eco-friendly blowing agent and fire retardant alternatives should be employed in polyurethane foam formulations.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Klemper D, Sendijaveric V. Handbook of Polymeric Foams and Foam Technology. 2nd Ed. Hanser Publishers. Munich. 2004;339-378.
2. Lee ST, Ramesh NS. Editors of Polymeric Foams: Mechanisms and Materials. CRC_Press, U.S.A; 2004
3. Ajayi J. Lecture delivered on Chemistry of polyurethane at training programme organized by Manufacturers Association of Nigeria in conjunction with TEMM Consulting Ltd, Ikeja. 1999;1-11.
4. Oertel G. Polyurethane Handbook, second ed, Munich Cari Hanser Publishers, Germany; 1993.
5. Kobushi K. Polyurethane foams, New York, Journal of Polymer Science, John Wiley, 1967;3:119
6. Gowariker VR, Viswanathan NV, Sreedhar Jayadev. Polymer Science, New Age International Publishers, New Delhi, India. 2007;306-321.
7. Seymour Raymond, Charles Carraher. Polymer Chem New York, Marcel Dekker, New York. 1992;3(2):10-15.
8. Chinn Henry, Akihiro Kishi, Uwe Loechner. Polyether Polyols for Urethanes (abstract only without subscription)", SRIConsulting, April, 2006. Accessed on10th March; 2010. Available: www.sriconsulting.com/CEH/Public/Reports/688.3000/.
9. Herrington R, Hock K. Flexible Polyurethane Foams. Dow Plastics; 2006.
10. Ionescu M. Chemistry and Technology of Polyols for Polyurethane. RAPRA Technology Limited. 2005;13-30.

11. Kaszynski Poitr, Oleg Kadkin, Karol Osajda, Thomas A, Barber. Polyester Polyols: Synthesis and Characterization of Diethylene Glycol Terephthalate Oligomers (PDF), Journal of Polymer Science,Part A: Polymer Chemistry. 2003;41(8):1114–1123. Accessed on 9th August, 2010.
    Available: www.vanderbilt.edu/AnS/Chemistry/omrg/Articles.
12. Lysenko Z, Babb DA, Stutts KJ, Zhang M, Schrock AK. Ployestherpolyols containing secondary alcohol groups and their use in making polyurethanes such as Flexible polyurerthane foams; 2010. Patent No: 7750108.
13. Sure Chem. Polyurethane foam sealing material and process for producing the same, Document USPTO; 2011, Patent No: 4264743
14. U S Patent Nos: 5171759, 33835 ,3304273, 3325421, 4374209; 1998.
15. Makanjuola D. Hand book of flexible foam manufacture, Temm consulting Ltd. Ikeja, Lagos, Nigeria. 1999;3–6.
16. Ikeh PO, Abdulrahman FW, Kolawole EG. Monitoring the Temperature Profile with changes in blowing agent concentration for castor oil based flexible polyurethane foams, Paper presented at 18th Annual Conference of Polymer Institute of Nigeria, Jos, Plateau State Nigeria, 24th-27th October; 2007.
17. Lefebvrte J, Basin B, Bras ML, Duguesne S, PaleJa R, Delobei R. Thermal Stability and Fire Properties of Conventional Flexible Polyurethane Foam Formulations. Polym. Degradation and Stability. 2004,88:28-34.
18. PaPa AJ, Runyan WW. Method of producing Flexible Flame Retarded Polyurethane Foam; 2000. US Patent No:62353.
19. Ilaboya R, Umukoro L, Omofuma FE, Atipko E. Effects of Formulation Parameters on the Properties of Flexible Polyurethane Foams, World Applied Sciences Journal. 2011;14(1):167-174.
20. ASTM D 1639–90. Standard Method for Acid Value of Organic Materials, Annual book of American Society for Testing and Material Standards, Philadelphia, PA. 1994;06(01):260-1.
21. Abdul-Rani AM, Hopkinson N, Dickens P. Analysis of Polyurethane Foam Processing and Surface Texture. In: Rapra Conference, Hamburg; 2004.
22. Nigeria Industrial Standard (NIS, 152). Methods of Test for Flexible Cellular Materials; 2006.
23. Alper H, Garcia JL, Jang EJ. New heterogeneous catalysis for the synthesis of poly(ether polyol)s"(abstract), Journal of Applied Polymer Science. 2002;86(7):1553–1557. Accessed on 9th August, 2010.
    Available:www.interscience.wiley.com/cgi-bin/abstract.
24. Abraham TW, Carter JT. Polyurethane Foams Comprising Oligomeric Polyols; 2010. US Patent No: 7691914B2.
25. Commomwealth of Massachusett. Crest foam toxics use reduction, case study elimination of Methylene Chloride (MC) use in manufacturing process. Executive Office of Environmental Affairs, office of technical assistance. (OTA); 1997.
26. Di Gani J, Bhum A, Bergman A, Wit CA, Lucas D, Mortimer D, Schecter A, Scheringer, M. 2010 San Antonio Statement on Brominated and Chlorinated flame Retardants. Environ. Health Perspect. 2010;118(12):12.
27. IPCS. Environmental Health Criteria 181: Chlorinated Paraffins. Genva. World Health Organization International Programme on Chemical Safety; 1996.
28. Jimoda LA. An environmental audit of Methylene Chloride blown batch and continuous polyurethane foam production process: Emission qualitative distribution, Auxilliary Blowing Agent tunnel concentration and diffusion coefficient estimations, FACT Universitatis-working and living environmental protection. 2011;8(1):55-62.

29. Wolfgang G, Peter E. Recycling of blowing agents (Chlorofluorocarbons) in the production of polyurethane flexible foams"; Results from the operation of a pilot installation proceedings, 7th world clean air congress, Sydney, Australia; 1986.
30. Wu J, Dillon D, Crooker R. Hydrochlorocarbons/Pentanes chloblown PUR Foams for Improved Fire Performance. Polyurethanes. 2002;144-149.
31. IPCS. Fourth Assessment Report: Intergovernmental Panel on Climate Change: Working Group 1 Report. The Physical Science Basis; 2007.
32. Jayakody C, Myers D, Crocker M, Bures K, Bridge J, Brown M. Flame Retardant and Physical Characteristics of Flexible Hybrid Foam Materials Prepared Using Foam One Technology. Polyurethanes Expo. 2001;409-416.
33. OECD. Selected Paris Organization for Economic Co-operation and Development, Environmental Directorate. 1994;52.
34. Pettigrew A. Halogenated Flame retardants. In: Kirk-Othmer encyclopedia of chemical technology. 4thed. New york. John Wiley & Sons. 1993;10:954-976.
35. Parenti V, Kramer H, Kohu SDK. Novel formulations offering outstanding performance in rigid foams for domestic appliance insulation: improved energy efficiency combined with productivity is now a reality for the appliance industry, Congress, Orlando, USA; 2009.
36. Polyurethane foams. Accessed on 10th October, 2012.
Available: www.qualityfoam.com/polyurethane- glossary.asp.
37. Susu AA. Lecture delivered on changes in ozone depleting substances technologies; economic, social and political impacts of available options organized by the federal environmental protection agency in collaboration with United Nations Environmental programme and united national development programme. 1992;1-28.
38. Troitzsch JH. Plastics Flammability Handbook, 3rdedn, HanserPublihs, Munish/Hanser Gardner Publications, Inc., Cincinnati; 2003.
39. Zeus. Flammability of Polymers", Zeus Technical White Paper. 2005;1-6. Copy right (c) Zeus Industrial Products Inc. Accessed on 20th June, 2013.
Available: www.zeusinc.com.

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