Rigid Polyurethane–Clay Nanocomposite Foams: Preparation and Properties

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ABSTRACT: Rigid polyurethane–clay nanocomposite foams considered in this work are made with different clay types and for different clay concentrations. The densities of the foams are in the range of 140–160 kg/m^3 with possible application as structural materials and for underwater buoyancy-related uses. Wide-angle X-ray diffraction and transmission electron microscopy studies confirm the formation of nanocomposites. The compressive modulus and the storage modulus of the foams increase and the mean cell size decreases with addition of clay. However, the hydraulic resistance of the nanocomposite foams, a measure of the strength of the foam lamellae, is lower than that of the foams without clay. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2802–2809, 2007

Key words: nanocomposites; structure–property relations; polyurethanes; rigid foam; hydraulic resistance

INTRODUCTION

Rigid polyurethane foam is extensively used for thermal insulation, construction and packaging.[1,2] In water blown rigid polyurethane foam, the ingredients are polyol, water, catalyst, surfactant and isocyanate. Initially the polyol is mixed with water, catalyst and surfactant, and then the polyol mixture is mixed with isocyanate to initiate reaction and foaming. The polymerization reaction between isocyanate and polyol occurs along with the blowing reaction between isocyanate and water, which produces carbon dioxide and blows the foam. The foam structure consists of large number of small cells in the shape of irregular polyhedra. The typical structure of a rigid polyurethane foam is shown in Figure 1. The lamella of foam material that separates two adjacent cells is called a cell window. A strut (also called Plateau border) is formed when three windows of three different cells meet.

We investigate here synthesis and properties of rigid polyurethane–clay nanocomposite foams. Extensive research on polymer–clay nanocomposites has shown that properties of the polymers can be improved by reinforcing them with clay.[3–5] There are two previous reports of clay–polyurethane foam nanocomposites. Kresta et al., found a decrease in thermal conductivity with addition of clay.[6] Cao et al. studied the effect of clay on the properties of the low density (58–77 kg/m^3) rigid polyurethane foams.[7] They used two trifunctional polyols of different molecular weight to give different crosslink densities in the foams. For the nanocomposites made with polyol of higher molecular weight (foam with low crosslink density) they observed a 780% increase in the reduced compressive modulus (to eliminate the effect of foam density the compressive modulus of different foams were normalized by dividing by their respective density). However, when the foams were made with polyol of lower molecular weight (foams with higher crosslink density) the reduced compressive modulus decreased by 55% on addition of clay. They attributed this negative effect of clay on the interference by the clay particles in forming hydrogen bonds among different urethane groups. The hydrogen bonds among different urethane groups improve the stiffness of the polyurethanes. Interestingly, for the pure foams, the reduced compressive modulus of the foam made with polyol of lower molecular weight is nearly 100 times more than that of the foam with higher molecular weight (increases from nearly 1.9 to 192 MPa cm^3 g^{-1}). This increase in modulus is due to higher crosslink density. There are also some reports regarding the use of nanoclay for making thermoplastic foam. Different polymers such as polypropylene,[8] polystyrene,[9] poly(methylmethacrylate),[9] polycarbonate,[10] and biodegradable polycaprolactone[11] and polylactide[12] have been used for making such foams.

The objective of this work is to study the synthesis method and properties of rigid polyurethane–clay
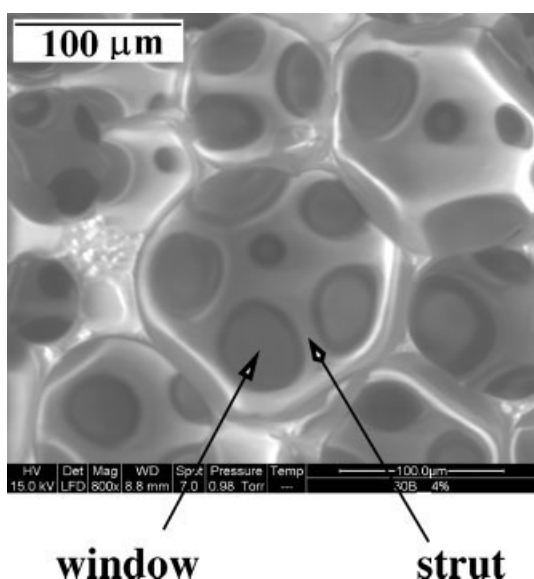
Figure 1 Sample scanning electron micrograph showing a cell window and a strut.

nanocomposite foams with densities in the range of 140–160 kg/m³. Such foams are suitable for structural applications and for underwater buoyancy applications. The main system parameter varied in the study is the nature of the clay used. Commercially modified[13] clay (Cloisite® 30B), clay modified by p-aminophenol and unmodified clay are considered. The organic cations present in the modified clays have pendant hydroxyl groups (organic cation present in Cloisite 30B has two hydroxyl groups[13] and p-aminophenol has one hydroxyl group). These hydroxyl groups can react with the isocyanate and thereby establish a chemical linkage between the clay and the polyurethane matrix. Foams produced by dispersing the clay initially in polyol or in isocyanate are thus compared. In addition to standard mechanical characterization, cell level mechanical properties are investigated by hydraulic resistance studies. In such studies, foam samples are completely submerged in water and exposed to elevated hydraulic pressures causing foam lamellae to rupture and resulting in percolation of water into the foam.[14–18] The variation of the volume fraction of water percolated with increasing hydraulic pressure gives an indication of the strength of the cell windows. We have shown that one method of achieving stronger cell windows is by catalyzing the polymerization so that less time is available for drainage of the liquid from foam lamellae resulting in thicker cell windows.[16] Using appropriate surfactant to reduce the mean cell size also results in improved hydraulic resistance.[14] The morphology of the foams is also characterized. In the following sections the experimental details are given first followed by results and discussion. The conclusions are given in the final section.

EXPERIMENTAL

Raw materials

The raw materials required to make water-blown rigid polyurethane foam are polyol, isocyanate, catalysts, and surfactant. The polyol used was a sucrose-based polyether polyol (DC 9911, Huntsman International, India). The polyol had a hydroxyl number of 440 mg of KOH per gram of the polyol and an equivalent weight of 128 g/mol. The isocyanate was a polymeric diphenyl methane diisocyanate (MDI) (SUPRASEC 5005, Huntsman International). The isocyanate had an equivalent weight of 132 g/mol. The catalysts used were dibutyltin dilaurate (DBTDL) (Lancaster, England), a polymerization catalyst and triethanolamine (TEA) (Spectrochem, India), which catalyzes both the polymerization and blowing reaction. Tegostab B8404, silicone surfactant, used in this study was donated by Goldschmidt AG Germany. The montmorillonite clays, Cloisite Na⁺ and Cloisite 30B, were purchased from Southern Clay Products, USA. In the remaining part of this article, these two clays are referred as Na⁺ and 30B, respectively. The cation exchange capacities of the Na⁺ and 30B are 92.6 and 90 mequiv./100 g of the clay, respectively.[13] The unmodified Na⁺ was also modified by p-aminophenol, which was purchased from Spectrochem, India. p-Aminophenol was added in a dilute dispersion of Na⁺ in distilled water, protonated (by concentrated hydrochloric acid) and the precipitate was filtered off, washed, and dried to obtain the p-aminophenol-modified clay (clay_PAP). All materials were used as received without further purification.

Foam formation

Foams were made by dispersing the clay first either in polyol or in isocyanate. Foams for which clay was dispersed in polyol were prepared as follows. Initially the clay was dispersed in the polyol by stirring for 48 h at 80°C. After cooling, the required amounts of water, catalysts, and surfactant were added to the dispersion and stirred for half an hour. The polyol mixture was mixed thoroughly with predetermined amount of isocyanate for 15 s using a high-speed stirrer at 2800 rpm. For the foams made by dispersing the clay in isocyanate, clay was added to isocyanate and kept for 12 h in a sealed container. The clay-dispersed isocyanate was stirred for 5 min before reacting with the polyol mixture (containing surfactant, water, and DBTDL). Then the clay dispersion was reacted with the polyol mixture by stirring at 2800 rpm for 15 s. The same speed and mixing time was maintained for all formulations. In the nomenclature adopted here to describe the foams, both the clay type and the percentage of clay in the foam are indicated. The nomenclature 30B__4% indicates

TABLE I
Formulations Used for Making Different Foams

Formulation (pphp[a])	Foams with DBTDL and TEA as catalyst	Foams with DBTDL as the only catalyst
Polyol	100	100
Water	1.0	1.0
TEA[b]	0.5	
DBTDL[c]	0.5	2.53
Surfactant	3.0	3.0
	Isocyanate index 105	
	Clay 0–4% of total weight of the foam	

[a] Parts per hundred grams of polyol.
[b] Molecular weight 149.
[c] Molecular weight 631.11.

that the foam was made with 4% of 30B. If the foam was made by dispersing the clay first in isocyanate then suffix iso is used and if only DBTDL is used as a catalyst the suffix D is appended. Thus foam 30B__4%_iso_D was made by initially dispersing 4% of 30B in isocyanate and only DBTDL was used as catalyst in the foam formulation. The details of the formulations used are given in Table I. The mixing time was the maximum time possible that still left adequate time for pouring into the mold before the foam started rising. The mixture was immediately poured into a stainless steel mold, which was closed and kept at room temperature for 15 min. The foam was then removed from the mold and allowed to cure at room temperature for at least 1 day before any characterization. The mold had the dimensions of $127 \times 127 \times 317$ mm^3 and was coated with a mold-release agent (wax). All foams were visually uniform in color, indicating reasonably uniform mixing of the reactants.

Characterization

Wide-angle X-ray diffraction

Wide-angle X-ray diffraction (WAXD) studies of the samples were carried out using an X-ray Diffractometer (model X'Pert PRO; PANalytical B.V; Almelo; Netherlands). A K-α wavelength of 1.54 Å was used and the samples were scanned in the range 0.5°–10°.

Transmission electron microscopy

A foam sample was powdered using a mortar and pestle and then dispersed in isopropanol. A small drop (using micro pipette) of the dispersion was placed on a 300 mesh copper grid. After evaporating the solvent, sample transmission electron micrographs were taken at an accelerating voltage of 120 kV on a twin transmission electron microscope (model Tecnai G^2 12; FEI; Brno, Czech Republic) focusing on the thin edge of the powder particles.

Cell window and strut width measurement

The cell window area and the strut width distributions were measured using an optical microscope (Model BX60 Olympus; Tokyo, Japan). Thin slices, less than 1 mm, were cut from each foam sample. Images were captured by an online CCD video camera (Model XC 77CE Sony; Tokyo, Japan) and frame grabber (Model Occulus MX, Coreco; Quebec, Canada). The captured images were analyzed to measure cell window area and strut width by manually selecting the window area and strut width using an image analysis software (Image Pro Plus version 4.1; Media Cybernetics, Silver Spring, MD). Only those cell windows for which the entire window came into focus were taken. Seventy measurements were made for each foam. Scanning electron micrographs of selected samples were taken on an environmental scanning electron microscope (model Quanta 200; FEI; Brno, Czech Republic).

Compressive modulus

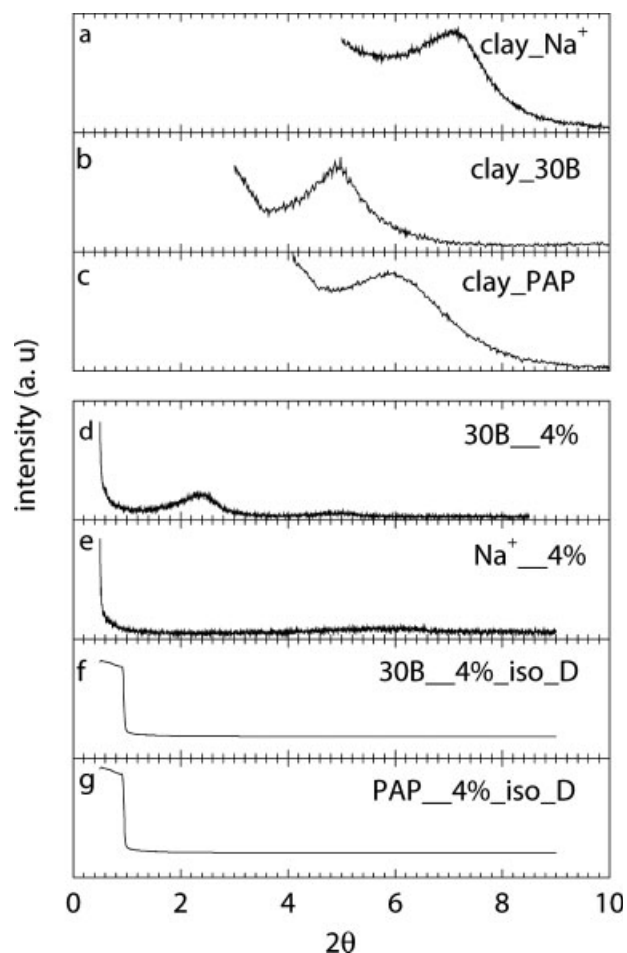The compressive modulus of the foam samples was determined according to ASTM D 1621 73 using a

Figure 2 Wide angle X-ray diffraction profiles of the clays (a, b, and c) and composite foams (d, e, f, and g).

Universal Tensile Testing Machine (UT 2000 series; R and D Electronics, India), using a compression cage. Test specimen dimensions were $51 \times 51 \times 30$ mm^3. The crosshead speed was 3 mm/min. The compressive modulus was measured for compression in both parallel (PL) and perpendicular (PR) directions to the foam rise. A total of five samples were used for each measurement. For all samples the compressive modulus were corrected to a density of 150 kg/m^3 using the following relationship,[19]

$$E_{\rho=150} = E_{ob}\left[\frac{150}{\rho_{ob}}\right]^{1.57}$$

where $E_{\rho=150}$ is the corrected compressive modulus for density 150 kg/m^3, E_{ob} and ρ_{ob} are the observed compressive modulus and density, respectively.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was performed in the cantilever bending mode on bar-like samples in a dynamic mechanical analyzer (Model Tritec 2000; Triton Technology, Notts, UK). All the samples were tested from room temperature to 180°C at a heating rate of 4°C/min. The frequency of bending was fixed at 1 Hz.

Hydraulic resistance

Four samples of cubical shape with side 45–48 mm in length were cut from each foam. The weight of the samples was measured and then the samples were immersed in a sealed container completely filled with water. The container was connected to a pressure gauge and a hydraulic hand-operated pump. The pressure inside the container was raised to a specific value using the hydraulic pump. After 1 h the foam samples were taken out, and water from the surface of the samples was removed by a piece of cloth and again weighed. During the 1-h equilibration period the pressure was found to decrease because of water absorption by the foam samples. Thus the pressure was checked at intervals of 5–10 min, and if there was any decrease, the pressure was raised to the specified value using the hand pump. The buoyancy loss was calculated by using the following formula,

$$\text{percentage buoyancy loss} = \frac{\rho_f' - \rho_f}{\rho_w - \rho_f} \times 100$$

where ρ_f, ρ_f', and ρ_w are the initial foam density, density of the foam after water absorption, and the density of water, respectively. The buoyancy loss was measured for different hydraulic pressures in the
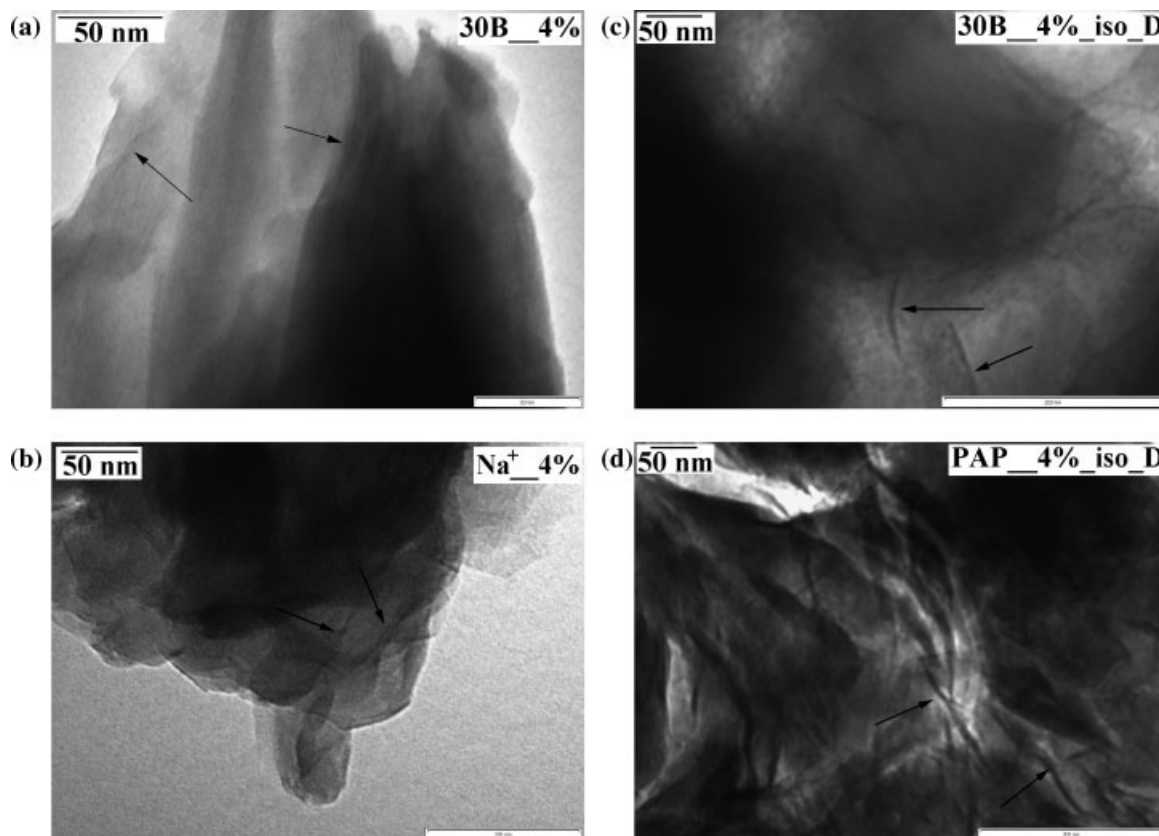

Figure 3 Sample transmission electron micrographs of some selected foams. The clay-rich regions (a) and the clay layers (b, c, and d) are marked by arrows.

range 0–3 MPa. It was assumed that volume of the foam samples remained constant in the experiment.

RESULTS AND DISCUSSION

The WAXD profiles of different clays and nanocomposite foams are shown in Figure 2. The shift of the XRD peak for the foam with 30B [Fig. 2(d)] toward a lower value of 2θ indicates formation of an intercalated nanocomposite. In case of the foam with Na$^+$ [Fig. 2(e)], no such peak is visible within the scan range (0.5°–10°). Thus in this nanocomposite the spacing between the clay layers is significantly more than that in the foam with 30B and the layers may be exfoliated. These results indicate that the unmodified clay is better dispersed in the polymer matrix as compared to the modified clay. This is due to the affinity of the polyether to the unmodified clay. It is reported in the literature that polyethers form an intercalated nanocomposite with the unmodified clay.[4,5,20–23] The polyol used in this study is a polyether-based polyol.

Foams made by dispersing the clay first in isocyanate (30B__4%_iso_D and PAP__4%_iso_D) also have exfoliated morphology [Fig. 2(f,g)]. This is due to the reaction of isocyanate with the hydroxyl groups present in the clay modifiers.

Sample transmission electron micrographs of some selected foams 30B__4%, Na$^+$__4%, 30B__4%_iso_D, and PAP__4%_iso_D are shown in Figure 3. The micrograph in Figure 3(a) shows an intercalated morphology for the foam 30B__4%. The micrographs in Figures 3(b)–3(d) respectively, for the Na$^+$__4%, 30B__4%_iso_D, and PAP__4%_iso_D show that clay layers are randomly distributed in the polyurethane matrix, indicating an exfoliated nanocomposite. These results corroborate the findings from the WAXD measurements (Fig. 2).

The distributions of the cell window area and strut width of the foams with clay (Na$^+$__4%, 30B__4%) and without clay are shown in Figure 4. The average value and the standard deviation of the measured quantity are also given in each graph. The figure
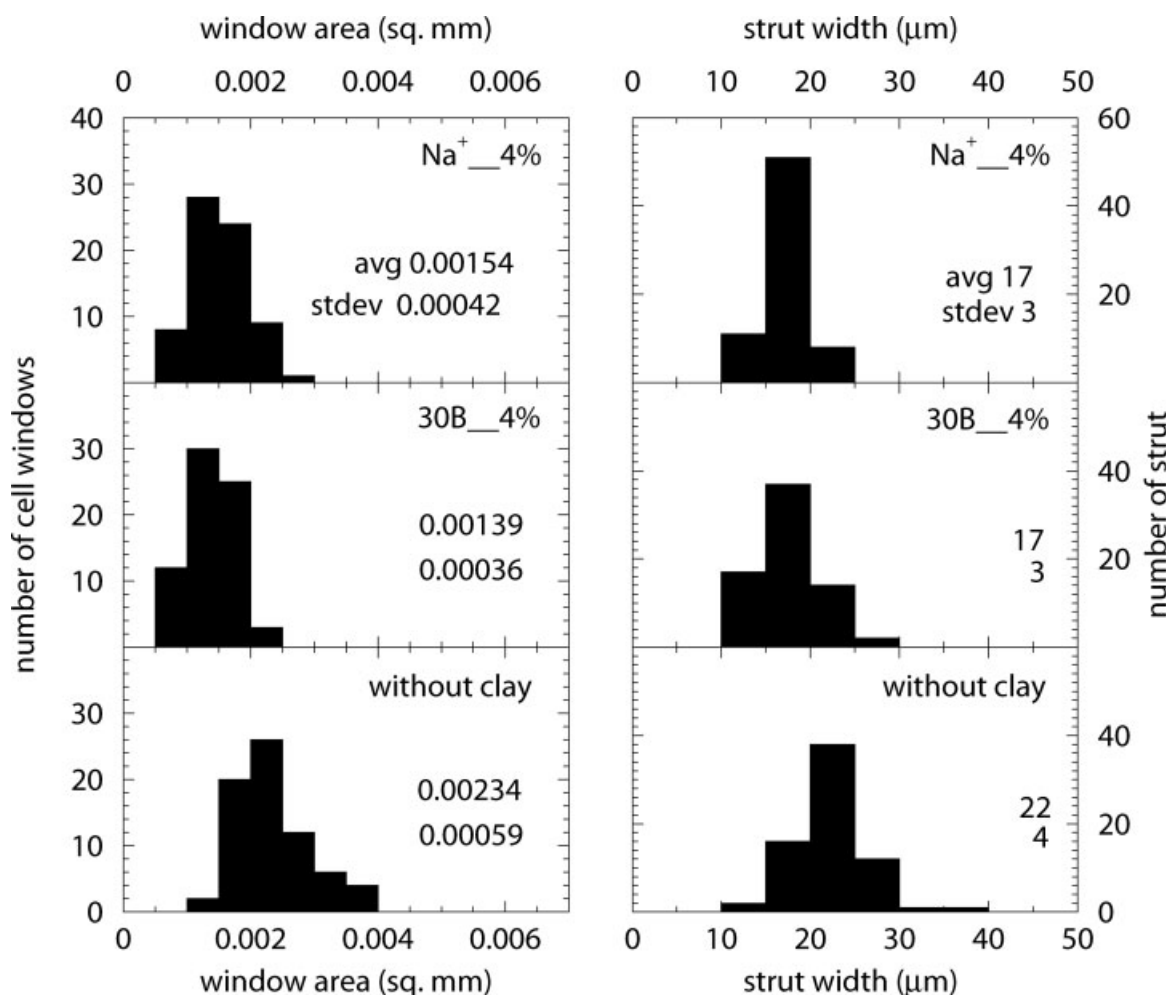
Figure 4 Effect of clay on the distribution of cell window area and strut width. The average values (avg) of cell window area and strut width and standard deviation (stdev) are given in each graph.
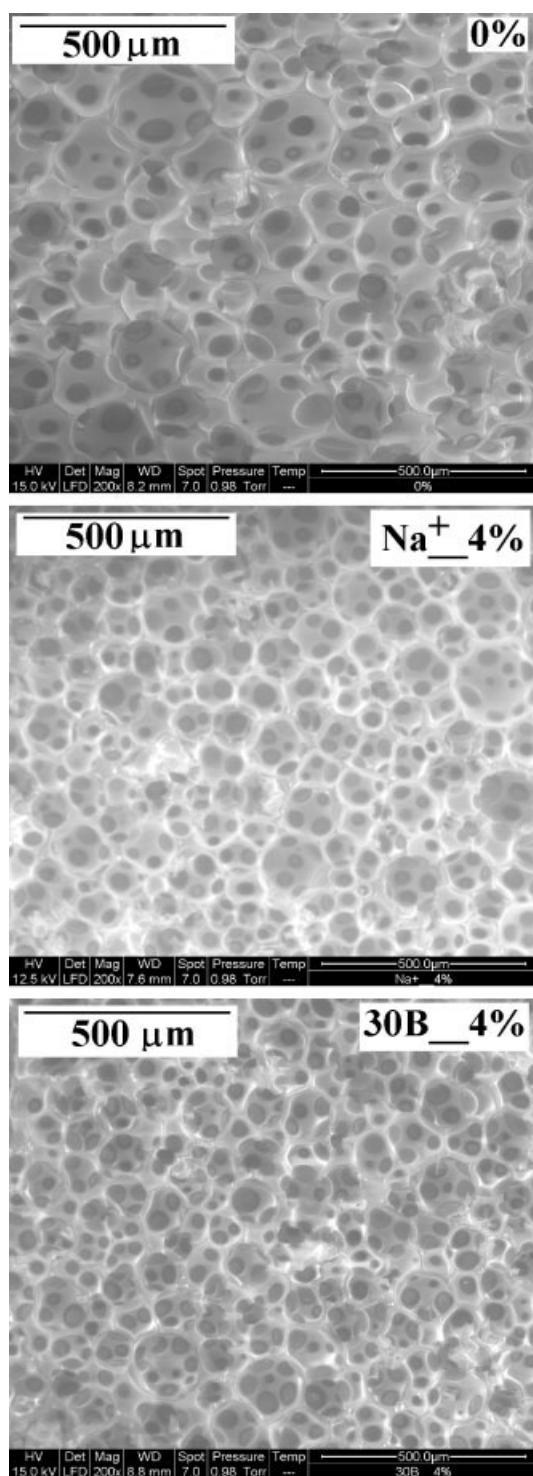
Figure 5 Sample scanning electron micrographs of the foams.

clay particles can act in two ways to cause reduction in cell sizes. They can act as nucleation sites for gas bubbles and they can increase the viscosity of the medium thus reducing coalescence. A consequence of both is that cell number density increases resulting in smaller cells.

The compressive modulus of some of the foams is given in Table II. The table shows that there is significant increase in modulus with addition of clay in the direction parallel to the foam rise, but modulus in the direction perpendicular to the foam rise is nearly constant. The anisotropy results from elongation of the foam cells in the direction of rise. The compressive strength of the foam is essentially determined by the framework of struts. Elongation results in a greater fraction of struts oriented in the rise direction than in the direction perpendicular to rise, resulting in greater compressive strength in the direction of rise. The greater anisotropy in the foams with clay is because the clay catalyzes the foaming reaction resulting in a faster foam rise. The compressive modulus for the Na^+ clay is not significantly higher than 30B in spite of the better dispersion of the Na^+ clay. The compressive modulus improvement with addition of nano clay is significantly lower than that found by Cao et al.[7] This is because the densities of the foams prepared for this work are much higher than those used by Cao et al.,[7] and the compressive modulus of the unmodified foam is already quite high.

The storage modulus of the foams is shown in Figure 6. The figure shows that storage modulus increases with addition of clay. At 35°C the storage modulus at 4% clay is about 25% higher than the foam without clay and is nearly the same for both modified and unmodified clay. At 1% clay loading, the storage modulus for the 30B is higher than the pure foam; however, the storage modulus of the foam with 1% Na^+ is less than that of the foam without clay, at all temperatures.

The effect of clay on the hydraulic resistance of the foam is shown in Figure 7. The error bars in the figure represent standard deviation for four samples. A lower buoyancy loss corresponds to a higher hydraulic resistance. The percentage buoyancy losses at 0.068 MPa (equivalent to pressure at nearly 7 m under water) for all foams (made with and without clay) are very small (Fig. 7). At this low pressure the

shows that both cell window area and strut width decrease with addition of clay. Thus cell size decreases due to addition of clay. Typical scanning electron micrographs of these foams are shown in Figure 5. The decrease in cell size due to addition of clay is visually apparent in the micrographs. The

TABLE II
Compressive Moduli of the Foams

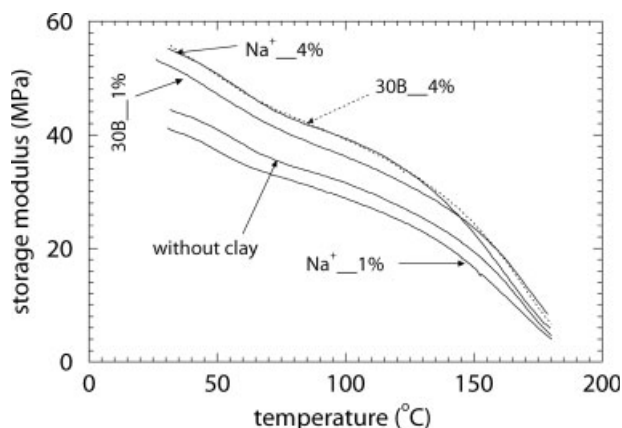| Foam	PL (MPa)	PR (MPa)
Without clay	17.71 ± 0.61	15.28 ± 0.53
Na^+__1%	18.36 ± 0.85	17.19 ± 0.71
Na^+__4%	19.39 ± 0.62	16.22 ± 0.69
30B__1%	20.03 ± 0.79	16.67 ± 0.40
30B__4%	21.79 ± 0.85	14.82 ± 0.52

Figure 6 Storage modulus of selected foam samples.

buoyancy loss is related to the closed cell content and would be low for a foam whose closed cell content is high.[14] Figure 7 shows that buoyancy losses of all foams are very low and nearly same up to a water pressure of 0.30 MPa. Therefore, the closed cell content of all foams (made with and without clay) is high. This indicates that most of the windows of the foams made with clay are closed, i.e., they are not ruptured during foam formation.

Figure 7(a) shows the effect of unmodified clay, whereas the Figure 7(b) shows the effect of one of the modified clays 30B on the hydraulic resistance of the foam. Both the figures show that the hydraulic resistance decreases due to use of clay. We observed that if the foam is made with only the catalyst for the polymerization reaction then the hydraulic resistance of the foam is much higher than any other foam made with any combination of the catalysts for both the polymerization and blowing reaction.[16] The hydraulic resistance of the foams made with unmodified clay in presence of the catalyst for the polymerization reaction (DBTDL) is shown in Figure 7(c). The figure shows that the hydraulic resistance of the foams (both with and without clay) increases in comparison to the foams [shown in Fig. 7(a,b)] made with both the catalysts for polymerization and blowing reaction i.e., DBTDL and TEA. However, in this case also the hydraulic resistance of the nanocomposite foams is lower than that of the foam without clay. The hydraulic resistance of the foams made by dispersing the clay first in isocyanate is shown in Figure 7(d). The figure indicates that dispersing the clay first in the isocyanate does not improve the hydraulic resistance of the foam. The Figure 7 indicates that hydraulic resistance of the foam decreases due to use of clay regardless of clay type and concentration.

The results indicate that although the clay improves the macroscopic properties of the foam, the cell level property, the lamellae strength, decreases. The compressive properties of the foam depend on the strength of the struts, whereas the strength of the windows determines the hydraulic resistance of the foam. In an earlier work,[14] we found that smaller cell windows give higher hydraulic resistances. In this work, though we get smaller cell windows on addition of clay, the hydraulic strength is lower. We thus conclude that the clay weakens the windows, most likely by introducing defects in the windows. This is supported by recent work,[24] which shows that in low density foams, clay has a significant tendency to rupture windows resulting in a greater fraction of open cells.

CONCLUSIONS

Water-blown rigid polyurethane foams are made with modified and unmodified montmorillonite clay. Foams are made by dispersing the clay first either in polyol or in isocyanate. WAXD and transmission electron microscopy of the prepared foams indicate the formation of nanocomposites. The unmodified clay forms an exfoliated nanocomposite. One of the modified clays (30B) having hydroxyl groups in the clay-modifier forms an intercalated nanocomposite when
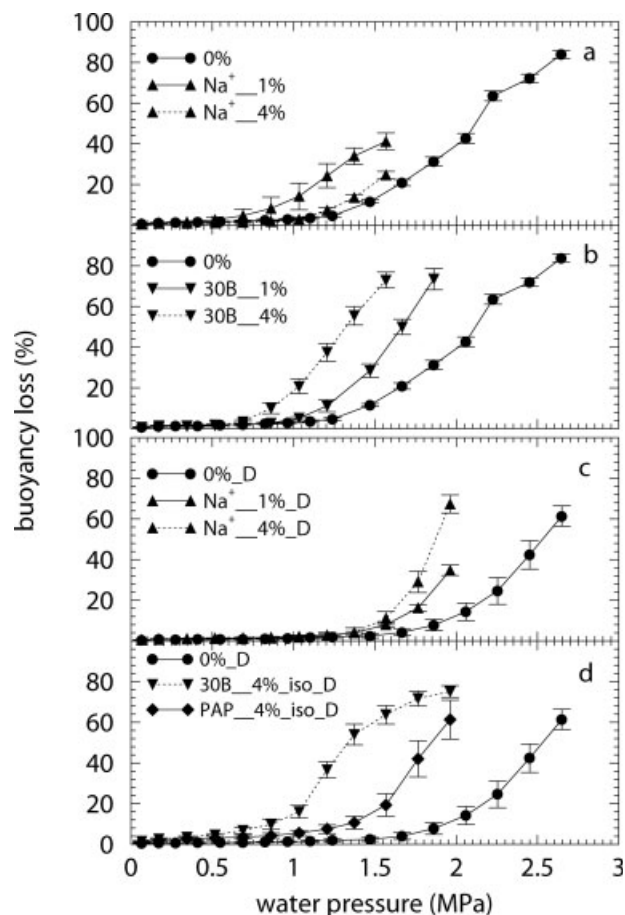

Figure 7 Effect of clay on the hydraulic resistance of the foams. The error bars represent the standard deviation for four samples.

the clay is initially dispersed in the polyol. However, the morphology changes from intercalated to exfoliated by dispersing the same clay first in isocyanate and then reacting the dispersion with the polyol mixture. The clay is modified with *p*-aminophenol and an exfoliated nanocomposite foam resulted when the clay is first dispersed in isocyanate. The compressive modulus of the nanocomposite foams measured in the direction parallel to the foam rise is significantly higher than that of the pure foam. The storage modulus of the nanocomposite foams is also higher than that of the pure foam. The mean cell size decreases due to addition of clay. However, the hydraulic resistance of the nanocomposite foams is lower than that of the pure foam. This indicates that the clay improves the overall mechanical properties of the foam; however, the cell windows are weakened. The mechanism for the latter needs further investigation.

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