Effect of a Nanoclay on the Mechanical, Thermal and Flame Retardant Properties of Rigid Polyurethane Foam

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Effect of a Nanoclay on the Mechanical, Thermal and Flame Retardant Properties of Rigid Polyurethane Foam

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Water blown rigid polyurethane foams (PUF) with organoclay/organically modified nanoclay (ONC) were prepared and their properties such as density, mechanical, morphological, insulation, thermal and flame retardant properties were studied. In this investigation, the ONC content was varied from 1 to 10 parts per hundred of polyol (php) by weight. It was observed that the compressive strength of ONC filled PUF increased up to 3 php of ONC loading and then it decreased. Wide angle X-ray diffraction and transmission electron microscopy studies indicated the exfoliated dispersion of ONC in PUF. The thermal conductivity of ONC filled PUF decreases up to 5 php and then increases. The glass transition temperature (Tg) of PUF decreases on loading of ONC. The TGA analysis shows that there is slight increase in degradation temperature with increase in ONC loading. The flame retardant properties (LOI and flame spread rate) are improved slightly on addition (3 php) of ONC filled PUF.

Keywords: Nanoclay, polyurethane foam, compressive strength, morphology, thermal properties, flame retardant properties

1 Introduction

Rigid polyurethane foams (PUFs) are used in many applications such as insulation, cushioning, packaging and structural materials. As structural materials, they have very good mechanical properties and energy absorption capabilities. The properties of PUF depend on the structure and geometry of the foam and their density (1–4). In general, the mechanical properties of the polymeric materials are improved by adding reinforcing fillers. The effects of different fillers on the mechanical properties of PUF have been reported (5). Interaction of fillers with different raw materials (like isocyanates) influences the properties of the PUF. In many cases, a large amount of fillers are required to get the desired properties of PUF. Nanocomposites are a new class of composite materials in which one of their constituents has a dimension in the nanometer (10^{-9}m) range. Use of nanofillers such as clay, silica, $CaCO_3$, ZnO, and metallic oxides greatly enhance the contribution of the contact area/interphase with the matrix materials and thus improve the overall properties of the nanocomposites (6–8). Generally, inorganic materials (fillers) exhibit low interaction with organic polymer which leads to poor dispersion

of the filler in the organic polymer matrix. However, it may be improved by enhancing the organophilicity in the filler surface. Among the polymer nanocomposites, the clay layered silicates are used in many applications such as automotive, medical, food, coatings and fire resistance. These clay layered nanocomposites exhibit increased mechanical, thermal and flame retardant properties, reduced gas permeability and increased solvent resistance when compared with the virgin polymers or conventional composites. The dispersion and properties of layered silicate nanocomposites depend on various factors, including intercalations (melt, solution, *in-situ* polymerization), mixing temperature, mixing time, solvent, size of monomer or polymer and intercalating agent. When the clays are dispersed in a polymer matrix, they are either intercalated or exfoliated the polymer molecules. The improvement in polymer properties with nanoclay is related to various factors including nature of clay, its aspect ratio, method of preparation of nanocomposite, orientation of the matrix and interaction between the nanoclay and the matrix (9, 10). In recent years, these kinds of materials have attracted great interest in polyurethane materials and polymer foams, as they lead to improvement in many prominent properties (11–17). This investigation reports an extensive study on the effect of an organonanoclay (ONC) at different concentrations on the mechanical, morphological, thermal conductivity, thermal properties and flame retardant properties of the water blown rigid PUF and compares these properties with those of neat foam.

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Table 1. Characteristic of the raw materials used for making filled PUF

Materials	Equiv. weight	Functionality	Role/Characteristics
Polymeric methane diphenyl diisocyanate (PMDI)	136.6	2.7	NCO content = 30.8%
Polyether polyol	127.5	3.0	OH value = 440 mg KOH/g
N,N,N′,N″,N″-Penta methyl diethylene triamine (PMDETA)	—	—	Catalyst
Polyether dimethyl siloxane (Tegostab B 8460)	—	—	Surfactant
Distilled water	9.0	2.0	Blowing agent
Organoclay (Cloisite-30B)	—	—	Reinforcing agent/filler

2 Experimental

2.1 Materials

The polymeric methane diphenyl diisocyanate (PMDI) and polyether polyol were obtained from Huntsman International Pvt, Ltd., Mumbai, India. Distilled water was used as a chemical blowing agent. N,N,N′, N″,N″-pentamethyl diethylene triamine (PMDETA) obtained from Aldrich, USA was used as a catalyst, polyether dimethyl siloxane (TEGOSTAB B 8460) supplied by Goldschmidt, Germany was used as a surfactant. Organically modified nanoclay-Cloisite-30B (density = 1.98 g/cc, particle size = 2–13 μm, thickness = 0.1 nm, cation exchange concentration = 90 meq/100 g, MT2EtOH, Methyl tallow-bis-2-hydroxy ethyl quaternary ammonium) obtained from Southern Clay products; Gonzales, TX, USA was used as organoclay in our formulations. The characteristics of different materials used in the preparation of filled PUF are shown in Table 1.

2.2 Preparation of Foam

The organoclay containing PUF samples were prepared by a one-shot and free-rise method and their chemical compositions were shown in Table 2. The polyol and organoclay were first mixed well in a plastic beaker by using high speed mechanical stirrer (3000 rpm) for 15 min and then other ingredients (except PMDI) were added and mixed into a homogenous mixture. Finally, the PMDI was added into the beaker with vigorous stirring for 10 sec. The resulting mixture was immediately poured into an open mold (30 × 25 × 15 cm) to produce free-rise foams. After the preparation, the foams were kept in an oven at 70°C for 24 h to com-

plete the polymerization reaction. Samples were cut into specific shapes by rubbing with fine emery paper and then the different properties of the foams were analyzed. The amount of PMDI required for the reaction with polyether polyol and distilled water was calculated from their equivalent weights. For the completion of the reaction, excess PMDI was added in this ratio; NCO/OH ratio = 1.1/1.0.

2.3 Measurements

2.3.1. *Mechanical properties*

The density of the PUF samples was measured according to ASTM D 1622-03 and the average value of three samples were reported. The mechanical properties of the PUF samples were measured under ambient conditions using Instron UTM Hounsfield testing equipment (model H10KS). The compressive stress at 10% strain in the parallel to foam rise direction was performed according to ASTM D 1621-00. The size of the specimen was 55 × 55 × 25 mm (length × width × thickness), and the rate of crosshead movement was fixed at 2.5 mm/min for each sample and the load cell used was 10 kN. The strength of five specimens per sample was measured and the average of these values was reported.

2.3.2. *Analysis of morphology*

The morphology of the PUF samples was studied with a JEOL, JSM 5800 scanning electron microscope (SEM), Japan. The samples were gold-coated before scanning in order to provide an electrically conductive surface. The accelerating voltage was 20 kV in order to avoid degradation of the sample. The cell size was measured by measuring a minimum of 20 cell areas and averaged out by Leica Q WIN Plus software appended to the polarizing microscope (Leica DMLM, UK).

2.3.3. *FT-IR analysis*

The FTIR spectra were recorded in a Perkin-Elmer FTIR spectrometer (Model Spectrum RX 1). The organoclay were prepared in the pellet form by mixing the powdered sample with KBr in the ratio 1:10.

2.3.4. *Wide angle x-ray diffraction analysis*

The wide angle x-ray diffraction analysis was performed using Rigaku Dmax 2500 diffractometer using CuKα radiation. The samples were scanned from $2\theta = 2°$ to $10°$

Table 2. Chemical compositions of organoclay filled water blown rigid PUF

Materials	*php
Polyether polyol	100
PMDETA	0.5
Tegostab B 8460	2.0
Distilled water	0.3
Organoclay	1–10
PMDI	122

*Represents as parts per hundred of polyols (php) by weight.

and the diffraction pattern was recorded using a scintillation counter detector.

2.3.5. *Transmission electron microscopy analysis*

The distribution of nano particles into the PUF was studied using a HR-TEM (JEOL 2000, Japan). The filled PUF samples were placed in the copper grid and observed through the microscope.

2.3.6. *Thermal conductivity measurement*

The thermal conductivity of the PUFs was measured as per ASTM C 177-97 standard for which the size of the sample was $100 \times 100 \times 25$ mm.

2.3.7. *Differential scanning calorimetry analysis*

The glass transition temperatures (Tg) were measured by differential scanning calorimetry (DSC) Q100, TA Instruments, USA under nitrogen atmosphere at a heating rate of 20°C/min over a temperature range of 30–150°C.

2.3.8. *Thermogravimetric analysis*

The degradation temperature was determined by thermogravimetry analyzer (TGA) Q50, TA Instruments, USA under nitrogen environment at a heating rate of 20°C/min over a temperature range of 30–600°C.

2.3.9. *Limiting oxygen index test*

The flammability test was performed using a limiting oxygen index (LOI) test instrument (Stanton Redcroft FTA unit) as per ASTM D 2863-97 standard. The specimens for the LOI measurement were $12 \times 1.2 \times 1.2$ cm (length $\times$ width $\times$ thickness) and the five specimens per sample were measured and their average values were reported.

2.3.10. *Flame spread rate measurement*

The rate of flame spread was measured as per the Federal Motor Vehicle Safety System (FM VSS) no 302 (18). A PUF specimen of $15 \times 1.0 \times 1.0$ cm (length $\times$ width $\times$ thickness) was exposed horizontally at its one end to a small flame for 15 sec. The distance and time of burning or the time to burn between two specific marks were measured. The burn rate is expressed as the rate of flame spread in mm/min according to the following formula, B = 60 (L/T) where B, L and T are burn rate in mm per minute, length of the flame travels in mm and time in sec for the flame to travel L mm, respectively. The three specimens per sample were measured and their average values were reported.

2.3.11. *Char residue analysis*

The char yields (CY) of the foams were measured on a muffle furnace at 550°C for 30 min. The char yield was calculated in this way; $CY = W_b/W_o \times 100$. (Where, W_o and W_b are the weights of the sample before and after burning, respectively).

3 Results and Discussion

3.1 Density

The foam density is a very important parameter to control the mechanical properties of rigid PUF (19). The density of the PUF may be varied by varying the amount of the blowing agent and proportion of filler materials. In the present study, the amount of blowing agent (distilled water) was fixed, the organoclay content was varied from 1 to 10 php (parts per hundred of polyol). Table 3 shows the density of rigid PUF filled with different amounts of ONC. It was observed that the density of PUF increases slightly with inclusion of a lower amount of ONC and then decreased with further increasing the ONC content. The increase in density is probably due to the higher density of ONC (1980 kg/m³) than that of neat PUF (20). However, the density of PUF decreased substantially at the higher amounts of ONC, due to the formation of highly porous cell structure having bigger voids. Harikrishnan et al. (21) also reported the formation of more voids and broken cell structure during the preparation of PUF at higher loading of nanoclay.

3.2 Mechanical Properties

Mechanical properties of a PUF are important parameters which determine its applications. Polyurethane foam nanocomposites with varying ONC content were prepared in the laboratory and they were subjected to compressive stress at 10% strain. To study the effect of ONC on the compressive properties of PUF and to eliminate the effect of foam density, the compressive strength of different foam

Table 3. Effect of organoclay on the density and compressive strength of the PUF

| S.No.	ONC loading (php)	Density (kg/m³)	Compressive strength at 10% strain (MPa)	Reduced compressive strength [MPa/(g/cm³)]
1	0	103	0.80	7.77
2	1.0	115	0.94	8.17
3	3.0	106	0.89	8.40
4	5.0	74	0.30	4.05
5	10.0	72	0.26	3.61

were normalized by dividing by their respective density (22).

Table 3 shows the compressive strength and reduced compressive strength of the PUF filled with organoclay at different loadings. It indicates that the reduced compressive strength increased marginally up to 3 php ONC loading. However, at higher loading (>3 php) of ONC, there was a tremendous decrease in reduced compressive strength. Moreover, the strength properties are linearly dependent on the foam density. The presence of reinforcing fillers in a polymer matrix improves the physical and mechanical properties of the polymer. Reinforcement plays a major role in this process which depends on surface activity and particle size of the fillers and the characteristics of the polymer-filler interaction (5). The increase in mechanical properties by the addition of a small amount of organoclay is due to the uniform and smaller cell size of the ONC filled PUF. The increased mechanical strength may also be due to the internal strength of the polyurethane matrix due to the higher degree of hydrogen bonding among the urethane groups (23, 24). The decrease in the properties of PUF with a higher amount of ONC is due to the collapse of the cells because of excessive coalescence and rupture of cells. It is shown later in the morphology section.

3.3 Fourier Transform Infrared Spectroscopy

Figure 1 shows the FT-IR spectra of organoclay, as well as their interaction with PMDI. The peak at 3628 cm^{-1} is due to –OH stretching of organoclay and hydrogen bonded water (free and bound, which is also confirmed from TGA analysis) bending peak at 1645 cm^{-1} and the -OH stretching peak (3400 cm^{-1}) of the organoclay, which are groups capable of reacting with –NCO group of PMDI. In addition, the peaks at around 2925 and 2853 cm^{-1} correspond to –CH stretching peak of hydrocarbon chains of

organically modified nanoclay (ONC). The chemical structure of the organoclay is given below,

$$CH_3 - \underset{\underset{CH_2CH_2OH}{|}}{\overset{\overset{CH_2CH_2OH}{|}}{N^+}} - T$$
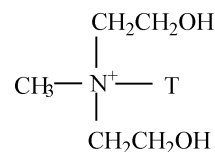
In the above structure of quaternary ammonium salt T denotes tallow consisting of ca.65% C18; ca.30% C16 and ca.5% C14. FT-IR spectra show the characteristic -NCO peak of PMDI at 2274 cm^{-1} (Figure 1).

In the model experiment when the organoclay was mixed with PMDI, the –OH group in the organoclay disappeared and the area of the –NCO group diminished indicating the reaction between –OH group of the organoclay and –NCO group of PMDI. Pattanayak et al. also reported the interaction of -OH of clay with –NCO group in the isocyanate (11, 12).

3.4 Dispersion of Organoclay into PUF

The distribution of organoclay in the PUF was analyzed by wide angle X-ray diffraction (WAXD) and transmission electron microcopy (TEM) techniques. Figure 2 shows the WAXD pattern of the organoclay and PUF filled with a different amount of organoclay. It clearly indicates that the peak at $2\theta = 4.8$, which is characteristic of the crystallinity in the organoclay disappears in PUF-nanocomposites. It indicates that the stacks/layers of the clay are delaminated or exfoliated in this case. Therefore, the exfoliation of the clay layers is achieved during the preparation of rigid PUF in the presence of ONC.

The dispersion and agglomeration behavior of organoclay with PUF was also confirmed by the study of the transmission electron microscopy (TEM) in the PUF
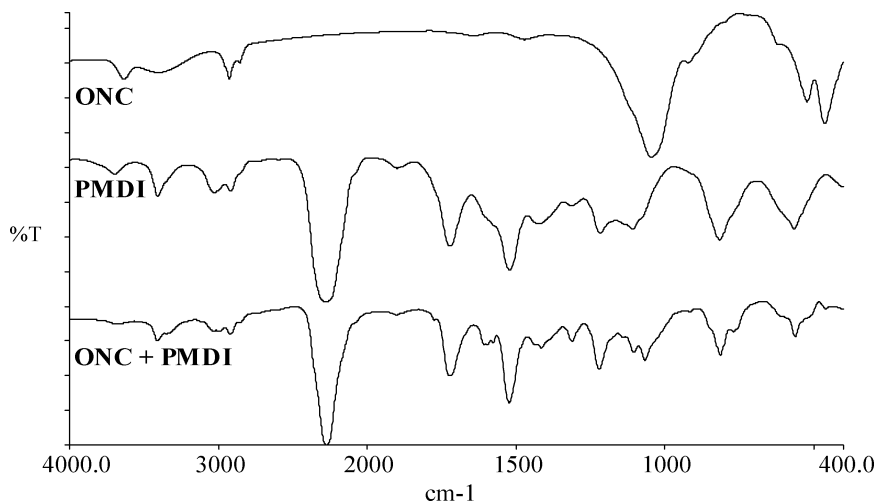

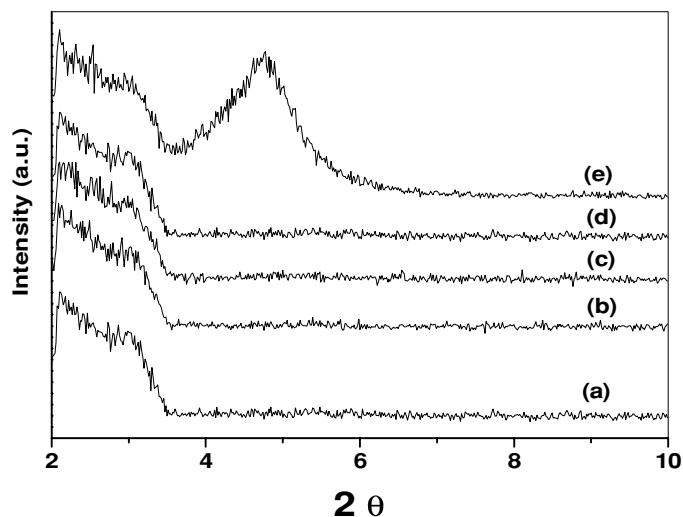**Fig. 1.** FTIR spectra of organoclay and its reaction with PMDI.

Fig. 2. WAXD of organoclay filled PUF samples: (a) ONC-1 php; (b) ONC-3 php; (c) ONC-5 php; (d) ONC-10 php; (e) Organoclay.

nanocomposites. TEM micrographs of PUF filled with 3 and 5 php of ONC are depicted in Figure 3 (a) and (b).

The PUF filled with a lower amount of ONC shows that the large portion of the plates were exfoliated, whereas some local agglomeration is obtained at a higher amount (5 php of ONC) in PUF as shown in Figure 3 (b). It was reflected in the mechanical properties of PUF. Table 3 showed that PUF filled with 3 php ONC has better compressive strength than the PUF with 5 php ONC.

3.5 Morphology

In general, the physical properties of foam depend on the rigidity of the polymer matrix, as well as on the cellular structures of the foam. Figure 4 (a, b, c, and d) shows the SEM microphotographs of the fracture surfaces for ONC

filled PUF. It indicates that the addition of 1 php of ONC into PUF imparts the decrease in cell size and finer cell structure compared to PUF filled with higher loading of ONC. The decrease in cell size is due to the nucleation effect of ONC during foam preparation. On addition of the higher amount (>5 php) of ONC the foams collapsed due to the excessive coalescence and rupture of cells. This effect resulted in the mechanical properties of PUF, which has been explained earlier (Table 3).

The cell size of PUF was obtained by calculating the average of at least 20 cells (25) shown in Figure 5. It indicates that the cell size continuously decreases up to 5 php of ONC filled PUF, and then increases with a further increase in ONC loading. The decrease in the cell size may be attributed to that fact that the ONC acts as a nucleation site for gas bubbles and can also increase the viscosity of the mixture, thus reducing the coalescence (26). The increase in the cell size of PUF filled with a higher loading of ONC may be due to the excessive coalescence of the nucleating sites.

3.6 Thermal Conductivity

In general, the thermal conductivity of PUF depends on the foam density, cell size, cell orientation, ratio of close to open cell content, and also on the thermal conductivity of the filling materials (5). Figure 6 shows the effect of organoclay on the thermal conductivity of the PUFs. It indicates that the thermal conductivity of PUF nanocomposites decreases up to the addition of 5 php ONC, and then it increases. It is known that the PUF with a small cell size shows low thermal conductivity (27). The results of thermal conductivity show similar behavior with the results of the cell size with the ONC filled PUF. Seo et al. also reported the decrease in thermal conductivity in the PUF clay nanocomposite (28). However; we observed that at higher loading of 10
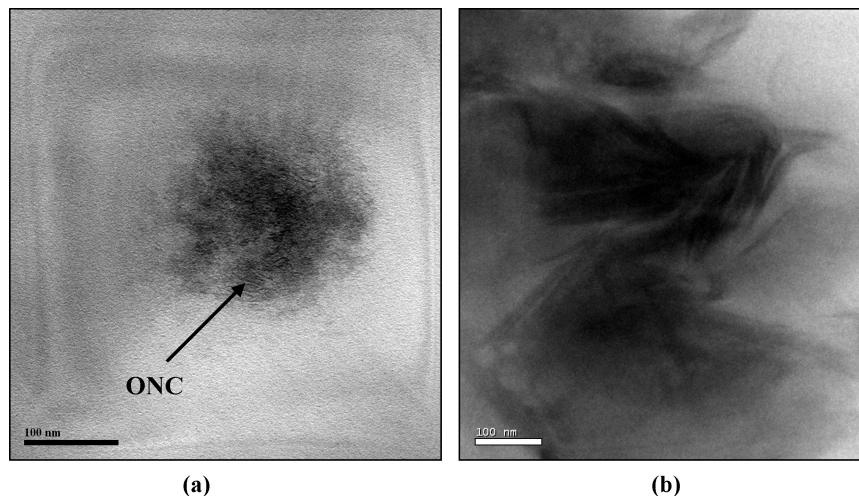

Fig. 3. TEM images of organoclay filled PUF samples: (a) ONC-3 php; (b) ONC-5 php.
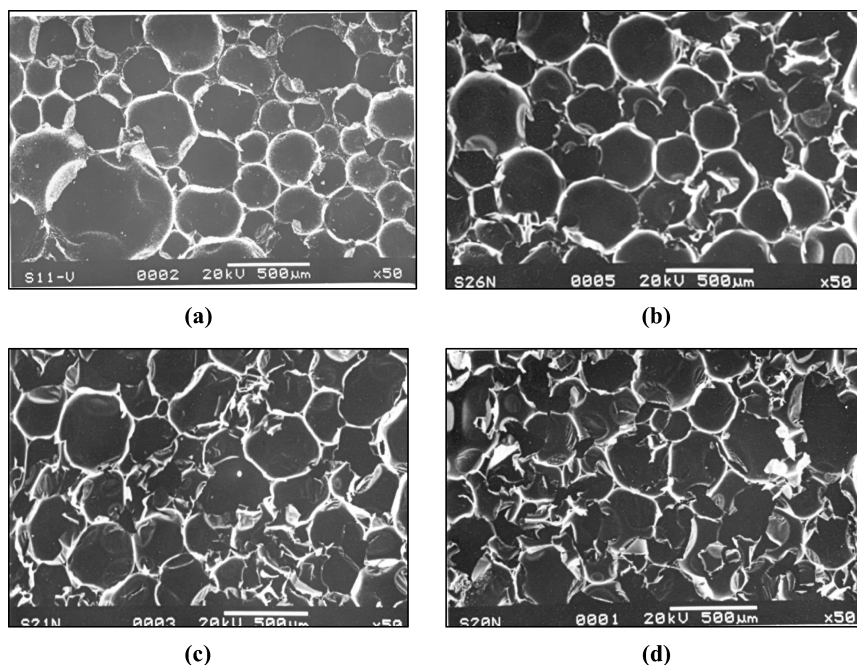
Fig. 4. SEM microphotographs of filled PUF samples: (a) Neat; (b) ONC-1 php; (c) ONC-5 php; (d) ONC-10 php.

php of ONC, the thermal conductivity increases due to the coalescence and collapse of cells in PUF.

3.7 Thermal Analysis

The glass transition temperature (Tg) depends mainly on chain flexibility, branching or crosslinking, molecular weight, intermolecular attraction, steric hindrance, etc. As the chain flexibility of a polymer increases, the Tg of the polymer decreases. The T_g of the ONC filled PUF samples were measured by differential scanning calorimetry (DSC) and are shown in Table 4.

The results indicate that the Tg of ONC filled PUF decreases with an increase in loading of ONC in PUF. The presence of ONC causes exfoliation in the clay-polyurethane matrix, which decreases the intermolecular attraction in the polyurethane macromolecular chains (29). So, the PU backbone chains gain more segmental mobility
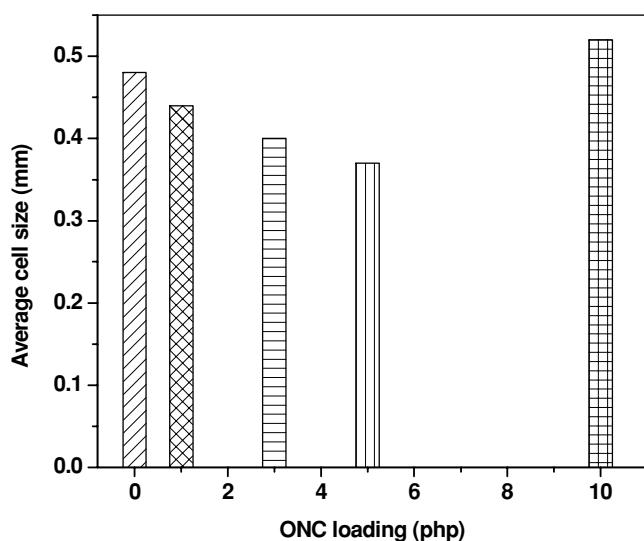

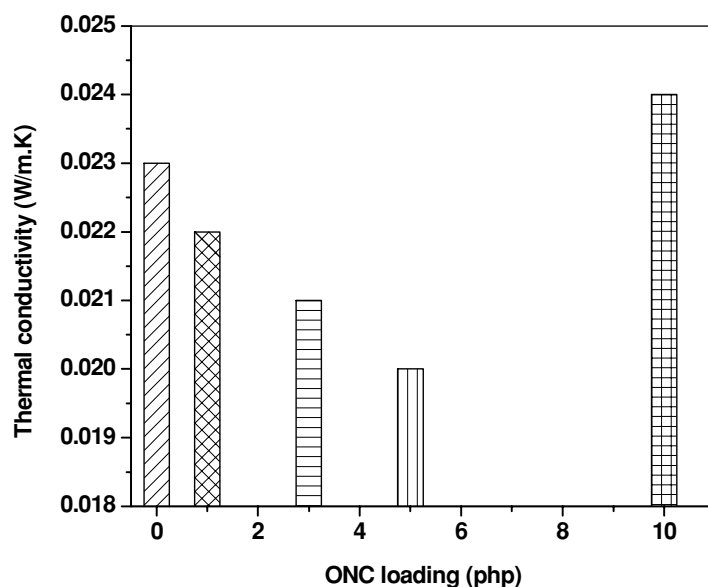**Fig. 5.** Effect of organoclay on the cell size of PUF.

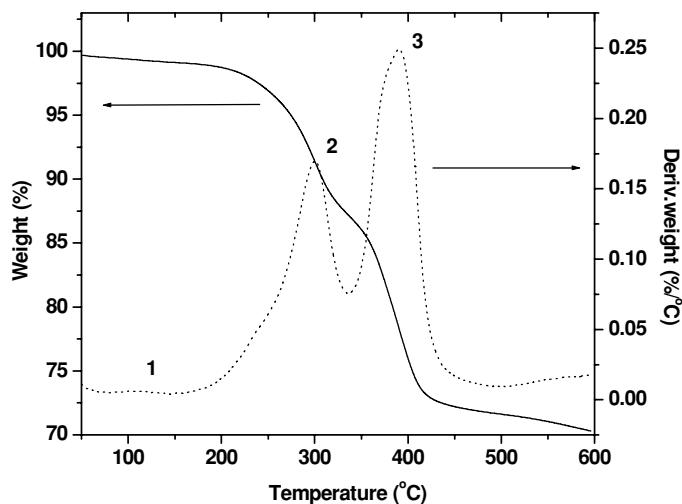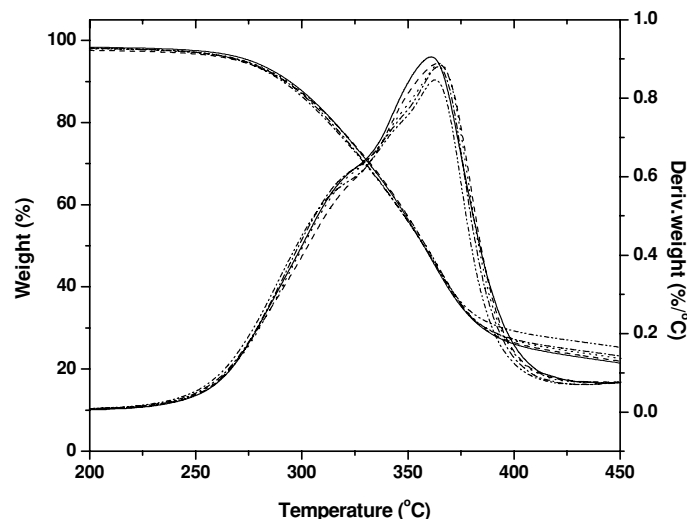**Fig. 6.** Effect of organoclay on the thermal conductivity of the PUF.

Table 4. Effect of organoclay on the glass transition temperature (Tg) and degradation temperature (T_{max}) of the PUF

S.No.	ONC loading (php)	Tg (°C)	T_{max} (°C)
1	0	105	361
2	1.0	96	364
3	3.0	91	365
4	5.0	92	364
5	10.0	87	363

and its Tg decreases with the increase in ONC content in PUF.

The TGA analysis of organoclay under nitrogen atmosphere is shown in Figure 7. It reveals that the decomposition of ONC is shown in three steps. The first region at (~105°C) shows a small hump, which is due to the evolution of absorbed water. The second and third decompositions takes place in the region of 200–330°C and 340–450°C, respectively. The second degradation is probably due to evolution of water, which is present in between the aluminosilicates layers (interlayer residing water), is also confirmed from FTIR studies discussed earlier and are evolved at higher temperature. The third step of degradation is due to the decomposition of surfactants/intercalating agents (30). The amount of residue (char yield) of ONC was greater (71%) at 550°C.

The TGA/DTA curves for the decomposition of ONC filled PUF and their maximum decomposition temperature (T_{max}) values are shown in Figure 8 and Table 4. The result shows that the maximum degradation temperature was slightly increased with an increase in ONC loading as compared to that of neat PUF as shown in Table 4 and Figure 8. This is due to a barrier effect generated by clay platelets which delays the escape of volatile degradation products from the nanocomposite (31).

Fig. 7. TGA thermograms of organoclay under nitrogen.

Fig. 8. Effect of organoclay on thermal stability of PUF under nitrogen.

3.8 Flame Retardant Behavior

The flame retardant behavior of PUF filled with organoclay at different loading was analyzed by determining the limiting oxygen index (LOI), rate of flame spread, and char yield (CY) measurement. Table 5 shows the effect of organoclay on the LOI behavior of PUF. It is clear that the LOI value slightly increases up to 3 php and then starts decreasing with an increase in organoclay loading. The reduction of flammability of PUF with up to 3 php of organoclay loading can be explained by the formation of a multi-layered carbonaceous silicate structure in the condensed phase. This carbonaceous silicate char generated on the surface of burning polymer insulates the underlying polymer and thus slows down the heat and mass transfer between the gaseous and condensed phases. In addition, it acts as a barrier layer generated by clay plates which delays the escape of volatile combustible degradation products from the nanocomposites (32–35). Interestingly, all the PUFs filled with organoclay had slightly higher LOI than that of neat PUF. However, in the case of higher loading of ONC, the LOI values slightly decreases. It is due to the decrease in density which facilitates the mass and heat transfer.

Table 5 indicates the effect of organoclay on the rate of flame spread of PUF at room temperature. The rate of flame spread depends on the physical and thermal properties of the material, the method of mounting and orientation of the specimen, the type and magnitude of fire and heat exposure, the availability of air and the properties of the surrounding area. It reveals that the neat PUF burns very fast after ignition and reaches a 100 mm distance in a very short time. Whereas, in ONC filled PUF the time required to burn 100 mm distance increases initially and then starts decreasing with an increase in the organoclay loading. With the loading of ONC, the density decreases, hence, the flame spread

Table 5. Effect of organoclay on LOI, flame spread rate and char yield of the PUF

S.No.	ONC loading (php)	LOI (%)	Flame spread rate (mm/min)	Char yield in TGA (N_2) at 550°C (%)	Char yield in muffle furnace at 550°C/30 min (%)
1	0	22.0	200.0	15.01	0.05
2	1.0	24.0	115.4	15.35	0.55
3	3.0	25.0	142.9	15.93	2.09
4	5.0	23.0	172.9	16.50	3.94
5	10.0	22.5	214.3	18.57	5.92

rate increases. However, at very higher loading (10 php) of ONC, the density is drastically reduced as well as there is agglomeration of ONC. Hence, its rate of flame spread is even higher than the neat PUF. The rate of flame spread depends not only on the flame retardant additive, but also on the density of matrix and distribution of the additives. As evidenced from the present investigation, the nanoclay marginally improves the fire retardant properties in PUF, which is not enough to provide benefit even in a small fire situation. As a result, the nanoclay may not be useful as a fire retardant additive alone. But, it can be used with other conventional fire retardant additives to get the synergistic effect with a lower dosage of fire retardant additives (32).

3.9 Char Formation

There is a strong correlation between char yield and flame resistance. This is because the char formation occurs at the expense of combustible gases and the presence of a char inhibits further propagation of flame by acting as a thermal barrier around the unburnt material (36). Table 5 shows the effect of organoclay on the char yield determined by TGA (heating at 550°C under nitrogen atmosphere), as well as by burning in a muffle furnace at 550°C for 30 min. It shows that the char yield increases linearly with increasing the organoclay loading. The organoclay enhances carbonaceous char formation by catalytic effect of clay. At higher temperature, organoclay degrades to form acidic protons on the clay layer (30). These acidic protons have further favored the depolymerization, crosslinking and charring process and finally increased the char yield.

4 Conclusions

Polyurethane nanocomposite foam was prepared by the *in situ* preparation of PUF in the presence of an organoclay. The studies show that,

1. The density of PUF increased marginally with the addition of a small amount of ONC.
2. At lower loading of ONC (up to 3 php), there is a slight improvement in mechanical properties of rigid PUF. This is due to the formation of a uniform and smaller cell size of the PUF as evidenced from SEM studies. At higher loading of ONC, there was rupture and collapse of cells which affect the mechanical properties.
3. Exfoliated nanocomposite PUF morphology was obtained and is confirmed by WAXD and TEM studies.
4. Thermal insulation properties of the ONC filled PUF improved at lower loading of ONC (∼5 php). This is because of a decrease in the average cell size.
5. The flame retardant properties (LOI and flame spread rate) of PUF are slightly improved with the addition of ONC up to 3 php.

Acknowledgements

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