

Polyurethane Syntactic Foams Filled with Nanoclay

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Abstract— The neat and nanoclay polyurethane syntactic foams were prepared to investigate the effects of microballoons and nanoclay on their properties. The desired densities of all syntactic foams were 0.6 g/cc. The microballoon loadings filled in the neat syntactic foams were 3, 5, 7 and 9 wt%. All nanoclay syntactic foams contained 7 wt% microballoons. The nanoclay loadings used to produce the nanoclay syntactic foams were 0, 0.5, 1, 2, and 3 wt%. The compressive properties and hardness of the syntactic foams were examined. It was found that the hardness and compressive strength of the neat syntactic foams significantly enhanced as increasing the microballoon contents. For the nanoclay syntactic foams, the compressive strength decreased with the incorporation of the nanoclay. Specific hardness of the syntactic foams was, however, enhanced by the addition of nanoclay.

Keywords—polyurethane foams, syntactic foams, nanoclay, microballoons

I. Introduction

Glass microballoons have been widely used as a filler to reduce density and high cost of polymeric materials. The microballoons are round and hollow particles with diameter of 10 to 200 micrometers and wall thickness of 4-5 micrometers. Polymeric materials filled with the hollow spheres exhibited the cellular structure and defined as syntactic foams. Polyurethane syntactic foams have been developed for many decades for example: US Pat. No. 4,916,173 disclosed a polyurethane syntactic foam composition for production of modeling stock applications [1].

Nanoclay, montmorillonite, is nano-filler for polymeric materials. The nanoclay particles show a layer structure with 100 to 200 nm in width and 1 nm in thickness. If only one gram of the nanoclay was completely separated into single layer, its combined area is 750 m², resulting in high aspect ratio of 57-69 [2]. With large surface areas and one nanometer thickness, only a small amount of nanoclay has potential to improve properties of polymeric materials. The polymers filled with only 4 wt% of the nanoclay exhibited the outstanding properties such as high tensile modulus and strength without brittleness, high thermal resistance, flamed retardation, and low gas permeability. Rigid polyurethane foams from polyol with hydroxyl value (HV) of 245 KOH/100g filled with modified and unmodified nanoclay had intercalated and tactoid structure, respectively [3-4]. It was found that their specific compressive properties (compressive modulus and strength divided by density) were significantly improved.

The aim of the research was to use the nanoclay to reinforce the polyurethane syntactic foams that were prepared from the polyol with hydroxyl value of 245 KOH/100g. It was expected that the compressive properties of the nanoclay syntactic foams were significantly enhanced such as found in the rigid polyurethane foam/clay nanocomposites. The application of the neat and nanoclay syntactic foams will be used as modeling boards for making models, patterns, jigs and fixtures.

II. Experiment

A. Materials

The nanoclay used was Nanomer I.28E (montmorillonite clay modified with trimethyl stearyl ammonium) and purchased from Sigma-Aldrich. The nanoclay exhibited interlayer distance of 2.4-2.6 nm [5]. Polyol with hydroxyl value of 245 mg KOH/g and Isocyanate (4,4'-diphenylmethane diisocyanate with %NCO of 31.5 were purchased from IRPC Co., Ltd. Silicone surfactant, Tegostab B8418, was purchased from EVONIK. Dibutyltin dilaurate (DBTDL) was purchased from Sigma-Aldrich used as a foam catalyst. The hollow glass microballoons used are K20 with density of 0.2 g/cc and purchased from 3M Thailand. Particle size of K20 was in the range of 25 to 105 micrometer. K20 provides crush strength of 2.75 MPa (4000 Psi).

B. Preparation

The amount of nanoclay used to prepare nanoclay syntactic foams was 0, 0.5, 1, 2, 3, and 4 % by weight of entire foam weight. The nanoclay was dried in an oven at 100 °C for 24 hours prior to use. The nanoclay was first dispersed in polyol in a plastic cup by stirring at 500 rpm for one hour at room temperature. Then catalyst (0.01 g at 100 g polyol), surfactant (4.0 g at 100 g polyol) and K20 (14.0 g at 100 g polyol) were added and stirred at 1000 rpm for several minutes. The microballoon concentration was about 7.0 wt% or 30 vol%. The isocyanate (isocyanate index of 1.3) was added into the polyol mixture and stirred at 1000 rpm for two minutes. The foam mixture was poured into an aluminum box with the size of 112(L) mm x 82(W) mm x 65(H) mm and then the mould was tightly closed. The desired density of all foam samples was 0.6 g/cc. Therefore the weight of foam mixture poured in the mould was about 360 g. The foams were removed from the mould after two hours and left for further curing in an oven at 70°C for 24 hours before characterization. The neat syntactic foams containing 3, 5, 7 and 9 wt% were prepared with the same procedure.

C. Characterization

The distance between clay layers in the polyurethane syntactic foams were examined by using a wide angle X-ray or

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XRD. Cu K α radiation with a wavelength of 0.154 nm was used for X-ray source. The nanoclay and nanoclay syntactic foams were scanned for 2θ between 1° and 10° at scanning rate of $6^\circ/\text{min}$. Scanning Electron Microscopy (SEM), JEOL model JSM-5800LV, was used to observe on fracture surfaces of the neat and nanoclay syntactic foams. Apparent densities of the foams were obtained from the ratio between the weight and the volume of cubic specimens. Compression test was performed by using a universal testing machine according to ASTM D1621.

III. Result and Discussion

A. X-ray diffraction

XRD results of the polyurethane syntactic foam filled with nanoclay were shown in Fig. 4.1. Due to absence of nanoclay, none of XRD peak appeared in the unfilled polyurethane syntactic foam. There was also no XRD peak for the syntactic foam filled with 0.5 wt% nanoclay because the nanoclay content was too low to be detected. When 1, 2, and 3 wt% of nanoclay was filled in the syntactic foams, the XRD peaks appeared at 2.3° and 2.4° , corresponding to the clay-interlayer distance of 3.83 and 3.67 nm. The interlayer distances of the nanoclay increased from 2.6 nm to 3.8 nm, indicating that the polyurethane molecules intercalated between layers of the nanoclay.

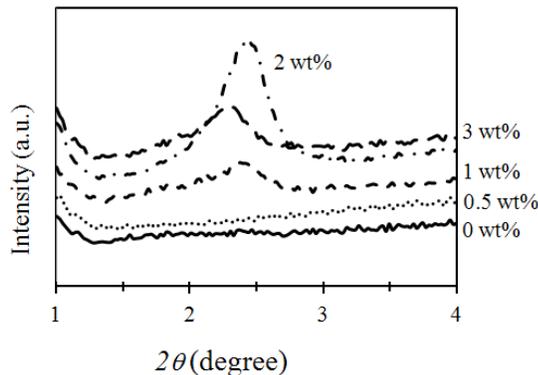


Figure 4.1 XRD results of polyurethane syntactic foams filled with nanoclay.

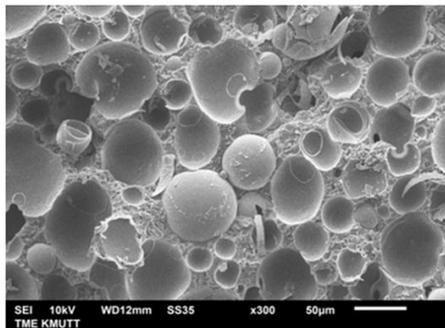


Figure 4.2 SEM image of polyurethane syntactic foams filled with nanoclay.

B. Morphology

SEM fracture image of the polyurethane syntactic foam filled with nanoclay was shown in Fig. 4.2. The syntactic foams obtained exhibited three phases of polyurethane matrices, hollow glass microballoons and gas bubbles as shown in the SEM image. Although any blowing agents such as water were not in the formulation, there was some water (0.2% max) in the polyol used. The blowing reaction of the water in polyol and isocyanate produced carbon dioxide to form gas bubbles. It was observed that all nanoclay syntactic foams showed similar numbers of gas bubbles with average diameter of $50\ \mu\text{m}$. The nanoclay particles were unable to observe because they were beneath the polymeric matrix.

C. Apparent density

The apparent densities of the neat and nanoclay syntactic foams were investigated according to ASTM D1622-98. The desired apparent densities of all syntactic foams were $0.6\ \text{g/cc}$. However, the free rise density of the nanoclay syntactic foams were also examined. The neat syntactic foams filled with 3, 5, 7, and 9 wt% of microspheres were produced to study the effects of microballoons on their properties. These neat syntactic foams exhibited apparent densities of 0.65, 0.65, 0.62 and $0.62\ \text{g/cm}^3$, respectively, closing to the required density. The free rise densities of the nanoclay syntactic foams containing 0, 1, 2, and 3 wt% of nanoclay and 7 wt% of microballoons were 0.205, 0.166, 0.15, and $0.14\ \text{g/cm}^3$ respectively. This indicated that when increasing nanoclay, the gas bubbles increased, resulting in the reduction of the foam densities. More gas bubbles in polyurethane were formed due to the effect of nanoparticles acted as heterogeneous nucleation site [6]. In this work, the weight of foam mixture poured in a closed mould must be equal to obtain the syntactic foams with the same density of $0.6\ \text{g/cc}$. The apparent densities of the nanoclay syntactic foams were shown in Figure 4.3. The nanoclay syntactic foams without nanoclay showed density of $0.62\ \text{g/cc}$, closing to the required density. With presence of the nanoclay, the densities of the nanoclay systems decreased with increasing nanoclay content. The decrease in density of the nanoclay syntactic foams was due to difference in the weight of each foam mixture poured in the closed mould.

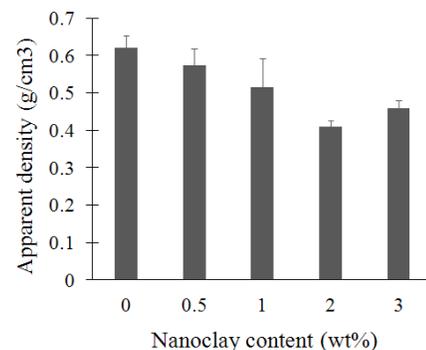


Figure 4.3 Apparent densities of polyurethane syntactic foams filled with different nanoclay content.

D. Hardness

Shore D hardness scale measures the resistance of a material to indentation of hard rubbers, semi-rigid plastics and hard plastics. The hardness of the foam samples was carried out according to ASTM D2240. Polyurethane matrix in this study has density of 1.15 g/cc and Shore D hardness of 75. Fig 4.4 shows the hardness of the neat syntactic foams. It was seen that the hardness of these syntactic foams increased with increasing microspheres contents. At 7wt% (or 30 vol%) of microspheres, the syntactic foams exhibited the highest hardness of about 60 Shore D. When microspheres content was 9 wt% (or 36.5 vol%), the hardness of the syntactic foams did not increase. Therefore, the microballoon content used to prepare the nanoclay syntactic foams nanocomposites was 7 wt%. Because density of the nanoclay syntactic foams obtained in this work decreased with increasing nanoclay content, the effect of the density on their hardness had to be removed. The hardness of the nanoclay syntactic foams was, hence, divided by its density to get specific density. Fig 4.5 shows the specific Shore A hardness of the free-rise nanoclay syntactic foams and Fig 4.6 shows the specific hardness of the nanoclay syntactic foams prepared from a closed mold. It was observed that the specific hardness was improved with presence of 1-2 wt% of nanoclay compared to the unfilled system. The improvement agreed with a few literature reports in the hardness improvement of polymeric materials due to the nanoclay [7-8].

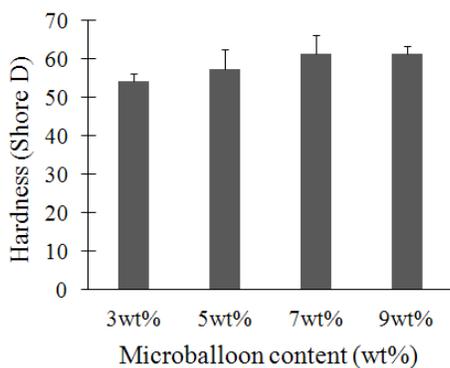


Figure 4.4 Hardness of the neat polyurethane syntactic foams filled with different content of microballoons.

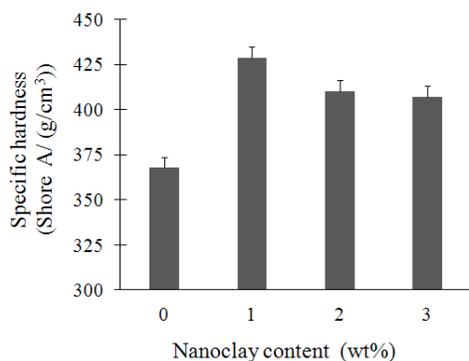


Figure 4.5 Hardness of the free-rise syntactic foams filled with different content of nanoclay.

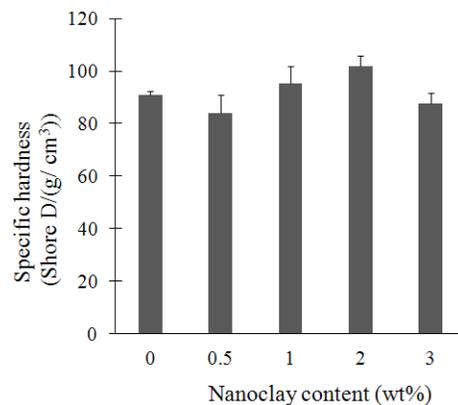


Figure 4.6 Hardness of the nanoclay polyurethane syntactic foams filled with different content of nanoclay.

E. Compression properties

The effect of microballoons on the compressive strength of the neat syntactic foams was shown in Fig 4.7. Densities of the neat syntactic foams approach 0.6 g/cc as explained in the section C. The compressive strength of the foams was, therefore, not affected by their densities. It was observed that the compressive strength significantly increased with the addition of microballoons. The foams with a high content of microballoons displayed higher compressive strength than the syntactic foams with a low microballoon content due to higher crush strength of microballoons than that of the matrix. The structure of syntactic foams exhibited three phases of microballoons, foam cells, and matrix. The foam cells resulted from CO₂ due to the reaction of isocyanate and the water in polyol used. The number of foam cells depended on the content of polyol used to produce the foams. Fig 4.8 (a) shows the diagram of foams with low content of microballoons and high content of polyol. When increasing microballoon content, polyol and isocyanate content used decreased, leading to a low number of foam cells as shown in Fig 4.8 (b). The foams with a high content of microballoons and a low number of foam cells provided higher foam compressive strength than the foams with a low content of microballoons and a high number of foam cells.

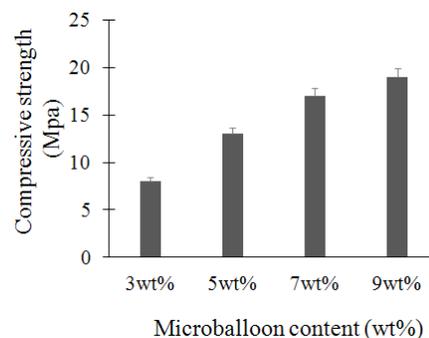


Figure 4.7 Compressive strength of the neat polyurethane syntactic foams with different content of microballoons.

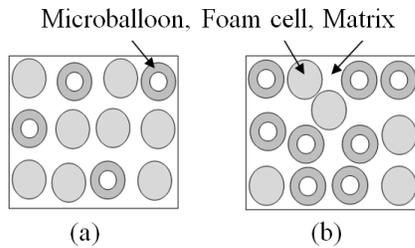


Figure 4.8 Diagram of structure of syntactic foam shows three phases of microballoons, foam cells and matrix, (a) low and (b) high microballoon contents in the similar volume.

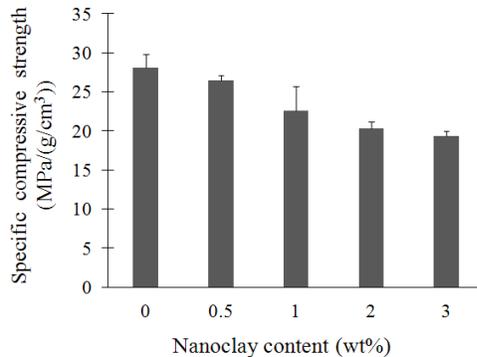


Figure 4.9 Specific compressive strength of the nanoclay polyurethane syntactic foams filled with nanoclay.

Fig 4.9 shows the specific compressive strength of the nanoclay syntactic foams with different nanoclay contents. It was clearly seen that the compressive strength decreased with increasing the nanoclay loadings. In our previous work, it was found that the rigid polyurethane foams from a polyol with HV of 245 KOH/100g filled with 4 wt% modified nanoclay possessed intercalated structure and provided the significant increase in the specific compressive properties [3]. This improvement resulted from the increase in cross-linking density of the rigid polyurethane foams due to the presence of the nanoclay. For the nanoclay syntactic foams from the same polyol, such enhancement did not appear. The reason for this was that adding the nanoclay in the syntactic foams with 7 wt% microballoons provided the increase in gas bubbles. The other probable cause was the decrease in the matrix-microballoon interface due to the presence of nanoclay as explained in Fig. 4.10.

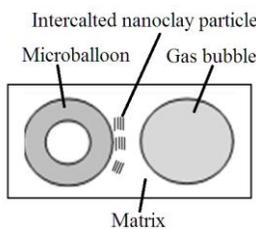


Figure 4.10 Size of intercalated nanoclay particles was around two micrometer while size of microballoons is around 70 micrometer. Nanoclay might locate between microballoons and polymer matrix, resulting in decrease interfacial adhesion of between microballoons and polymer, leading to decrease in the compressive properties of the syntactic foams.

IV. Conclusions

For the neat polyurethane syntactic foams with the desired density of 0.6 g/cc, their compressive strength and hardness significantly increased with increasing microballoon contents. This was attributed to high number of microballoons and less number of foam cells when increasing the microballoon contents. For free-rise nanoclay syntactic foams, their densities decreased with the increase of nanoclay content. It implied that nanoclay acted as nucleation site to form the foam bubbles, resulting in increase of foam volume when increasing nanoclay contents. Unlike nanoclay, microballoons did not act as nucleation site of foam cells. The nanoclay syntactic foams displayed intercalated structure as evidenced by XRD results. The specific hardness of the nanoclay syntactic foams increased with the presence of nanoclay as compared to the neat syntactic foams. For the nanoclay syntactic foams, the specific compressive strength was decreased with the presence of the nanoclay. For future work, the effect of nano-silica on the compressive properties of the polyurethane syntactic foams will be investigated.

Acknowledgment

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