Rigid polyurethane foam nanocomposites with unmodified clay

Somchoke Sontikaew

Abstract—Rigid polyurethane nanocomposite foams filled with 1, 2, 3 and 4 wt% of unmodified clay (Na-clay) were prepared by in situ polymerization. Hexadecyl trimethyl ammonium bromide (HTAB), was added during dispersion of Na-clay in isocyanate to modify Na-clay. The morphology and compressive properties of the foams were examined. All nanocomposite foams possessed tactoid structure as evidenced by X-ray diffraction (XRD) results. The specific compressive properties of the filled polyurethane foams were significantly increased at the Na-clay content of 1 to 2 wt%. The overall crosslink density increased with the presence of Na-clay. This was the reason for the improvement in the compressive properties. HTAB might act as a plasticizer, resulting in decreased the specific compressive properties.

Keywords—Rigid polyurethane foam, Nanocomposites, Nanoclay, Intercalation

I. INTRODUCTION

In 1986, Toyota showed that the addition of small amount of nanoclay into polymer such as nylon 6 resulted in great improvement of mechanical and thermal properties [1]. Afterwards, the nanocomposite of nanoclay and polyurethane has been greatly developed and it was found that the nanoclay significantly increased properties of polyurethanes in many applications: for example, only 1 wt% of nanoclay led to great enhancement in properties of polyurethane elastomer by a two-fold increase in the tensile strength and a three-fold increase in the elongation as compared to those of pure polyurethane elastomer [2]. Polyurethane adhesive used in producing laminates for food packaging exhibited the reduction in the oxygen transmission rate and the water vapor permeation by 30% and 50% respectively when 3 vol% of nanoclay was added [3]. With the addition of 5% nanoclay, rigid polyurethane nanocomposite foams prepared from a high molecular weight polyol showed a 650% increase in specific compressive strength and a 750% increase in specific modulus. The opposite result was observed in rigid polyurethane nanocomposite foam prepared from a low molecular weight polyol [4]. The shear and peel strength of polyurethane adhesive filled with only 1 wt% of nanoclay were increased by 170-195% and 30-40% respectively [5].

To obtain outstanding the property improvements of polymer-clay nanocomposites, the stack of clay layers must be separated into single layers and dispersed throughout the polymer matrix. Therefore, there are many techniques used to obtain the highest level of nanoclay dispersion: for example, the use of ultrasonic [6] or microwave [7] to disperse nanoclay in polyol or isocyanate prior to blend with other chemical agents to obtain the rigid polyurethane/clay nanocomposite foams. It was found that the technique by dispersing nanoclay in polyol with microwave offered the best intercalation [7]. The influence of clay surface modifiers on compatibility between nanoclay and polyurethane was also studied. Among commercial organoclay, Cloisite 30B coated with methyl tallow bis(2-hydroxyethyl) quaternary ammonium chloride (MT2ETOH) was significantly compatible with polyurethane due to hydroxyl (OH) groups in MT2ETOH that was able to react with NCO groups in isocyanate to promote nanoclay dispersion. Rigid polyurethane foam filled Cloisite 30B showed the combination of intercalated and exfoliated structures [8]. Nanoclay coated with cetyltrimethyl ammonium bromide (CTAB) that is commonly used provided the intercalated structure for rigid polyurethane foam nanocomposites [8]. For waterborne polyurethane system, nanoclay coated with didodecyl(dimethyleneammonium bromide (DMAB) dispersed at the highest level [9].

It was clearly seen that nanoclay must be modified prior to blending it with polymer to obtain intercalated or exfoliated nanocomposites. Dispersion of unmodified clay in polyol or isocyanate by using ultrasonic or microwave provided insignificant intercalation of polymer into nanoclay layers [7]. In this work, the unmodified clay was dispersed in isocyanate by using a high speed mixer. The organic modifier, HTAB, was added into the clay suspension during the dispersion. The cation exchange reaction of between the sodium cations on clay surfaces and the modifier molecules would be occurred and promoted the intercalation of the isocyanate molecules into the clay layers. The nanoclay suspension was then used to prepare rigid polyurethane nanocomposite foams. It was expected that the nanocomposite foams obtained exhibited an intercalated structure.

II. EXPERIMENT

A. Raw materials

The unmodified clay used was Sodium bentonite (Mac-Gel, grad SAC) and kindly supplied by Nippon Thai chemical. Hexadecyl trimethyl ammonium bromide (HTAB) was purchased from Sigma-Aldrich. Polyol, RAYPOL 4162 (HV
of 245 mg KOH/g), and Isocyanate B 9001 (4,4’-diphenylmethane diisocyanate with %NCO of 30.5-32.5) were purchased from IRPC Co., Ltd. Silicone surfactant, Tegostab B8418, was kindly supplied by EVONIK. Distilled water purchased from Lab Scan Ltd, Thailand used as blowing agent. Dibutyltin dilaurate (DBTDL) was purchased from Sigma-Aldrich used as a catalyst.

B. Preparation of RPUF/clay nanocomposites

The isocyanate index (NCO/OH ratio) used was 1.3 for all foam samples. The amount of sodium bentonite (Na-clay) with cation exchange capacity (CEC) of 90 meq/100 g used to prepare all nanocomposite foams was 1, 2, 3, and 4 % by weight of entire foam weight. The Na-clay was dried in an oven at 100 °C for 24 hours prior to use. The Na-clay was first dispersed in the isocyanate in a plastic cup by stirring at 2000 rpm for two hours at room temperature. The polyol (100 g), DBTDL (0.01 g), surfactant (2.0 g) and distilled water (0.05 g) were mixed in another plastic cup by stirring at 2000 rpm. The isocyanate-clay and polyol mixture were added together and stirred at 2000 rpm for 30 seconds. Then, the foam mixture was poured into an open mould. These PU foams filled with 1, 2, 3 and 4 wt% of Na-clay were labelled as PC1, PC2, PC3 and PC4. The PU foams named as PCH1, PCH2, PCH3 and PCH4 were the PU foams filled with Na-clay and HTAB. HTAB equivalent to 1.0 CEC (Cation Exchange Capacity) of Na-clay was added during dispersion of Na-clay in isocyanate for 2 hours. The isocyanate-clay-HTAB suspension was then mixed with the polyol mixture to form the PU foams. The unfilled foam was denoted as PU.

C. Foam Characterization

The distance between clay layers in the polyurethane foam were examine by using a wide angle X-ray. Cu Kα radiation with a wavelength of 0.154 nm was used for X-ray source. The nanoclay and nanocomposite foams were scanned for 2° between 1° and 10° at scanning rate of 6 °/min. The foam apparent density was measured to the ASTM D 1622. The apparent density of the foams was obtained from the ratio between the weight and the volume of a cubic specimen. Compression test was performed by using a universal testing machine according to ASTM D1621 with sample size of 40 mm x 40 mm x 30 mm. To examine swell behaviour of the foams, small blocks with size of 10 x 20 x 5 mm were weighed and immersed in toluene at room temperature for one week. The samples were then removed from the solvent, rapidly blotted with tissue and weighed to obtain % swollen weight.

III. RESULTS AND DISCUSSION

A. X-ray diffraction (XRD)

The XRD results of the polyurethane/Na-clay composite foams without adding HTAB are shown Figure 4.1(a). It was found that Na-clay showed the diffraction peak at 2θ = 7°, corresponding to the interlayer distance of 1.26 nm. Similar to the unfilled foams, the polyurethane foams filled with 1 and 2 wt% of Na-clay did not display any peaks. The reason for this is that the amount of Na-clay used was too low to be detected and the clay was not uniformly dispersed throughout the polymer matrix. When the clay content was 3 and 4 wt%, the peaks were present at the same peak position of Na-clay. These results confirmed that the polyurethane molecules did not intercalate into the clay layers. Therefore, it can be concluded that all nanocomposites obtained exhibited a tactoid structure.

![XRD results of Na-clay, unfilled PU foam, and PU composite foams filled with (a) Na-clay, (b) Na-clay with HTAB.](image-url)
B. Compressive properties

The compressive properties of all polyurethane foams were examined according to ASTM D-1621. All specimen foams were compressed in foam rising direction. Fig. 4.2 showed the apparent density of the unfilled and filled PU foams. The average apparent density of the unfilled foams was 0.158 g/cc while the filled systems had a higher density in the range of 0.165 to 0.22 g/cc. The specific compressive properties (the compressive properties/the apparent density) were used to compare the mechanical properties of all PU foams due to the difference in the density. The specific compressive moduli and strength of all foams were shown in Fig. 4.3 and 4.4 respectively. It was seen that both compressive moduli and strength of the rigid polyurethane foams increased with adding the Na-clay. The compressive properties of the composite foams were highest at 2 wt% of the Na-clay as compared to the unfilled foams and gradually decreased with increasing Na-clay.

Fig. 4.2 The apparent density of the filled and unfilled PU foams.

Fig. 4.3 Specific compressive modulus of unfilled and filled rigid polyurethane foams.

For the composite foams with adding Na-clay and HTAB, the maximum compressive properties were at 1 wt% of Na-clay as compared to the unfilled foams. For the foams filled with 2, 3 and 4 wt% Na-clay, the compressive properties were similar to those of the unfilled systems. This was possibly due to the additional HTAB acting as a plasticizer. For the 1wt% Na-clay foams, the amount of HTAB used was too low to act as the effective plasticizer.

C. Crosslinking of PU composite foams

It was generally known that the crosslink density of polymer networks, such as polyurethane, influences on the degree of swelling or the amount of solvent absorbed [10]. A polymer with a high crosslink density exhibited a low degree of swelling due to less solvent absorbed, resulting in small increase of foam weight. The degree of crosslink density of polyurethane foams can be observed by examination of % gain in weight after in toluene for one week. It was reported that when modified nanoclay was added into polyurethane foams, the overall crosslink density increased for low crosslink polyurethane foams and decreased for high crosslink polyurethane foams [11].

Fig. 4.4 Specific compressive strength of unfilled and filled rigid polyurethane foams.

Fig. 4.5 % gains in weight of all foams after in toluene for one week.

The polyurethane foams prepared in this work had a low crosslinking. Therefore, the increase in the overall crosslink density of these filled foams was expected. Fig 4.5 showed the % gain in weight of all foams after in toluene for one week. It seemed that the presence of Na-clay led to decreases in the % gain in weight as compared to the unfilled system (PU). This indicated that the filled foams showed a higher crosslink
density than the unfilled system, especially in PC1 and PCH1. The increase in the crosslink density might be the reason for the improved compressive properties of the composite foams filled with Na-clay, especially in PC2 and PCH1.

IV. CONCLUSION

XRD results of all foam samples showed that the clay interlayer distances did not increased. It indicated that the isocyanate and HTAB were unable to intercalate into the clay layers. Consequently the cation exchange reaction between HTAB and sodium cations on the clay surfaces did not occur as expected. Due to absence of isocyanate in the interlayer of Na-clay, there was no occurrence of polymerization reaction of polyurethane between the clay layers, resulting in the nanocomposite foams with tactoid structure. The dispersion of Na-clay in polyol with adding HTAB prior to preparation of the nanocomposite foams will be further investigated.

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REFERENCES