FABRICATION OF NOVEL POLYURETHANE ELASTOMER COMPOSITES CONTAINING HOLLOW GLASS MICROSPHERES AND THEIR UNDERWATER APPLICATIONS

H. Im[1], C. K. Kim[1]*, O. C. Kwon[2]
[1] School of Chemical Engineering and Materials Science, Seoul, Rep. of Korea
[2] Naval Technology Directorate, The 6th R&D Institute, Agency for Defense Development
* Corresponding author(ckkim@cau.ac.kr)

1. Introduction

Polyurethanes are a class of polymers that exhibit a wide range of mechanical properties. Among various polyurethanes, thermoplastic polyurethane elastomers (TPUs) are frequently used in underwater applications such as encapsulants for undersea sonar devices, electric wires, and communication lines.[1-5] TPUs used for sonar encapsulants must satisfy particularly stringent requirements. Sonar devices are dragged behind submarines or surface ships, and the encapsulant is filled with a paraffin oil to protect against the ingress of seawater. To adapt to operating conditions, TPUs used as sonar encapsulants should possess a low swelling ratio in seawater and paraffin oil and be able to withstand hydrolysis and prolonged extensional stress without significant deterioration of their properties.

TPUs prepared from methyldiphenyldiisocyanate (MDI) and polytetramethylene glycols (PTMGs) have received the most attention for use as sonar encapsulants. MDI with a symmetric molecular structure forms crystallizing hard segments and produces TPUs with higher mechanical strength and better packing ability than other isocyanates.[6-8] As compared to other types of polyols, PTMG is the most favorable material for use as a soft segment in the fabrication of TPUs since it provides outstanding mechanical stiffness and resistance to hydrolysis.[9] However, current commercially available TPUs, composed of MDI and PTMG, do not satisfy the stringent requirements for use as sonar encapsulants.[1-3] They exhibit high swelling in seawater and paraffin oil and reduced mechanical properties when immersed in these liquids over long periods.

Therefore, it is necessary to develop new materials that can address the drawbacks of TPUs. TPU composites containing inorganic fillers, such as glass fibers, aerosol particles, and clays, have been studied as sonar encapsulants.

Hollow glass microspheres (HGMs) show promise as a candidate inorganic filler for TPU composites of low density. HGMs consist of an outer stiff glass and inner inert gas, which results in some unique properties, such as light weight and low thermal conductivity. Based on these properties, HGMs have been used in preparing composites with various polymers.[9-17] HGM composites, i.e., syntactic foams, exhibited multifunctional properties, including high specific compressive strength, [13-15] high thermal stability, and low density and moisture absorption,[15-17] which makes them more suitable for applications such as aeronautical and marine structures compared to solid particle-filled composites and open cell structured foams.

Excellent interfacial adhesion between TPU and HGMs with a high level of dispersion of HGMs within the TPU matrix are required to produce TPU/HGM composites that have the desired mechanical and barrier properties, TPU/HGM composites exhibiting enhanced interfacial adhesion might be fabricated by using surface treated HGMs with proper organic materials. To date, TPU composites containing surface treated HGMs with proper organic materials have not been studied even though HGMs have often been treated with metal oxides for electronic applications.28-30 In this study, HGMs grafted with TPU (TPU-g-HGM) were prepared and then HGM composites with TPU were fabricated for underwater applications by melt mixing. The effects of TPU grafting with HGM on the morphology and mechanical and barrier properties of TPU/HGM composites were explored.

2 Experimental

The commercial grade thermoplastic polyurethane elastomers (TPUs) was (Skythane R-185A), supplied by SK Chemicals (Korea). According to the suppliers, these TPUs contain 4,4' diphenylmethane diisocyanate (MDI) as a hard segment and poly(tetramethylene glycol) (PTMG) as a soft segment. The weight average molecular weight of the PTMG used for the synthesis of Skythane R-185A (TPU-2) was 1,000 g/mole. Also, the hollow glass microsphere composed of sodium borosilicate (HGM, im30K) was obtained from 3M Corp. (USA). To prepared amino functionalized HGM, The NaOH treated HGM (5.0±0.05 g), the 3-propylaminetriethoxy silane (0.50±0.01 g), the solvent (100 ml cyclohexane) and n-propylamine (0.1±0.01 g) were stirred at room temperature for 30 min and then at 60±5 ◦C for additional 30 min at atmospheric pressure. PU grafted HGM was able to be prepared from amine terminated HGMs which can form a urea bonding in the presence of MDI. In first, 5g amine terminated HGMs were suspended in 200 ml DMF and 5g MDI was added to suspension and mixtures was stirred for 2hr at 80oC. Then, 10g PTMG with an average molecular weight of 1,000 g/mol and 1,4-buthanediol (chain extender) were added to the suspension to polymerization between MDI and PTMG. The reaction was conducted at 90 ^{o}C for 3hr. After cooling, the mixture was filtered using membrane filter which pore size is 0.4 um. And filtered cake was washed by using DMF several times to remove the residual monomer and un-grafted polyurethanes.

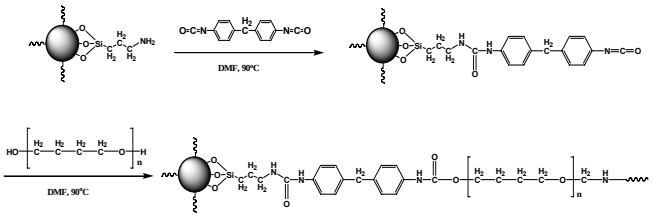

Fig.1 Chemical route for preparation of TPU-g-HGM

Specimens for tensile testing were prepared in accordance with American Standards Testing Method (ASTM) specification No. D412. Tensile tests were performed using a universal testing machine (UTM, R&B Corp, model: UTM-301, Korea) at a cross head speed of 500 mm/min. The tensile property values reported represent the averages of five specimens. The swelling ratios of the TPU and its composites with HGM were examined in seawater and paraffin oil. The specimens were cut into small pieces (length x width x thickness = 1 cm x 3 cm x 0.3 cm) and immersed into a seawater bath (or a paraffin oil bath) at 30oC. Changes in weight of the specimens were measured as a function of impregnation time. Synthetic seawater was prepared in accordance with ASTM specification No. D1141. Paraffin oil was supplied by SK Energy (grade YU-8, average molecular weight = 500 g/mol, Korea). According to the supplier, this oil is a long-chain normal paraffin that is bonded with about seven methyl side groups. Each experiment was performed at least five times, and the reported data are the means of these values. The swelling ratio (SR) was calculated using the following equation.

$$SR(\%) = \frac{100(W_t - W_o)}{W_o} \quad (1)$$

Here, W_o and W_t are the weights of the specimen before impregnation and after impregnation for a time, t, respectively.

3. Results and Discussion

3.1 FT-IR analysis

Figure. 2 shows FT-IR spectra of unmodified HGM, amine terminated HGM and polyurethane grafted

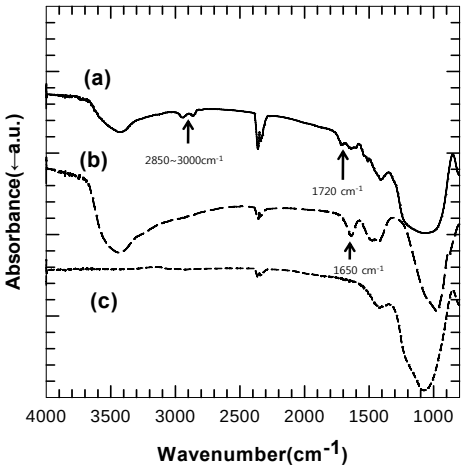

Fig.2 FT-IR spectra of various HGMs; (a) TPU-g-HGM; (b) HGM-NH2; (c) pristine HGM

HGM. The characteristic absorption bands of the any functional groups was not observed in pristine HGM except broad absorption bands which are associated with the stretching (1000~1250 cm^{-1}) of Si–O–Si as shown Figure 2. In the case of amino silane treated HGM (b), primary amine (N-H) absorption band appeared at 1650 cm^{-1}, clearly. As reaction was completed between isocyanate and diol, urethane bond containing carbony groups (C=O) was formed, and the stretching peak of carbonyl groups was observed at the 1720cm^{-1}. Also, methyl bonding (C-H) derived from PTMG used as soft segment was appeared in the 2850~3000cm^{-1} range, respectively.

3.2 ^{13}C CP/MAS NMR analysis

To confirm a surface modification of HGM by using 3-aminopropyltetrasthoxy silane, ^{13}C CP/MAS NMR was employed and the results spectra was shown in Figure 3. The spectra of amine terminated HGM showed peaks derived from the C atoms of the incorporated aminopropyl groups (1, 2, 3) were clearly observed. Also, any other peaks were not observed except aminopropyl groups. If amino silane coupling agent was not reacted with HGM surface, the carbon peaks in the ethoxy groups of coupling agent have to be observed in the spectra. However, as shown in Figure 3, the carbon resonance peaks of amino propyl groups was only observed because amino silane coupling agent was bonded with hydroxyl groups on the HGM in the presence of hydrolysis. Therefore, this result supports the conclusion that amino-moieties were successfully incorporated onto the HGMs.

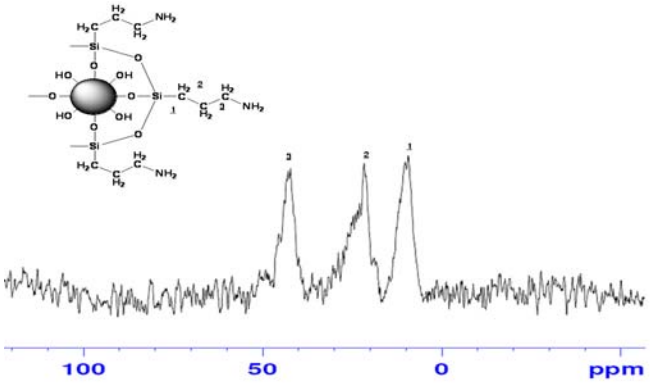

Fig3. Structure of HGM-NH_2 and its ^{13}C CP-MAS NMR spectrum

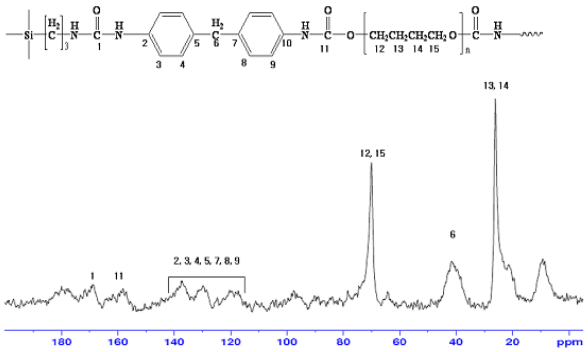

Fig4. Structure of TPU-g-HGM and its ^{13}C CP-MAS NMR spectrum.

Figure 4 shows the ^{13}C CP/MAS NMR spectra of PU-g-HGM and possible PU structures on the HGM surfaces. The spectrum of PU-g-HGM shows two strong and sharp peaks centered at 27.2 and 71.1 ppm are ascribed to the PTMG soft-segment carbons (12, 13, 14, 15). The peak at 158 ppm and 174 ppm are attributed to the resonance of urea carbon (1) and urethane carbonyl carbons adjust aromatic rings (11), respectively. The resonance at 40 ppm is ascribed to –CH_2– groups of MDI. The peak at 119 and 129 ppm are assigned to the protonated aromatic MDI carbons, while the peak at 136 ppm is associated with quaternary MDI ring carbons. These assignments are in agreement with those published values

3 SEM images

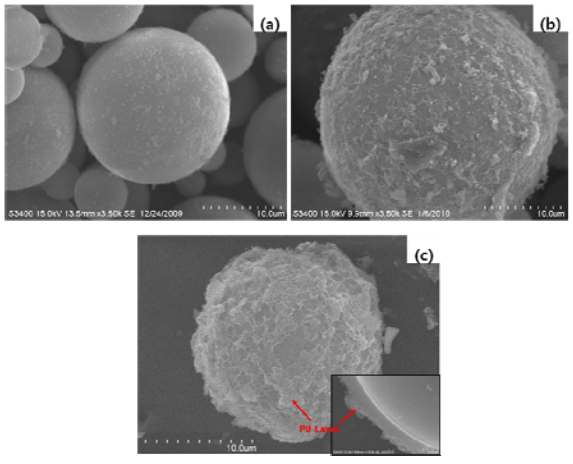

Fig5. Photomicrographs of various HGMs observed with SEM; (a) pristine HGM; (b) HGM-NH_2; (c) TPU-g-HGM

To ascertain the confirmation whether HGM have been incorporated into the polyurethane by described mechanisms during the reaction process scanning electron microscope was employed. Figure 5 shows the SEM images of pristine hollow glass microspheres(a), amine terminated hollow glass microspheres (b) and hollow glass microspheres coated with polyurethane. Figure 5(a) is the high quality individual HGM whose diameter of around 5~10um is clearly observed. The appearance of HGM, by contrast, in the Figure 5 (b) and (c), become a more thick and had a rougher surface compared with HGM in the Figure 5 (a) because of reactive silane coupling agent and polymerized polyurethane onto HGM surfaces

3.4 Effect of Surface Modification on Mechanical Pr operties

In this study, the effect of the interfacial interaction on the mechanical properties was investigated by tensile tests. Figure 6 shows the tensile stress of pure HGM, amine terminated HGM and PU grafted HGM at various elongation state. As expected, the tensile stress of composite filled with surface modified HGM were showed stronger tensile stress

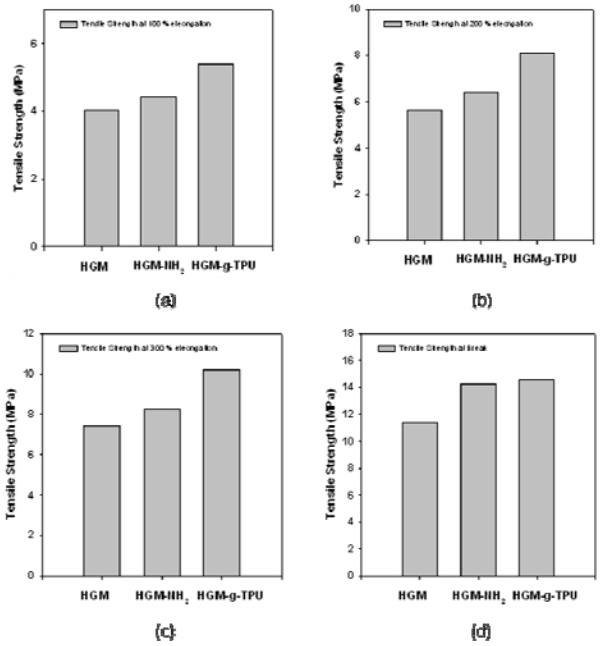

Fig.6 Tensile strengths of the TPU composites at various strain. (a) 100%, (b) 200%, (c)300% and (d) ultimate

than that of untreated HGM composite because of interfacial bonding that enables an effective stress transfer to particle, as explained above it.

Also, PU-g-HGM showed the stronger tensile stress than amine terminated HGM at the fixed HGM concentration, as shown in Figure 6. In the amine terminated HGM composite, the possible interaction forces which can lead to bonding with polymer matrix is a hydrogen bonding between urethane bonding and amine on the HGM. And that of PU-g-HGM is the compatible interaction forces originated from miscibility of PU on the HGM and matrix.

Therefore, it can be concluded that compatible interaction forces established more strong interfacial adhesion than hydrogen bonding of amine groups with urethane bonding of polymer matrix. Mechanical properties of the extruded TPU/HGM composites were investigated to examine the effect of filler concentration and surface modification.

3.5 Swelling properties

It is also necessary that the encapsulant materials have a low swelling ratio in the seawater and paraffin oil to protect the transducer from the ingress of seawater without significant deterioration of properties. Figure 7 shows the swelling ratios of the TPU composites containing various amounts of TPU-g-HGM in seawater and paraffin oil as a function of the impregnation time. The swelling ratio of TPU composite was decreased with increasing TPU-g-HGM content. Figure 8 shows the swelling ratio of the TPU composites containing 5 wt% of pristine HGM, HGM-NH_2, and TPU-g-HGM. When TPU composites contained the same amount of HGM, the swelling ratio of the TPU composites decreased in the order of TPU/HGM > TPU/HGM-NH_2 > TPU/TPU-g-HGM at equilibrium. Note that other TPU composites prepared at different HGM contents showed swelling behaviors similar to those of TPU composites containing 5 wt% of HGMs.

In summary, TPU composites satisfying stringent requirements for underwater applications could be fabricated by properly incorporating HGM surface modified with TPU.

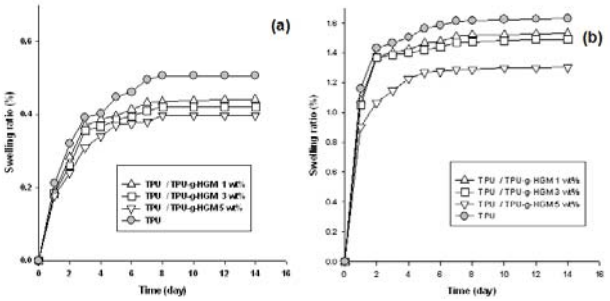

Figure7. Changes in the swelling ratios of the TPU composites containing various amounts of TPU-g-HGM as a function of the impregnation time in (a) seawater and (b) paraffin oil.

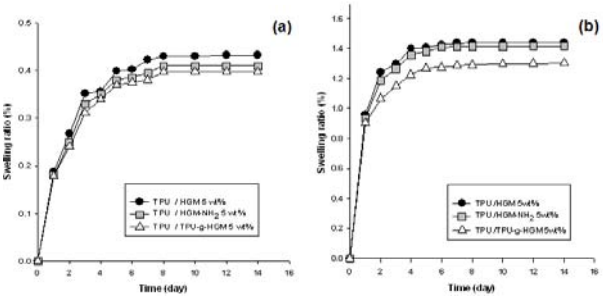

Figure8. Changes in the swelling ratios of the TPU composites containing 5 wt% of pristine TPU, TPU-NH_2, and TPU-g-HGM as a function of the impregnation time in (a) seawater and (b) paraffin oil

4. Conclusion

The hollow glass microsphere containing thermoplastic polyurethane composite was fabricated as a sonar encapsulating materials which have more enhanced mechanical properties and less water adsorption properties than pure TPU. To achieve the interfacial compatibility between TPU and HGMs, the surface of HGM was treated with 3-prorylaminetriethoxy silane. Also, PU was grafted on the HGM to investigate the effect of surface modifications. SEM images revealed the rougher surface of treated HGM than pristine HGM because of grafted PU and coupling agent.

The tensile stress of composite filled with surface modified HGM were showed stronger tensile stress than that of untreated HGM composite because of interfacial bonding that enables an effective stress transfer to particle. In the case of surface modified composite, PU-g-HGM showed the stronger tensile stress than amine terminated HGM at the fixed HGM concentration. Therefore, it can be concluded that compatible interaction forces established more strong interfacial adhesion than hydrogen bonding of amine groups with urethane bonding of polymer matrix.

In the water adsorption behaviors, surface treated HGM composite revealed the lower swelling ratio than untreated HGM composite. Also, PU-g-HGM composite showed the more reduced water absorption behaviors than amine terminated HGM composite because of reduction of void on the interface.

Therefore, it was concluded that polymer grafting surface modification method is more useful to improve mechanical and restrictive properties of water adsorption than providing of polar groups by using silane coupling agent.

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