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Soy-based Polyurethane Foam Reinforced with Carbon Nanotubes

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Abstract. The objective of this research is to develop soy-based polyurethane (PU) foam product reinforced with carbon nanotubes. The shortage of petroleum and the increasing concern on environmental issues have resulted in an interest in using renewable substances as building blocks for polymer applications. Multi-walled carbon nanotube (MWNT) was used in this study to reinforce the soy-based polyurethane foam. The compressive and mechanical properties of the composites were enhanced with adding carbon nanotubes. Neat polyurethane was used as a control. Soy-based polyurethane / carbon nanotubes composites with loadings of 0.5 and 1.0 wt% were fabricated. The compressive, flexural, and tensile properties of MWNTs-PU foams were improved by 24, 30 and 30 %, respectively, as compared with the neat PU foam. The greatest enhancements on compressive and flexural properties were shown at the 0.5 wt% MWNT loading, while the highest tensile stress enhancement of PU foam was shown at 1 wt% MWNT loading.

Introduction

Polyurethane is one of the most versatile and intensively used industrial materials. By the proper selection of reactants and changing percentage of the component in the formula, the resulting polyurethane can be elastomer, thermoplastic, thermosetting, rigid and flexible foams. Rigid polyurethane foams can be used as construction materials, such as polymeric concrete components, insulating materials, sealants and signboard. One of the major components to make polyurethane, polyol, is largely relying on petroleum crude oils and coals as feedstock. However, bio-based polyols have been developed from vegetable oils such as soybean oil, canola oil, palm oil and castor oil, due to the environmental and sustainable issues in recent years [1-5].

Developing bio-renewable feedstock for industry is crucial now for both the economic and environmental reasons. Soybean oil is an annually renewable natural resource for the polyols and is available in large quantities. For each pound of soybean oil produced, 2.67 pounds of carbon dioxide are removed from the air [1]. Soy-based polyols can be used in various polyurethane applications by selecting proper functional groups and side chains. Polyurethanes produced from soy-based polyols normally exhibit equivalent or improved physical and chemical properties due to the hydrophobic nature of triglycerides.

Carbon nanotubes have outstanding physical properties such as light weight, high aspect ratio, and high strength. Multiwalled carbon nanotubes (MWNTs) can be good candidates for improving the mechanical properties of polyurethane foam. Incorporating MWNTs could significantly improve the thermal and mechanical properties of PU foam [6-9]. A homogeneous distribution of carbon nanotubes in polymer matrix can be achieved by mechanical stirring, ultrasonication, melt blending, extrusion and spinning process.

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The main objective of this research was to develop soy-based polyurethane foam reinforced with multi-walled carbon nanotubes to enhance the compressive and mechanical properties. Soy-based polyurethane / carbon nanotubes composites with loadings of 0.5 and 1.0 wt% were synthesized. The effects of MWNTs content on the properties of soy-based polyurethane foam composites were investigated.

Materials and Method

Materials: Polymeric diphenylmethane diisocyanate (pMDI) from BASF Company and soy-based polyol from BioBased Technologies Company were used as reactants to make polyurethane foam. Distilled water was used as a chemical blowing agent. Dibutin Dilaurate (DBTDL) and N, N-dimethylethanolamine (DMEA) were used as catalysts. Tegostab B8404 from Goldchmidt Chemical was used as surfactant. Multi-walled carbon nanotubes in 40-90 nm diameter and aspect ratio > 100 were supplied from Nano Carbon Technologies (Tokyo, Japan).

Foam Preparation: Polyurethane foams were prepared by one-pot and free-rising method. The experiments were as followings: Weigh the polyol, catalysts, surfactant and blowing agent (B-side material) using disposable plastic cups; Mix them with a mechanical stirrer at 3000 rpm for 10 ~ 15 s; Allow the mixture to degas for 2 min; Rapidly add pMDI (A-side material) into the mixture and continue to stirring for another 10 ~ 15 s at the same speed; Allow the foam to rise and set at room temperature for 24 hr. Sonication and mechanical stirring were used to aid MWNTs thoroughly mixed with B-side material before adding pMDI.

Property Measurements: The density of PU foam was determined by averaging the mass/volume measurements of six specimens in accordance with ASTM D1622-03 standard. The compressive properties of the foams were measured using an Instron universal testing machine (model 5869, Canton, MA, USA) in accordance with ASTM D1621-04a standard. The compression test was conducted in the foam rise direction. Six replicates were measured and averaged. Flexural testing was conducted on six specimens according to ASTM D 790 standard. The flexural strength (FS) and modulus (FM) were calculated based on Eq. 1 and 2. Tensile strength testing was performed in accordance with ASTM D 1623-03. Five replicates were measured and averaged.

$$FS = (L^3M)/(4Wt^3). \tag{1}$$

$$FM = (3PL)/(2Wt^2). \tag{2}$$

Where P is the ultimate load of the specimen; L is the span, W is the specimen width, and t the specimen thickness, M the slope of the initial stage (straight line) for the load-deflection curve.

Results and Discussion

Effect of MWNTs Content on Foam Density and Compressive Property: The densities of the neat PU foam and the MWNTs-PU foam composites with 0.5 and 1 wt% of MWNTs are shown in Fig. 1. The Densities of MWNTs-PU foam composites were about 1.5–6.3 % higher than that of neat PU foam. As the MWNT loading increased, the density of the foam increased. The viscosity of the mixture was increased when the MWNTs were added to the B-side material and was significantly increased when 1 wt% of MWNTs was used. The increased viscosity would make the foams rise much slower than those without adding MWNTs.

Fig. 1 also shows the foam compressive modulus of PU foam as a function of MWNTs content. The compressive modulus of MWNTs-PU foams was about 12.0 – 24.3 % higher than that of the neat PU foam. This could be attributed to the increased density of MWNTs-PU foams. The compressive modulus increased at 0.5 wt% loading of MWNTs and then decreased at 1 wt% of MWNTs. Under our current lab mixing conditions, at a lower MWNTs loading, the homogeneously distribution of MWNTs could be easy to achieve. At a higher MWNTs weight fraction, MWNTs could be aggregated and thus degraded the compressive property of MWNTs-PU foams.

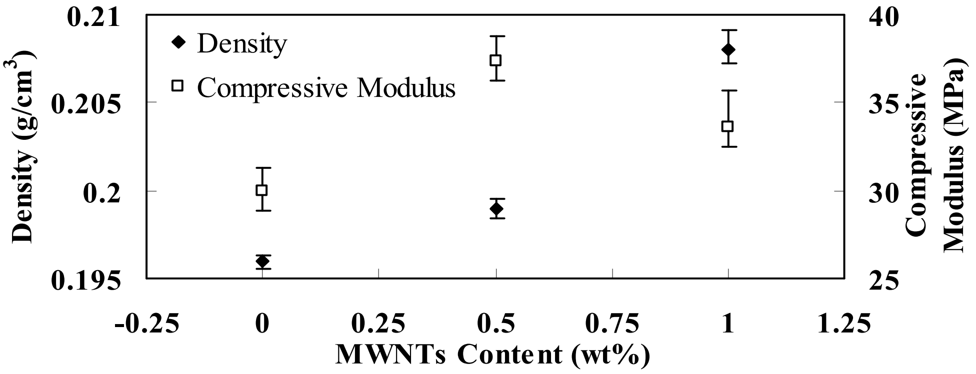

Fig. 1. Density and compressive modulus of PU foams as a function of MWNTs content.

Effect of MWNTs Content on Foam Flexural Property: The flexural properties of neat PU foam and MWNTs-PU foams are shown in Fig. 2. The overall flexural modulus and strength of MWNTs-PU foams were higher than those of the neat PU foam. The enhancements in flexural properties could be attributed to the outstanding physical properties of MWNTs, such as high mechanical strength/modulus and high aspect ratio. Also, the homogeneously distributed MWNTs throughout the foam matrix help with the load transfer from the matrix to MWNTs. Similar to compressive property, the maximum flexural property was achieved at 0.5 wt% loading of MWNTs. MWNTs could act as nucleation sites to promote a more efficient polymer network of PU foam at a lower loading. However, this process could be hindered when MWNTs weight fraction was high at a certain level. The aggregation of MWNTs at high weight fraction also reduced the stress transfer efficiency from the matrix to the MWNTs [7].

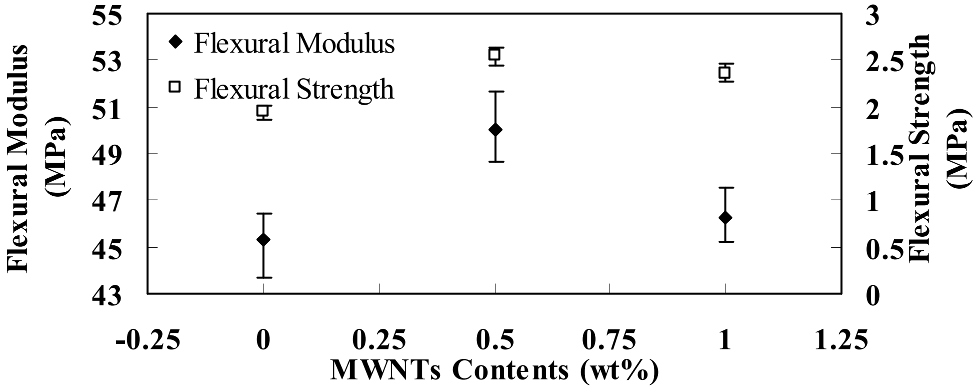

Fig. 2. Flexural modulus and strength of PU foams as a function of MWNTs content.

Effect of MWNTs Content on Foam Tensile Property: The tensile strength properties of both neat PU and MWNTs-PU foams are shown in Fig. 3. The tensile stress of PU foam was enhanced by incorporating MWNTs into the polymer matrix. As the MWNT weight fraction increased, the tensile strength of the foam increased. This might be due to the combined mechanisms of crack deflection and realignment of MWNTs under the tensile stress. The carbon nanotubes could slide and align with themselves under the tensile stress. Aligned carbon nanotubes had a higher tensile strength and were more effective for the load transferring from polymer matrix to carbon nanotubes than the unaligned ones. At the same time, aligned MWNTs could effectively deflect crack development pathway, resulting in an increased tensile strength, and thus creating a new energy-dissipation path for foam composites [10].

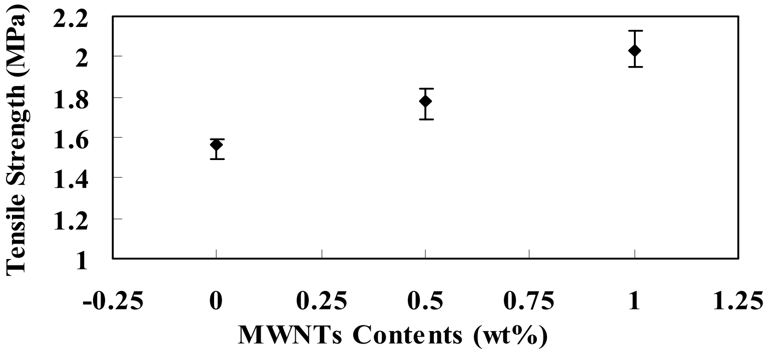

Fig. 3. Tensile strength of PU foams as a function of MWNTs content.

Conclusions

Soy-based polyurethane foam was successfully fabricated with the multiwalled carbon nanotubes incorporated into the foam for the property enhancement. The densities of MWNTs-PU foams were greater than that of neat PU foam and increased as the MWNT weight fraction increased. The compressive, flexural, and tensile properties of MWNTs-PU foams were improved as high as 24, 30 and 30 %, respectively, as compared with the neat PU foam. The greatest enhancement on compressive and flexural properties was shown at 0.5 wt% MWNT loading, while the highest tensile stress of PU foam was shown at 1 wt% MWNT loading.

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