

Original Research Article**Effects of CaCO_3 and Kaolin Filler Loadings on Curing Rates of Polyurethane Foams****ABSTRACT**

Commercial kaolin ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), a clay mineral obtained on the Upper Plateau (Jos, Central Nigeria) was characterized for physical properties such as moisture content (= 1.30%), sieved particle size (= 150 μm) and (Apparent Bulk Density (= 0.40g/cm³) and compared to CaCO_3 , a rock mineral and a conventional filler presently used extensively in the foam industry in Nigeria, with moisture content (= 0.60%), sieved particle size (= 150 μm) and (Apparent Bulk Density (= 0.75g/cm³). CPO and PPO Foam formulations using conventional polyols (CPO) and polymer polyols (PPO) with variations of Kaolin and CaCO_3 filler loading were investigated for curing rates. The results showed that curing decrease immediately after cream times for both fillers. The result also shows that the rate of curing is faster for kaolin filled foams than CaCO_3 with the free isocyanate content exhibiting increases with filler loading indicating that fillers delay curing rates. However, this effect is more pronounced for CaCO_3 filler than kaolin for the two types of polyols considered especially after aging for 720mins. This indicates that polymerization is usually incomplete because of the active isocyanate groups still present.

Key Words: Fillers, Isocyanate Content, Curing Rates, Conventional Polyol (CPO), Polymer Polyol (PPO),

1. INTRODUCTION

Certain additive materials have been used to impart foam plastics with cushioning and load bearing properties. Such additives include fillers either as bulk or reinforcing fillers. Fillers are substances added to other materials (plastics, composites e.t.c) to lower consumption of more expensive binder material or to improve some properties of the base material. In production of flexible polyurethane foams, fillers are used to modify the morphology and mechanical properties of the material [1]. Predominantly, fillers are used to cheapen end products, in which they are called extenders. Among over twenty most important fillers, calcite (CaCO_3) holds the largest market volume and is mainly used in plastic sectors. Other fillers include dolomite ($\text{CaMg}(\text{CO}_3)_2$), kaolin and talc [2].

Fillers are used in flexible urethane foams to reduce their flammability, increase the bulk and structural reinforcement. Fillers used in foam formulations are mainly inorganic in nature that need vigorous agitation to produce a stable suspension. Inorganic solid materials used in filled foam formulations include; hydrated alumina, carbonates, silicates, silica, glass fibers, and barium sulfate [1]. Historically, inorganic fillers such as barium sulfate and calcium carbonate have been used in flexible slab stock foams to achieve increased density and/or load bearing, and to reduce cost. Normal concentrations range from 20 to 150 parts per hundred parts polyol. The use of inorganic fillers have several disadvantages including difficulty of preparing and maintaining the dispersion; problems with removal of entrained air; difficulty of mixing and pumping the filler/polyol slurry; loss of the foam physical properties; difficulty of processing on all types of foam machinery, and, due to their abrasive nature, increased wear on machinery components [1]

Mineral fillers are also used to reduce costs, and to increase the comprehensive strength of rigid foams used in composite building panels. Finely divided fillers with a particle size ranging from a few microns up to about 100 microns are usually added as dispersers in the polyol component of the urethane systems. Care must be taken to dry the fillers or to know the precise water content available and factor data into the foam calculations. Fibrous fillers are reinforcers used to increase stiffness, and range of operating temperatures of rigid foams, integral foams and flexible RIM products. The degree of reinforcement obtainable depends on the strength of the fiber, the concentration, the modulus and extensibility of the polymer matrix, the interfacial adhesion and the shear strength at the fiber/polymer interface, and on the orientation of the fibers [3]. Mechanical properties of polyurethane foam affected by

filler loading include; density, creep recovery, elongation, tensile strength, % compression set and thickness [4]. Modification involving the use of fillers are to achieve desirable end use properties of polyurethane/filler composite products. Inorganic filler materials are available as nano-, micro- and macro-scale crystals. Their effects on plastic foam materials have been known to strongly depend on their sizes, filler/resin ratio, hybrid morphology, and dispersion quality. It is also well known that fillers increase cell density and decreased cell size thereby affecting the macroscopic cell and in this way act as reinforcement materials in polyurethane foam composites [5].

The maximum benefit from nano layer dispersal and reinforcement was demonstrated by Javni and co-workers in 2002. In their study, they found that nano-silica used as filler in flexible polyurethane foam increased the hardness and compression strength, but decreased the rebound resilience of the foam. In the same study, micro-silica filler was found to decrease all the mechanical properties of the foam [6].

Effects of various organoclays of nanosizes on the thermo mechanical properties and morphology of polyurethane foam have been investigated by Chen *et al*, (2002) [7]. The study shows that most clay layers were dispersed homogeneously into the matrix polymer. Moreover, the addition of only a small amount of organoclay was enough to improve the thermal stabilities and mechanical properties of the foam. Furthermore, they use nano- and micro- scaled calcium carbonate (calcite) to influence cell nucleation in the foaming process of polyethylene plastics. The nano-scaled calcite (ultra-flex CaCO_3) increased substantially the cell density of the foam thereby improving the mechanical properties, while the micro-scaled calcite (Hi-flex CaCO_3) has an effect that was less significant in reinforcing the strength characteristics of the foam.

1.1 Calcium carbonate (CaCO_3)

Calcium carbonate is a common substance found in rocks in all parts of the world, and is the main component of shells of marine organisms, snails, coal balls, pearls, and eggshells. Calcium carbonate is the active ingredient in agricultural lime, and is usually the hydrated lime in water treatment and leather manufacture and a principal cause of hard water. It is commonly used medicinally as a calcium supplement or as an antacid, but excessive consumption can be hazardous [8].

Calcium mineral compounds in clays are calcite (CaCO_3), aragonite (CaCO_3), and various calcium silicates and alumina-silicates such as feldspar, micas or alteration products. Smaller proportions of compound include Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), its anhydride (CaSO_4) and calcium-phosphate. The main effects of calcium compounds in clays are;

1. They act as fluxes by combining with alumina and silica to form low melting point liquids, and so reduce the vitrification temperatures and refractoriness of the clay.
2. They produce a mobile fluid/liquid of great corrosive power but form a glass when cooled causing the distortion of the body.
3. They reduce the shrinkage of clay and facilitate its drying temperatures below which they react.
4. Calcium compounds may combine with iron minerals and bleach it at dull red heat.
5. Calcium sulphate causes scum and efflorescence in common and facing bricks.
6. They increase the vitrification range in some brick making clays.
7. Calcium compounds reduce the expansion but raise the maturing temperature when they replace alkalis.
8. They act as a strong and viscous bond than simple silicate fluxes.

Calcium compounds can be identified by differential thermal analysis; microscope or X-ray techniques and the total calcium content can be assessed by spectrographic analysis [9].

1.2 Kaolinite

Kaolinite is a clay mineral, part of the group of industrial minerals, with the chemical composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. It is a layered silicate mineral, with high silica to alumina ratio and low plasticity, apparent bulk density, dry shrinkage and high refractory properties. It is popularly known as kaolin or china clay [10]. The name is derived from Kao-ling (Chinese: pinyin: Gaoling), a village near Jingdezhen, Jiangxi province, China. It is a soft, earthy, usually white mineral (dioctahedral phyllosilicate clay), produced by the chemical weathering of aluminium silicate minerals like feldspar. In many parts of the world, it is colored pink-orange-red by iron oxide, giving it a distinct rust hue. Lighter concentrations yield white, yellow or light orange colors. Commercial grades of kaolin are supplied and transported as dry powder, semi-dry noodle or as liquid slurry [11].

Silica occurs in clays and allied minerals (a) in the Free State as quartz or other form of crystalline, amorphous, hydrated or colloidal silica (b) in combination with alumina in the form of clay minerals with fluxes and alumina in the form of feldspar, mica or with various basis forming simple silicates as wollastonite (CaOSiO_2). The effect of free silica in clay is as follows;

1. It reduces the plasticity.
2. It lessens the shrinkages on drying and firing.
3. It reduces the tensile and crushing strength.
4. It reduces the refractoriness in many cases.

Alumina occurs in clays in the form of clay minerals, in feldspar, mica, hornblende, tourmaline, other alumina-silicates all of which are moderately fusible. Free alumina is also found in some clay derived from bauxites and laterites. Hallosite clays contain associated free alumina in the form of gibbsite ($\text{Al}(\text{OH})_3$) making such clays highly refractory because of the high total alumina content. Other clays may contain free alumina as gibbsite, diaspora (AlO.OH) or as a colloidal variety. Aluminous other than clay minerals have the following effect on clays in which they occur.

1. They reduce the plasticity of clay as they are non-plastic.
2. They increase the refractoriness of clay, provided that the total proportion of alumina is greater than 5%. The refractoriness of a silica brick is drastically reduced by alumina alkalis and other fluxes are usually associated with alumina compounds and these usually have a serious influence in the refractory properties.

Jong, 2013, (unpublished work) reported kaolin deposits in some villages on the upper Plateau as; Rarinsho 56.24%, Major porter 41.4%, Wereng 98.11% and Kwi 87.99% [12, Fig I].

foam industries in Nigeria) and kaolin (a clay mineral locally abundant on the Jos – Plateau) as fillers. Therefore, exploring and exploiting alternative local raw materials for the foam industry will reduce manufacturers' cost and invariably the prices of these goods.

2. MATERIALS AND METHOD

2.1 Sample collection

1 metric ton of castor seed pods were locally collected in Rukuba village in Jos, Plateau state and Korai village in Zaria, Kaduna state. The pods were deshelled to obtain the seeds and the oil was extracted by mechanical expression and also by solvent extraction for yields comparison. Industrial chemicals such as: Polymer Polyol (PPO), Conventional Polyol (CPO), Toluene Diisocyanate (TDI) (80/20), stannous octanoate, dimethyl ethanolamine, polysilicone Methylene Dichloride, and CaCO_3 were gratefully supplied by Vitafoam Nig. Plc, Jos Mega Factory. Pure white powdered commercial kaolin was purchased at Katako market in Jos Plateau State. 2 kg of Calcium hypochlorate ($\text{CaOCl}_2 \cdot \text{H}_2\text{O}$) was gratefully obtained from Plateau State Water Board, Jos.

2.1.1 Sample Treatments

The castor seed pods were deshelled using NARICT castor deshelling machine to obtain the seeds. The seeds were fed in 50kg batches into the NARICT Mosanto Expeller machine which ground it into a slurry and thereafter the slurry was mechanically pressed by NARICT hydraulic press to obtain the oil and cake. An oil yield of about 30% was collected into plastic containers. Similarly, solvent extraction was carried using n-hexane in a soxhlet extractor which gave an oil yield of 35-40%. However, the mechanical expression was adopted in this work, for bulk extraction.

The kaolin and CaCO_3 were dried at 100°C for 2 hours and thereafter sieved to $150\mu\text{m}$ particle sizes.

2.2 Materials and Industrial Chemicals

All the industrial chemicals used are products of Korean Fire Chemicals Ltd., BASF and Dupont, and were gratefully obtained from Vitafoam Nigeria Plc, Jos Mega factory

170 **2.3 Laboratory Reagents (AR Grades)**

171 All reagents used were analyte grades products of British Drug House and were used as
172 received.

173 **2.4 Equipment /Glasswares/ Moulds**

174	Motorised mechanical stirrer	Fabricated locally
175	Moulds (21.5x13.145cm)	Fabricated locally
176	Soxhlet extractor	Supplied locally
177	Toploading balance	
178	Ubbelohde Viscometer	
179	Automated Mosanto Tensometric Testing Machine	Standard Org. Nigeria
180		Laboratory Kaduna.
181	Automated IR Spectrometer	NARICT - Zaria
182	Digital thermometers	Source
183	Mosanto Expellers/hydraulic press	NARICT-Zaria
184	Refractometer	
185	Castor seed Pods Deshelling machine	NARICT – Zaria
186	Band knives	Vitafoam Jos, factory
187	Isol – Block machine	Vitafoam Jos, factory
188	Cutting knives /meter rules	

189

190 **2.5 Physical and Chemical Characterization OF CO, CPO and PPO**

191 The specific gravities, relative viscosities, refractive indices, colour, boiling points and acid,
192 hydroxyl, saponification and iodine values of CO, CPO and PPO were determined by Conventional
193 methods [13]. Furthermore, IR spectral analysis of castor oil samples were carried out neat on NARICT
194 FTIR spectrometer [14].

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2.6 Foam Formulation (Table 1)

One-shot technique of urethane foam formulation was used. The ingredients were measured accurately using syringes, micro-syringes, pipettes and measuring cylinders into moulds of dimensions (21.5cm x 13.7cm x 14.5cm), using the recipes on Table 1. The components were thoroughly stirred and TDI added with continuous stirring until the systems creamed. The foams were then allowed to rise undisturbed and left to cure 24 hrs after which physico-mechanical properties were determined.

2.7 Determination of Moisture Content of Fillers

3.0 g of sample in each case was weighed and dried in a drying cabinet at 103°C. Repeat weighings were carried out at intervals of 30 mins until three consecutive constant weights were obtained. Moisture content was calculated using the equation (1);

$$\text{Moisture content} = \frac{W_2 - W_1}{W_1} \times 100 \quad \dots\dots\dots (1)$$

Where W_1 = Initial weight of sample

W_2 = final weight of sample after drying.

2.8 Determination of Apparent Bulk Density of Fillers [15]

100g of filler was weighed and transferred into 250 cm³ measuring cylinder and kept on a flat horizontal surface. The measuring cylinder was tapped 50 times and repeated 4 times to obtain a constant the volume of sample. Apparent Bulk Density (ABD) was calculated using equation (2)

$$\text{ABD} = \frac{\text{weight of filler}}{\text{Tapped volume}} \times 0.6253 \quad \dots\dots\dots (2)$$

Table 1: Formulations with variations of CaCO₃ or Kaolin filler loading for CPO or PPO

Sample Identity	X ₁	X ₂	X ₃	X ₄	X ₅	X ₆	X ₇	X ₈	X ₉
CPO or PPO (g)	100	100	100	100	100	100	100	100	100
CaCO ₃ or Kaolin (g)	0	2	4	6	8	10	12	14	16
Silicone (g)	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Amine (g)	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13	0.13
Stannous(g)	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Water (g)	4.30	4.30	4.30	4.30	4.30	4.30	4.30	4.30	4.30
M.C (g)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
TDI (g)	50	50	50	50	50	50	50	50	50

2.10 Determination of Curing Times [16]

1.5g of sample aliquots were weighed at time intervals of 1, 5, 10, 15 and 720 mins and transferred into a 200 cm³ labeled conical flasks. 10 cm³ of toluene was added in each case to dissolve the sample. Next, 10cm³ of di – n – ethylamine was added, shaken and allowed to stand for about 20 mins after which 50 cm³ isopropyl alcohol was added. This was titrated with 1.0 M HCl to methyl orange end point. A blank titration was similarly carried out. The free isocyanate content was calculated using the formula;

$$\text{Free isocyanate content} = \frac{\text{sample size}}{(\text{BL}_1 - \text{EP}_1) \times \text{FA}_1} \times K_2 \dots\dots\dots (3)$$

Where BL₁ = Blank Level (cm³), EP₁ = Titrant Volume (cm³), FA₁ = Titrant Factor (1.00)

K₂ = coefficient (1000), Sample Size = Weight of Sample

3. RESULTS AND DISCUSSION

TABLE 2: Results of Moisture Content and Apparent Bulk Density of Fillers:

Fillers	Particle size (μm)	Apparent Bulk Density (g/cm^3)	Moisture Content (%)
CaCO_3	150	0.75	0.60
Kaolin	150	0.40	1.30

Table 2 compares the particles sizes, moisture contents and apparent bulk density of CaCO_3 and kaolin fillers. CaCO_3 , a rock mineral, is the conventional filler used in foam manufacture in Nigeria, while kaolin, a clay mineral, is employed in this research as a substitute or supplement for CaCO_3 . The result shows that CaCO_3 has a much lower moisture content of 0.6% compared to kaolin with 1.3%. It is very important to ensure that fillers are completely free from water molecules because excess water in the foam formulation leads to high exotherms and risk of fire and degraded products [17]. Similarly, CaCO_3 has a higher apparent bulk density of $0.75\text{g}/\text{cm}^3$ than kaolin with $0.4\text{g}/\text{cm}^3$. A low moisture content and high apparent bulk density are essential characteristics that make a filler suitable for polyurethane foam manufacture because these properties influence density (comfort/support factor) and mechanical properties [18]. In this respect of the present study, CaCO_3 is the preferred filler than kaolin in foam manufacture. However, it has been reported that kaolin exhibits high firing shrinkage and refractory temperatures at 1350°C and 1785°C respectively which means it can readily absorb the high exotherms evolved in the foam reactions than CaCO_3 [[12], equations 4 and 5]

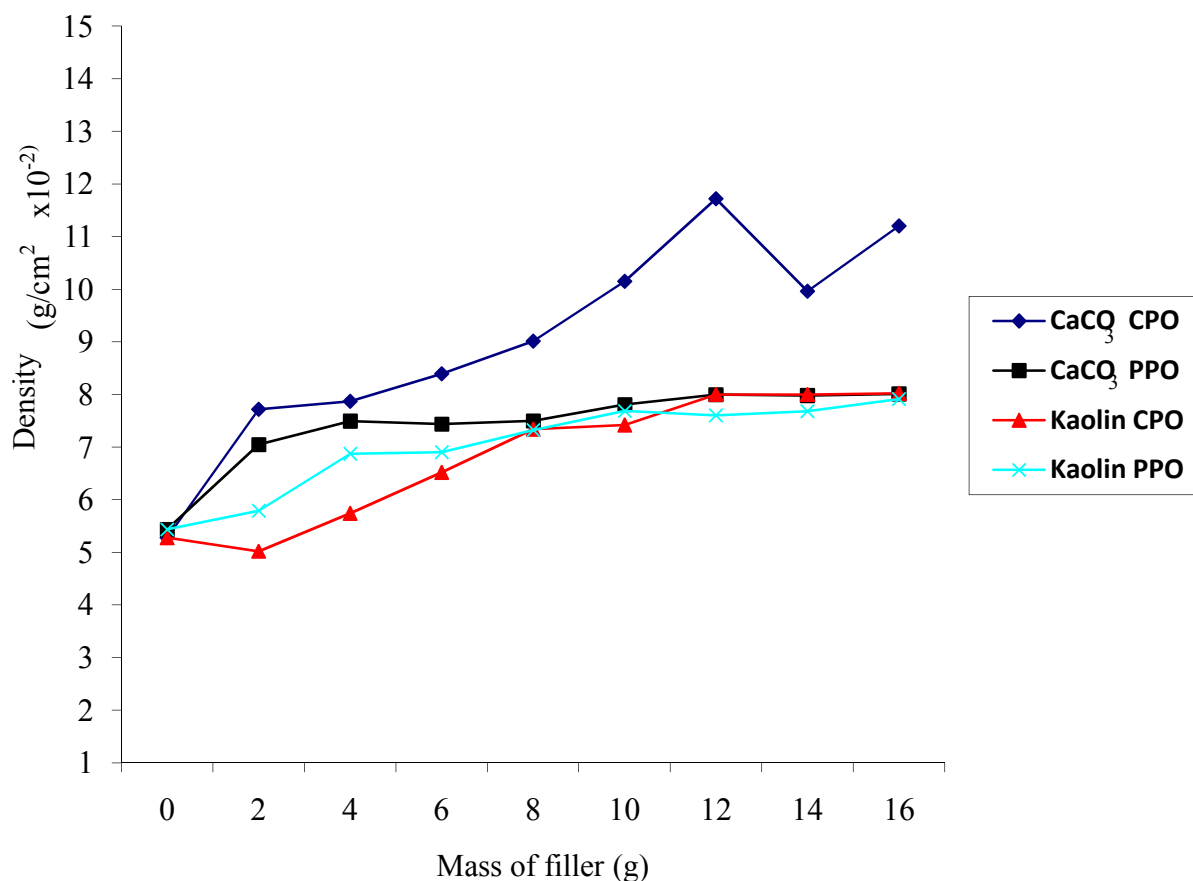


Fig. 2: Results of variations of CaCO₃ and kaolin filled CPO and PPO filler loadings with density.

Fig. 2 shows variations of density with CaCO₃ and kaolin filler loadings for CPO and PPO foam formulations. Density generally increases with filler loadings but higher increases are observed for CaCO₃ filled CPO and PPO than kaolin filled CPO and PPO. CaCO₃ filled CPO displays higher increases than CaCO₃ filled PPO. Kaolin filled CPO displays lower values up to 10g compared to kaolin filled PPO, however, at higher values above 10g, density values show little or no significant differences between CaCO₃ filled PPO and kaolin filled CPO and PPO. These density differentials are expected since the fillers have different apparent bulk densities [15].

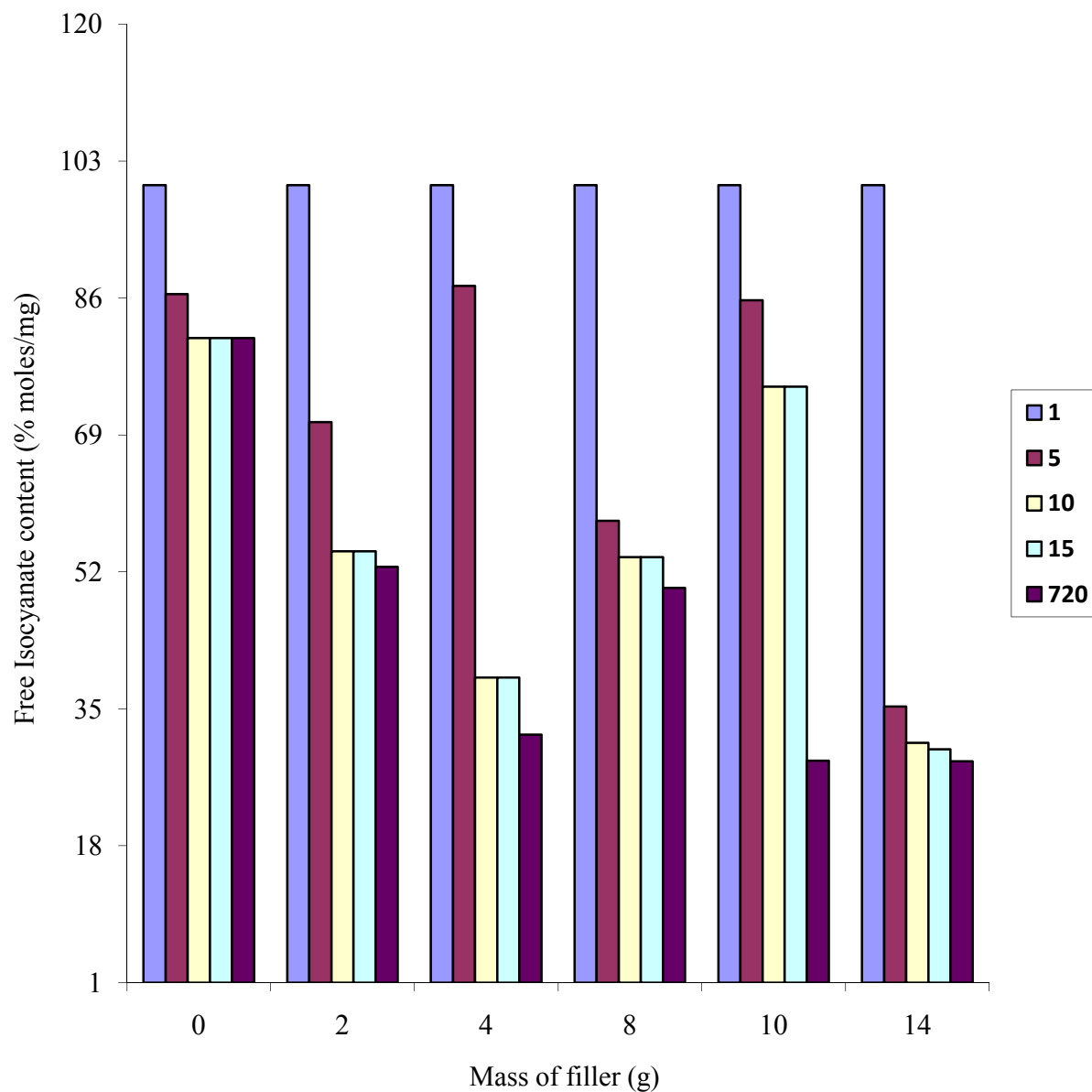


Fig. 3: Results of variations of CaCO_3 filled CPO with curing times.

* 1 = cream time (1min), 5 = 5mins, 10 = 10mins, 15 = 15mins, *720 = 720mins (aging time)

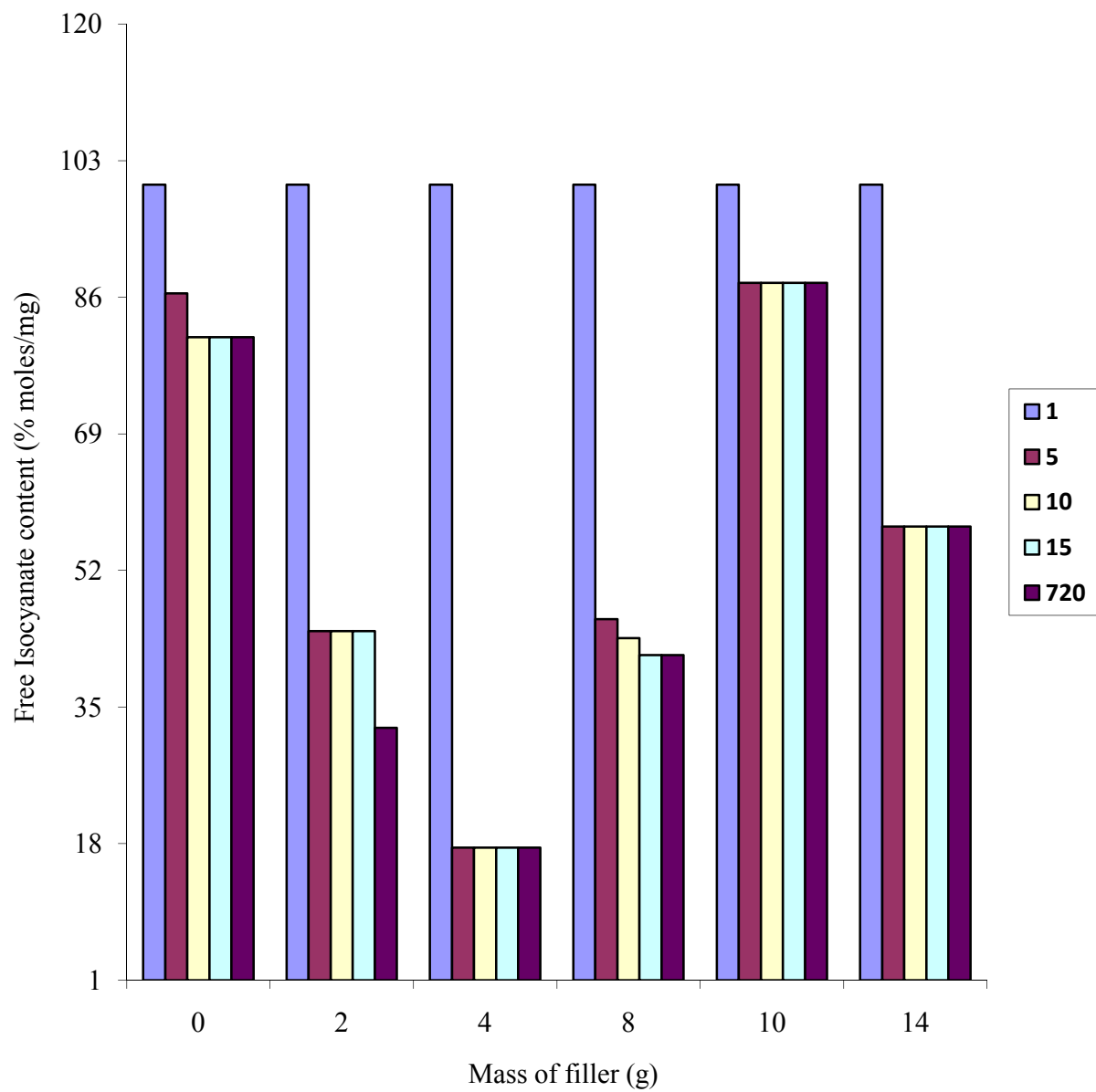


Fig. 4: Results of variations of Kaolin filled CPO with curing times.

* 1 = cream time (1min), 5 = 5mins, 10 = 10mins, 15 = 15mins, *720 = 720mins (aging time)

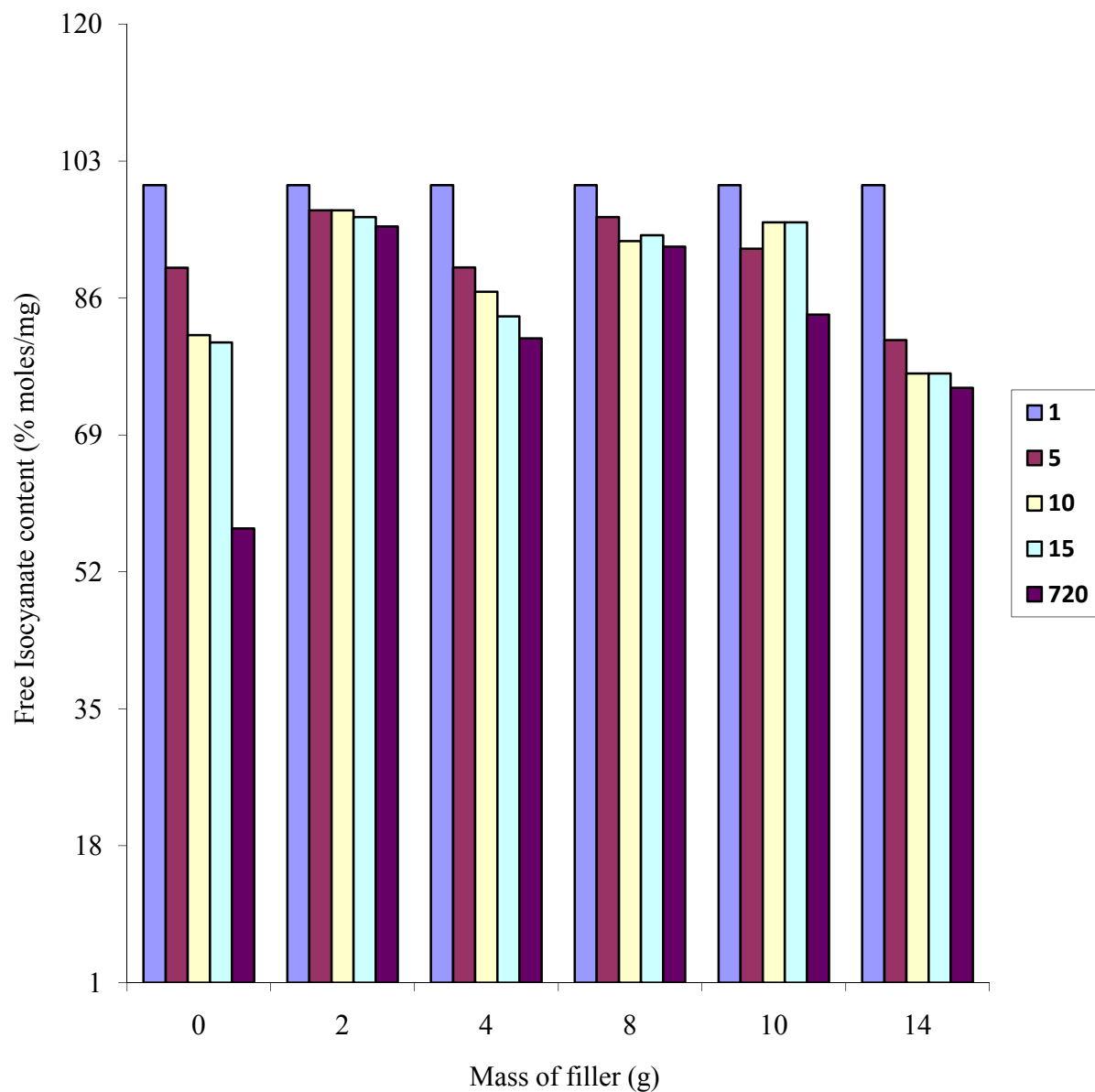


Fig. 5: Results of variations of CaCO_3 filled PPO with curing times.

* 1 = cream time (1min), 5 = 5mins, 10 = 10mins, 15 = 15mins, *720 = 720mins (aging time)

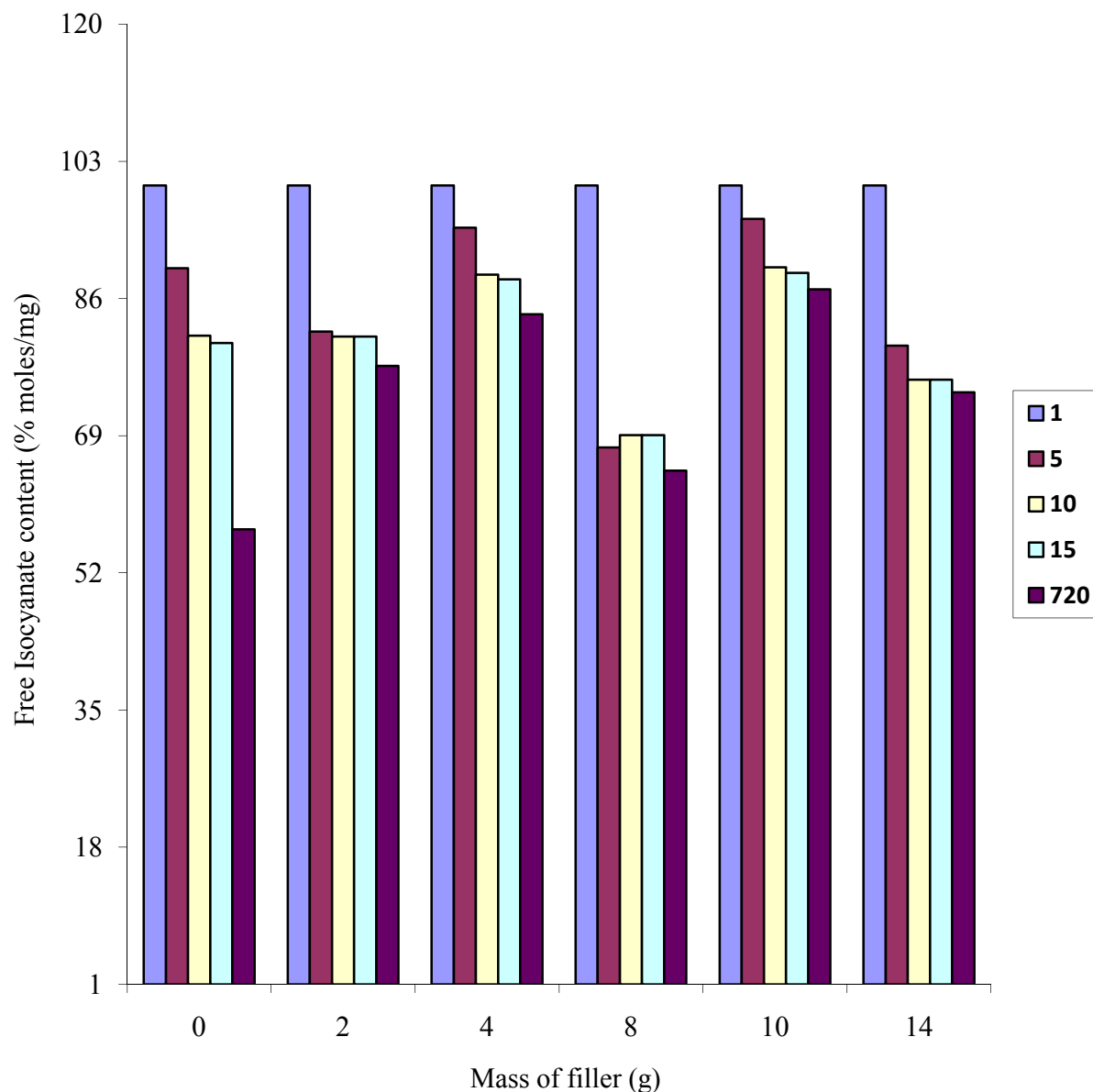


Fig. 6: Results of variations of Kaolin filled PPO with curing times.

* 1 = cream time (1min), 5 = 5mins, 10 = 10mins, 15 = 15mins, *720 = 720mins (aging time)

Figs. 3, 4, 5 and 6 show the effects of filler loadings on curing rates for CaCO_3 and kaolin filled CPO and PPO. Curing times are monitored by changes in % free isocyanate contents with respect to time which is an indication of degree of conversion (extent of reaction). Curing is the setting or stabilization process of the foam matrix, that is, the foam is cured (set) or hardened into a permanent shape. In foam

manufacture, the liquid polyols are the prepolymer resins possessing reactive functional groups which react with low molecular weight or polymeric substances (e.g., TDI, amines etc) with appropriate functional groups capable of reacting with the active groups of the polyols, thus curing takes place resulting in a cross-linked solid polymeric mass or solid foam or mattress [19]. Curing is an irreversible chemical reaction exhibited by the degree of cross-linking which usually occurs under heat or curing agents as indicated by equations 4, 5, 6 and 7 [19, 20]. Although the cured part can be softened by heat, it cannot be remelted or restored to the flowable state that existed before the plastic resin was cured. Therefore, the presence of CaCO_3 and kaolin fillers either hasten or slow the curing reactions. The higher the % free isocyanate content, the slower the curing rate and the lower the % free isocyanate content, the faster the curing rate.

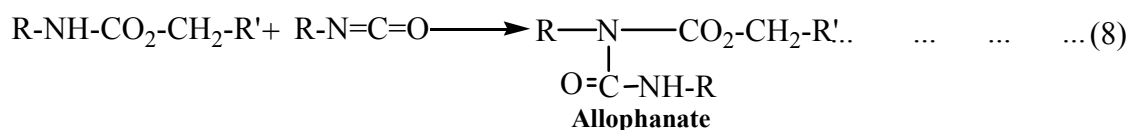
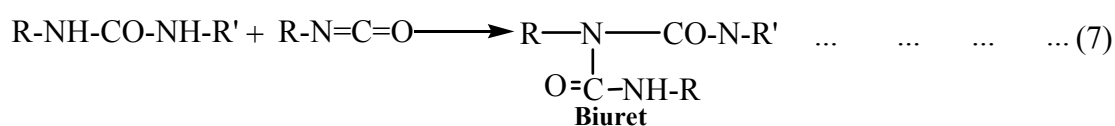
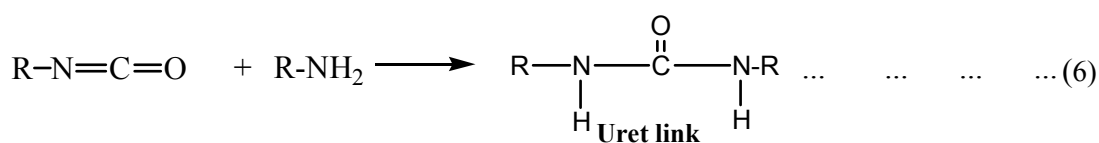
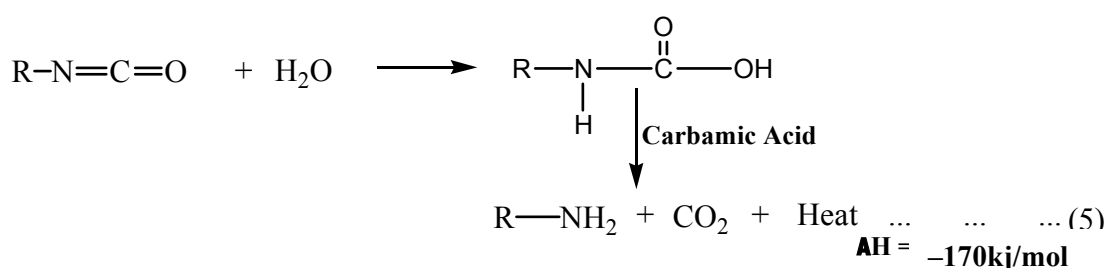
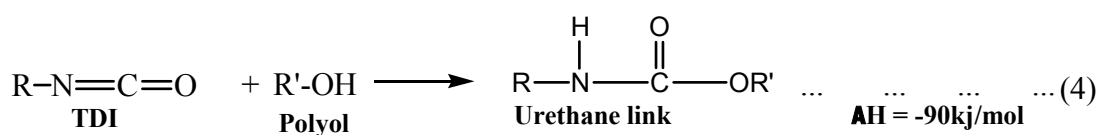


Fig. 3 shows that CaCO_3 filler loading of CPO foams decreases curing times (increases curing rates) compared to no filler addition. At zero filler loading, reaction terminated within 5 – 10 mins with % free isocyanate content decreasing from 100% at cream time to 86.5% at 5 mins and further decreases to 81.0% at 10 mins and remains constant at 720 mins aging time. This confirms the theory of no reaction after cream time within 75% foam rise [21]. This is apparent because the addition of CaCO_3 introduces amorphous regions within the polymer matrix making room for the penetration of molecules easily within the foam mix [22]. At 2g filler, decreases were observed from 100% free isocyanate content at cream time to 70.59% at 5 mins, 54.55% at 10 and 15 mins and 52.64% at 720 mins aging time. Comparing the values of % free isocyanate contents at 0g filler, it shows that CaCO_3 filler loading decreases curing times (increases curing rates) as a result of increases of the magnitude of the amorphous regions compared to the crystalline regions. At 4g, decreases in % free isocyanate content from 100% at cream time to 87.5% at 5 mins, 38.59% at 10 and 15 mins, 31.82% at 720 mins aging time, this indicates more sharper decreases than at 2g CaCO_3 loading observed above. At 8g, free isocyanate content decreases from 100% at cream time to 58.33% at 5 mins, 53.84% at 10 and 15mins and 50% at 720 mins aging time, much higher than the corresponding value at 4g, however, it displays the same value with the one at 2g, but still much lower than the value at 0g filler.

At 10g, decreases are observed from 100% at cream time to 85.7% at 5 mins, 75% at 10 and 15 mins and a sharp decrease to 28.67% at 720 mins aging time, much lower compared to the corresponding values at 0, 2, 4, and 8g filler loadings. This agrees with the 10% parts per hundred resin of CaCO_3 filler utilization in polyurethane foam manufacture also reported by Babolola and Dominic (2012) in their publication on comparative analysis of the effects of calcite (CaCO_3) and dolomite $\text{CaMg}(\text{CO}_3)$ as fillers in polyurethane foam production [23]. At 14g loading, decreases are observed from 100% at cream time to 35.3% at 5 mins, 30.8% - 30.00% at 10 and 15 mins, and 28.5% at 720 mins aging time. These trends indicate that 10g and 14g have the lowest decreases in % free isocyanate contents at aging times. This shows that increases in CaCO_3 filler loading increases curing rates (decreases curing times) as cross-linking reactions are easily achieved [19].

Fig. 4 shows the effects of kaolin filler loadings on curing times for CPO foam formulations. The 0g shows the same trend as stated above. At 2g, sharp decreases were displayed from 100% free

isocyanate content at cream time to 44.4% at 5, 10 and 15 mins, with further decreases to 32.4% at 720 mins aging time. Comparing these values with the corresponding values for CaCO_3 filled CPO shown on Fig. 3, the kaolin filled CPO shows more sharper decreases than the CaCO_3 filled CPO. At 4g loading, the decreases are the sharpest (lowest). This loading is critical for kaolin filled CPO, it decreases from 100% free isocyanate content at cream time to 17.50% at 5, 10, 15 and 720 mins aging time. Comparing this value with the corresponding value at 4g CaCO_3 filled CPO with (31.8%) shown on Fig. 3, is twice lower, suggesting that the 4g kaolin cures far better than CaCO_3 for CPO formulations at the same loading.

At 8g kaolin, 100% free isocyanate at cream time decreases to 50% at 5 mins, 55% at 10 mins and 41.2% at 15 and 720 mins aging time. Although, these values are higher compared to the values at 2g and 4g kaolin loadings, they are still lower than the corresponding values of CaCO_3 filled CPO shown on Fig. 3. At 10g kaolin, it was observed that decreases are minimal as 100% free isocyanate at cream time decreases to 87.8% at 5, 10, 15 and 720 mins aging time. This is completely a sharp contrast to what were observed at 0g and 10g CaCO_3 filled CPO which exhibit 81% and 28.5% free isocyanate contents respectively at aging times. Therefore, 10g kaolin filled CPO exhibits a very slow curing effects.

At 14g kaolin loading, decreases were observed from 100% free isocyanate content to 57.5% at 5, 10, 15 and 720 mins aging time. Although these decreases are higher than values at 2g, 4g, and 8g kaolin loadings, they are still lower than values at 0g and 10g. They are however, higher than the corresponding value at 14g CaCO_3 filled CPO (= 28.5% at aging time).

In summary, for CaCO_3 filled CPO, curing time decreases with filler loading in the order $14 > 10 > 4 > 8 > 2 > 0\text{g}$ while for kaolin filled CPO curing time decreases in the order, $4 > 2 > 8 > 14 > 0 > 10\text{g}$, with 4g kaolin gives the best (lowest) comparative decrease, over and above CaCO_3 . As mentioned earlier that increases in the magnitude of amorphous regions decreases curing times (increases curing rates), therefore, the faster the degree of cross-linking shown in equations 4 – 8.

Figs. 5 and 6 shows effects of CaCO_3 and kaolin filled PPO on curing times. Figs. 5 and 6 show generally that curing time increases with filler loading especially at aging times. These increases are more pronounced for CaCO_3 filled PPO than kaolin filled PPO.

Considering Fig. 5, at 0g CaCO_3 , % free isocyanate decreases from 100% at cream time to 89.7% at 5 mins, 81.4% at 10 mins, 80.5% at 15 mins, and 57.4% at 720 mins aging time. Although these decreases

are slower compared to the ones at 0g CaCO_3 filled CPO; PPO displays sharper decrease of % free isocyanate content at aging time than CPO at 0g filler at aging time.

At 2g CaCO_3 , slight decreases in % free isocyanate from 100% at cream time to 96.9% at 5 and 10 mins, 96.0% at 15 mins and 95% at 720 mins aging time. These decreases are marginal compared to the values at 0g CaCO_3 above, and significant compared to the corresponding value at 2g CaCO_3 filled CPO with (= 52.64% at aging time). The sharp differences can be attributed to the viscosity differences between CPO and PPO as PPO is more viscous than CPO, therefore addition of filler makes PPO even more viscous, since the reaction of active site is diffusion-controlled, PPO experiences difficulties in viscosity build up and therefore difficulties in the dissipation of heat [25]. At 4g CaCO_3 , decreases in % free isocyanate content are observed from 100% at cream time to 89.8% at 5 mins, 86.8% at 10 mins, 83.7% at 15 mins and 81% at 720 mins aging time. Again these decreases are much higher than the corresponding ones at 4g CaCO_3 filled CPO with 31.8% at 720 mins aging time.

At 8g, decreases show that 100% free isocyanate content at cream time decreases to 96% at 5 mins, 93.1% at 10 mins, 93.8% at 15 mins and 92.4% at 720 mins at aging time. Similarly, these values are higher than the corresponding ones for 8g CaCO_3 filled CPO with (= 50% at 720 mins aging time).

The same trend was observed for 10g CaCO_3 filled PPO; as 100% free isocyanate content at cream time decreases to 92.1% at 5 mins, 95.4% at 10 mins and 15 mins, and 83.9% at 720 mins aging time. Again these decreases are far greater than the corresponding values at 10g CaCO_3 filled CPO with 28.6% at 720 mins aging. At 14g CaCO_3 filled PPO, the same trend was observed with 100% free isocyanate content decreasing to 80.8% at 5 mins, 76.6% at 10 and 15 mins and 74.9% at 720 mins aging time comparing the value at 14g CaCO_3 filled CPO with 28.5% at 720 mins aging time. Conclusion can be drawn here that CaCO_3 displays favourable interactions (synergistic effects) with CPO than it engages with PPO.

Fig. 6 shows that at 2g kaolin filled PPO, 100% free isocyanate content decreases to 81.9% at 5 mins, 81.3% at 10 and 15 mins and 77.6% at 720 mins aging time. Although these decreases are higher compared to the values at 0g filler, they are comparatively lower than the corresponding values at 2g CaCO_3 filled PPO shown on Fig. 5, but much higher than the corresponding values for 2g kaolin filled CPO with 32.4% at 720 mins aging time. At 4g kaolin filled PPO, slight decreases are observed from

100% free isocyanate content at cream time to 94.8% at 5 mins, 88.9% at 10 mins, 88.4% at 15 mins, and 84% at 720 mins aging time. These values are higher than the ones obtained at 0g kaolin PPO. This shows that kaolin filled PPO at this loading cures more slower compared to values at 4g kaolin filled CPO with 17.5% at 5, 10, 15 and 720mins.

At 8g kaolin, 100% free isocyanate content decreases to 67.5% at 5 mins, 69% at 10 and 15 mins and 64.7% at 720 mins aging time. Again, these values are lower than the corresponding ones at 8g CaCO_3 filled PPO with (92.4% at 720 mins aging time). However, the values are higher than the ones at 8g kaolin filled CPO with 41.2% at 720 mins aging time and at 8g CaCO_3 filled CPO with 50% at 720 mins aging time. At 10g kaolin filled PPO, 100% free isocyanate content decreases to 95.8% at 5mins, 89.8% at 10 mins, 89.1% at 15 mins and 87.1% at 720 mins aging time. These values are similar to the corresponding ones at 10g CaCO_3 filled PPO. They are however, much higher than the corresponding values for 10g CaCO_3 filled CPO with 28.6% at 720 mins aging time and more or less similar to the value at 10g kaolin filled CPO with 87.8% at 720 mins aging time.

At 14g kaolin filled PPO, values indicate that, 100% free isocyanate content decreases to 80.2% at 5 mins, 75.9% at 10 and 15 mins and 74.4% at 720 mins aging time. These values are similar to the corresponding ones at 14g CaCO_3 filled PPO. They are, however, much higher than the corresponding ones at 14g CaCO_3 filled CPO with 28.5% at 720 mins aging time and at 14g kaolin filled CPO with 57.5% at 720 mins.

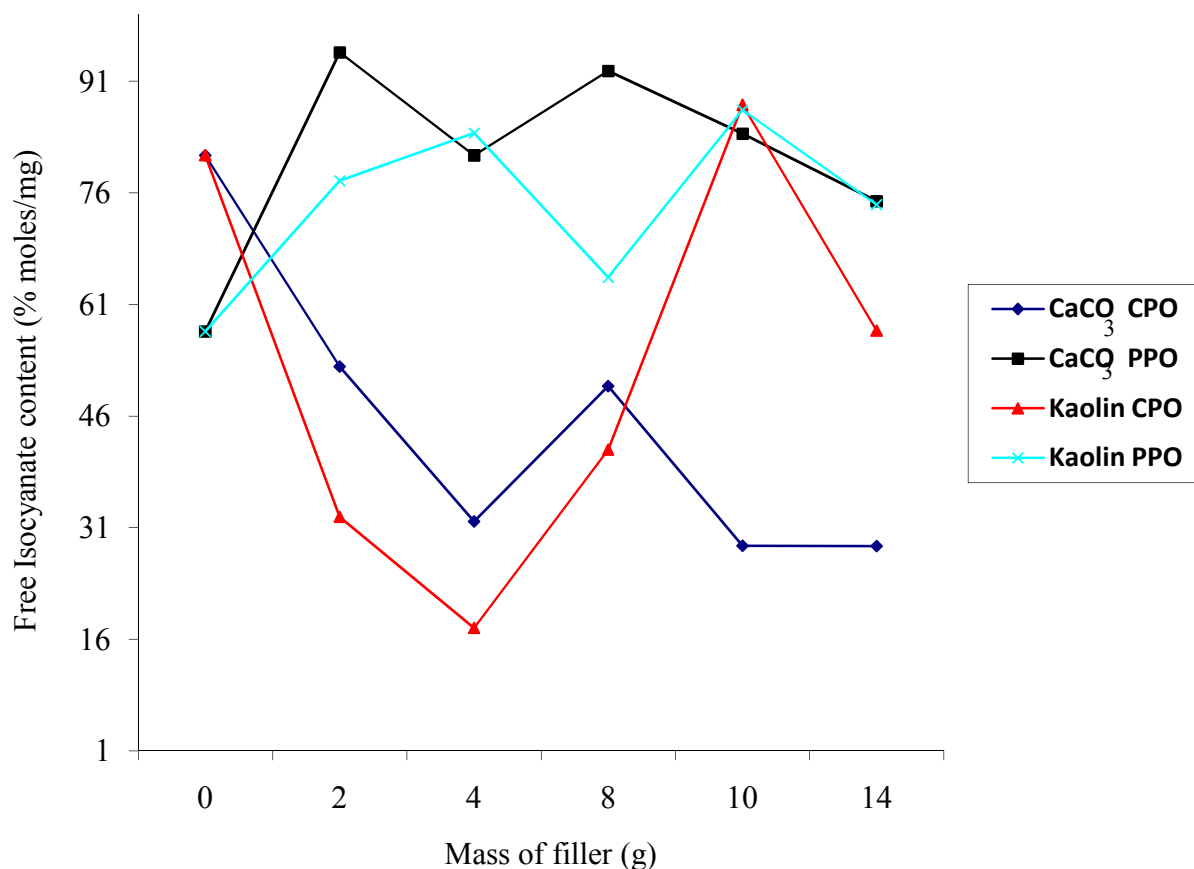


Fig. 7: Results of variations of % free Isocyanate content at aging times (720 mins).

Fig. 7 summarizes the % free isocyanate contents at aging times of 720 mins for CaCO₃ and kaolin filled CPO and PPO respectively. For CaCO₃ filled CPO, results showed that at; 0g = 81%; 2g = 52.5%, 4g = 31.8%, 8g = 50%, 10g = 28.6%, 14g = 28.5% as against kaolin filled CPO at; 0g = 81% , 2g = 32.4%, 4g = 17.5%, 8g = 41.5%, 10g = 87.8%, and 14g = 57.5%. These results show that kaolin cures faster between 2 – 8g with the fastest cure loading at 4g (= 17.5%) while CaCO₃ cures better between 2g – 14g with best results between 10g and 14g [24].

For CaCO₃ filled PPO, results show % free isocyanate contents at aging times as; 0g = 57.4%, 2g = 94.9%, 4g = 81%, 8g = 92.4%, 10g = 83.8%, 14g = 74.9% as against kaolin filled PPO which indicate; 0g = 57.4%, 2g = 77.6%, 4g = 84.0%, 8g = 64.7%, 10g = 87.1%, 14g = 74.4%. As mentioned

earlier, CaCO_3 or kaolin filled PPO show slower or longer curing times than CaCO_3 or kaolin filled CPO. This means that CaCO_3 or kaolin filled CPO cures faster than CaCO_3 or kaolin filled PPO.

Finally, as mentioned earlier, CaCO_3 or kaolin filled PPO displays slower or longer curing times than CaCO_3 or kaolin filled CPO. This suggests that CaCO_3 or kaolin filled CPO cures faster than CaCO_3 or kaolin filled PPO. This study has indicated that Kaolin cures faster due to its lower apparent bulk density compared to CaCO_3 . Furthermore, aluminum and silicon elements present in Kaolin hybridize at excited state to provide empty orbital that can be occupied by ligands (nucleophiles) which can fast track the curing reaction compared to CaCO_3 [24]. From the results, independent of the kind or amount of filler used, the isocyanate content reduces as the time increases, that is as curing takes place, the number of $-\text{N}-\text{C}=\text{O}$ groups decreases. Also, at certain point in time, constant free isocyanate content is attained, at that time the foam is believed to have cured. But even after the curing process has terminated, a zero number of $-\text{N}-\text{C}=\text{O}$ group is not reached. This means that the foam polymerization process is an incomplete one. That is, there are still active chain ends which of course is one of the characteristics of poly-condensation reactions [19].

4. CONCLUSION

Filler loading affects the curing rates of foams depending on whether a filler is inert or reactive and also the degree and amount of amorphous regions particle size and distribution as well as parameters such as firing shrinkage temperature and refractoriness. In this regard incorporation of between 2 – 8% of Kaolin as filler improves curing rates, tensile strength, creep recovery and compression set over and above CaCO_3 even though it lowers the density of foams. While calcium carbonate incorporation between 2 – 14% also improves the mechanical properties mentioned above at lower values. Kaolin filled foams can be used for light weight application such as upholstery, packaging, industrial filters, e.t.c.

Moreover, kaolin is much cheaper than Calcium Carbonate as 2kg of kaolin processed in Jos costs between 400 and 500 naira while a corresponding weight of processed calcium carbonate costs much higher. Therefore cost can be minimized and calcium carbonate can be freed for use in leather,

paint, and water treatments, e.t.c. This is because kaolin being a clay mineral is abundant naturally and cheaper with large deposits on the Jos plateau [12].

The evaluation of local raw materials is the principal requirement for any economic process and development. The comparison of the quality potentials of raw materials with process specifications and process economics are pre-requisite for industrial development. It is not enough to have a local raw material source but it is essential to study the properties and potentials before it is exploited. Supplement or substitute CaCO_3 with Kaolin, since kaolin is much cheaper and abundant locally than Calcium Carbonate. Furthermore, the present investigation has also firmly established the utilization of kaolin, a clay mineral with high refractory temperature of 1785°C locally abundant on Upper Plateau (Jos) as a filler which improves curing rates by ease of absorption of exotherms generated during foaming process and also enhances some important mechanical properties such as tensile strength, creep recovery and compression set of urethane foams for light weight, packaging and cushioning applications over and above the conventional CaCO_3 filler presently used by foam industries in Nigeria.

5. RECOMMENDATION

1. Raw Materials Research and Development Council of Nigeria should organize sensitization workshops and seminars for all stakeholders in the foam and allied industries on the development and use local raw material. It is also important to state that the future of the chemical industries would be better secured if Nigeria could install modest capacities for local production of intermediate chemicals from our locally available raw materials
2. The Federal Government of Nigeria should as a matter of urgency increase the tariff on importation of any raw material that can be sourced locally. This will go a long way in discouraging industrialists from importation and encourage local sourcing of the raw materials. Even where there is claim that the locally available ones do not meet the specification needed, value should be added so as to improve the quality.

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484 **COMPETING INTEREST**

485 Authors declare that there are no competing interests.

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