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Glass fiber reinforced rigid polyurethane foams

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Abstract Rigid polyurethane foam (RPUF)/glass fiber composites have been fabricated from glass fiber, polymeric 4,4′-di-phenylmethane diisocyanate (PMDI) and polypropylene glycols (PPG) using HFC 365mfc as blowing agent. Thermal conductivity, glass transition and decomposition temperatures as well as the mechanical strengths of the foam increased with the addition of glass fiber. This indicates that an optimum fiber content should depend on the balance between the mechanical reinforcement and thermal insulation.The results were interpreted in terms of cell size, closed cell content, density, fiber dispersion and a simple series model for heat transfer of the composite foam.

Introduction

Polyurethanes (PUs) are used in a variety of form as coating, adhesive, elastomer, fiber and foam because their properties can be readily tailored by the variations of their components [1, 2]. Among them rigid foam (RPUF) finds numerous applications as insulations of refrigerators, freezers, piping, tanks, ship building, and LNG cargos [3, 4]. In such applications, high compression strength especially at low temperature and thermal insulation are properties of prime importance [5].

Recently, many of the conventional blowing agents such as monofluorotrichloromethane (R11) and difluorodichloromethane (R12) have been suggested to contribute to the depletion of the stratospheric ozone layer and the use has been regulated in many countries [6–8]. Consequently, the use of environmentally friendly blowing agent which reduces ozone depletion potentials (ODP) and/or global warming potential (GWP) has become an important and urgent issue in the synthesis of polyurethane foam [5, 9]. We have earlier reported the effects of hydroxyl value and functionality of polyol [10, 11], isocynate index [12], surfactant [13], and type of blowing agent [14] in the preparation of RPUF using environmentally friendly blowing agents.

There have been demands for high impact, compression, and tensile strengths for RPUF with regard to their practical applications. Addition of glass fiber to RPUF is known to improve the stiffness, strength, and the high-temperature performance [15, 16]. In this study, we added glass fiber in the form of mat to synthesize RPUF from polymeric MDI and polypropylene glycols (PPG) in a broad range of composition using a physical blowing agent, HFC 365mfc ($CF_3CH_2CF_2CH_3$) which is known to have zero ODP. The effects of glass fiber have been analyzed in terms of cell structure, density, thermal conductivity, mechanical and thermal properties of the foams.

Experimental

Raw materials

Two types of propylene oxide based polyols, HR-450P (hydroxyl value = 450, equivalent weight = 124.65)

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and HD-401 (hydroxyl value = 400, equivalent weight = 140.26), were supplied by KPX, formerly Korea Polyol (Korea). HR-450P was synthesized using sucrose and glycerin as coinitiators, whereas HD-401 used glycerin as initiator. High functional polymeric 4,4′-di-phenylmethane diisocyanate (PMDI) having functionality of 2.7 was provided by Kumho Mitsui Chemicals (Korea). HFC 365mfc as physical blowing agent was provided by Solvay Chemicals (Belgium). PC 8 (Air Products) was used as blowing catalyst. Silicon surfactant (B 8409) was provided by Goldschmidt. Polyols were dehydrated before use at 90 °C for 24 h in a vacuum oven. Vetrotex (France) as received has been used as glass fiber mat. Other chemicals were used as received.

Preparation of samples

The basic formulations to prepare the foams are given in Table 1. The foams were synthesized by one shot method [17]. That is, all materials shown in Table 1 were first put into a mixing cup and mixed thoroughly at 3000 rpm and at room temperature until they become homogeneous. The NCO index (isocyanate equivalents/polyol equivalents) was fixed at 1.10. A continuous glass fiber mat was placed in a rectangular open mold. Then, the mixtures were poured into the open mold (200 × 200 × 100 mm) and cured for 1 week at room temperature. The closed cell content was determined by an air pycnometer following ASTM D 3574 with specimen dimension, 50 × 50 × 25 mm. Density of the foam was measured according to the ASTM D 1622 with sample size of 30 × 30 × 30 mm (width × length × thickness), and average of at least five measurements was taken to report. Thermal conductivity was measured using HC-074 (Laser Comp) according to the ASTM C 518. The cell morphology was observed under a scanning electron microscopy (SEM, HITACHI S3500N). Samples were cryogenically fractured in liquid nitrogen and gold sputtered before they were scanned in the free rising direction. Thermogravimetric analysis (TGA) has been done using TGA Q50 (TA instruments). An 8–10 mg of sample was put in an alumina crucible and heated at 10 °C/min under N_2 atmosphere, where the flow rate of N_2 was 60–40 L/min [18]. Thermal properties were measured using a differential scanning calorimeter (DSC, Du Pont 9900). Samples were sealed in DSC pan using a crimping and welding press (Du Pont). The DSC thermograms were taken from 60 to 250 °C at a heating rate of 20 °C/min. Mechanical properties were measured using a Universal Testing Machine (Ametek, Lloyd) at room temperature. Compression strength was determined according to ASTM D 1621 at a crosshead speed of 3.00 mm/min with the sample dimension of 30 × 30 × 30 mm (W × L × T). Tensile tests were done following the ISO 1926 with 20 × 100 × 6 mm (W × L × T) at a crosshead speed of 2.54 mm/min [17].

Results and discussion

Density

Density is a most important parameter to control the mechanical and thermal properties of closed cell foams [18, 19]. Figure 1 shows that the foam density increases with the addition and increasing amount of glass fiber. This in part is due to the addition of high-density glass fiber, but also to the decreased size of cell and increased open cell content that follow.

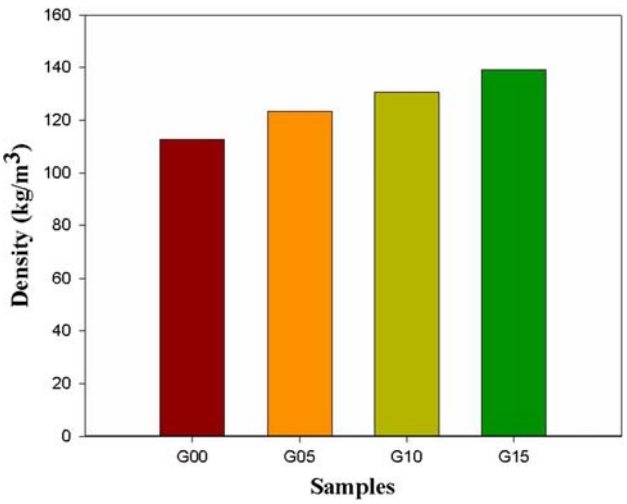

Fig. 1 Density of RPUF/glass fiber composites versus glass fiber content

Table 1 Formulations (unit: pphp)

Samples	Glass fiber mat (wt%)	HR-450P	HD-401	HFC 365mfc	B 8409	PC 8	PMDI
G00	0	80	20	12	2	0.6	114.2
G05	5						
G10	10						
G15	15						

The formulation is based on 100 parts of the polyol by weight (pphp)

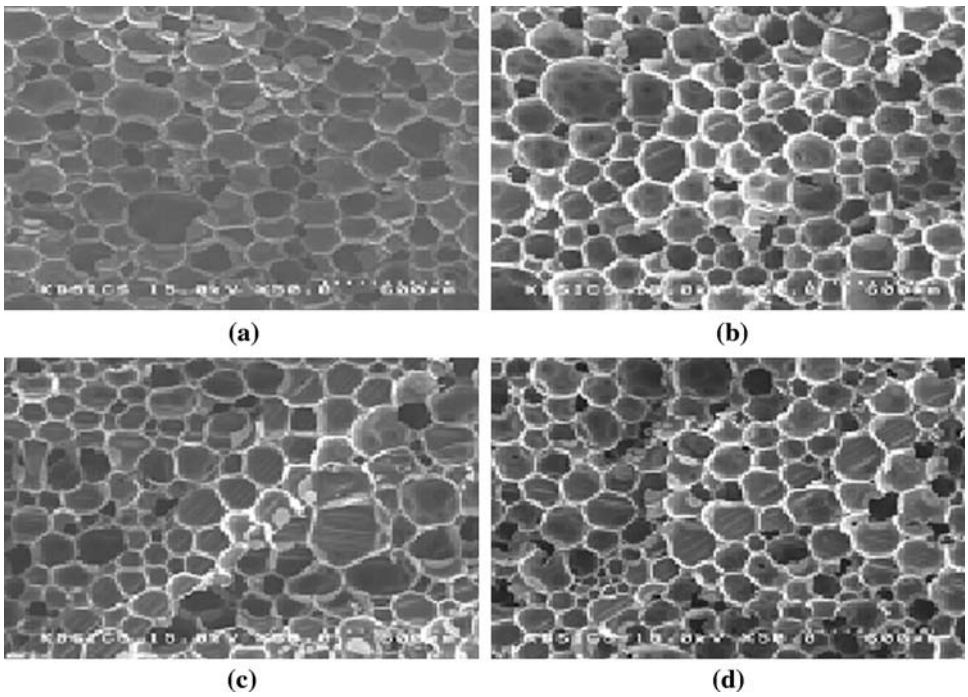

Fig. 2 SEM micrographs of RPUF/glass fiber composites versus glass fiber content. **a** 0 wt%, **b** 5 wt%, **c** 10 wt%, **d** 15 wt%

Cell morphology

Figure 2 shows the SEM morphology of the cell with their average size and closed cell content in Fig. 3. It is seen that the foams consist of spherical and polyhedral shape where the cell size generally decreases as the glass fiber content increases. The cells around the glass fiber are particularly small, indicating that cell growth is hindered by the fiber. In addition, bubble rise and growth are also physically hindered by the presence of glass fibers. The closed cell content linearly decreases with the glass fiber content. This implies that the surface of glass fiber helps cell opening as clay does [20]. This on the other hand allows uniform infusion of ingredients and thus more uniform RPUF foams of higher density. The size of cell gives significant effect on the thermal conductivity of foam. In general, smaller cells give smaller thermal conductivity since smaller ones provide the foam with more heat flow resistance for given volume [12–14]. However, when the reduction in cell size is accompanied by a significant density increase, thermal conductivity is virtually insensitive to the cell size reduction [10, 11].

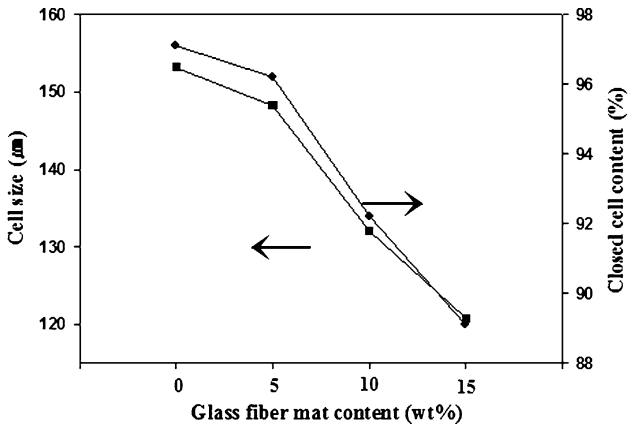

Fig. 3 Cell sizes and closed cell contents of RPUF/glass fiber composites versus glass fiber content

Mechanical properties

As the temperature goes up, gas pressure inside the cell increases, and the pressure difference relative to the atmospheric pressure becomes great. If the foam is to be dimensionally stable under these conditions, the compression strength must be greater than the pressure rise [21]. Minimum compression strength of 0.1 MPa is generally recommended for closed cell foam.

As expected, compression strength (Fig. 4), tensile modulus and strength (Fig. 5) almost linearly increase with the addition and increasing amount of glass fiber. It seems that the high modulus (78000 kg/m^2) and strength (1080 kg/m^2) of glass fiber are properly incorporated in the composite. Linear increase of the mechanical properties implies that the fibers are well dispersed in polymer matrix with sufficient interface adhesion [9]. In addition, the decrease of cell size should also contribute to the mechanical strengthening of the composite.

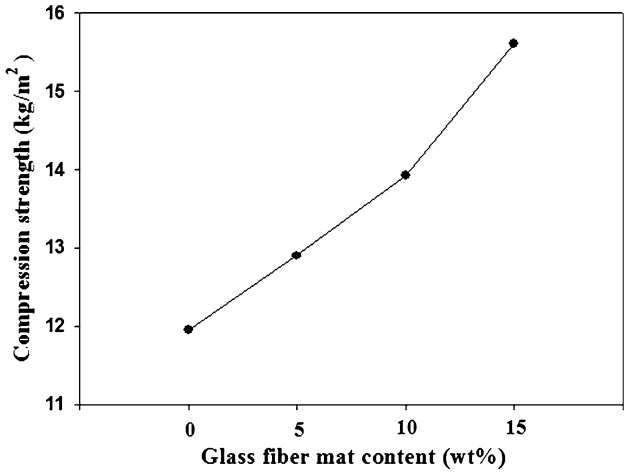

Fig. 4 Compression strength of RPUF/glass fiber composites versus glass fiber content

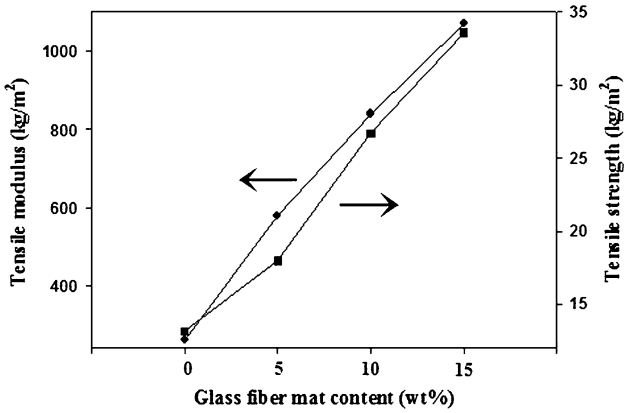

Fig. 5 Tensile modulus and strength of RPUF/glass fiber composites versus glass fiber content

Thermal insulation

Heat conduction through the closed cell foams can be approximated by a series model which is composed of polymer walls and gas cells in series [22, 23]. Conductive heat flux (q) through the composite wall is given by

$$q = \frac{\Delta T}{R} \tag{1}$$

where ΔT is the temperature drop across the foam and R is the conduction resistance given by the following equation.

$$R = \sum_{i=1}^{n} \left(\frac{X_{W,i}}{k_W} + \frac{X_{G,i}}{k_G} \right) \tag{2}$$

where $X_{W,i}$ and $X_{G,i}$ are the cell wall thickness and cell dimension and n is the number of polymer wall or cell, respectively. For uniform cells, wall thickness ($X_{W,i}$) and cell dimension ($X_{G,i}$) are constant to give

$$R = n\left(\frac{X_W}{k_W} + \frac{X_G}{k_G} \right) \tag{3}$$

In typical closed cell foam, the polymer walls occupy 3–6 vol.% of the foam. In addition, the conductivity of the polymer is much greater than that of the blowing gas. So, the first term, viz. polymer wall resistance can be neglected to give

$$R = n\left(\frac{X_G}{k_G} \right) \tag{4}$$

The above simple analysis shows that the thermal insulation of closed cell foams increase linearly with the number of closed cells, i.e., effect of insulation increases as the cell size decreases. In this regard, the decrease of cell size with the addition and increasing amount of glass fiber should lower the overall thermal conductivity of the composite.

Thermal conductivity (k) is the most important property of foam for insulation application [3]. The overall thermal conductivity of our foam increases with increasing the glass fiber content (Fig. 6). The overall thermal conductivity of the composite foam is increased due to the high thermal conductivity of glass fiber and decreased due to the decreased cell size. The former contributes to the thermal conductivity of cell wall (k_W) while the latter to the number of cell (n). Our results show that the effect of wall conductivity is more pronounced than that of cell resistance. Since the major application of RPUF is the thermal insulation, the overall conductivity increase should be considered along with the mechanical reinforcement by fiber or filler for an optimum filler loading.

Thermal properties

Figure 7 shows the DSC thermograms of the composites where the glass transition temperature (T_g) of the foam

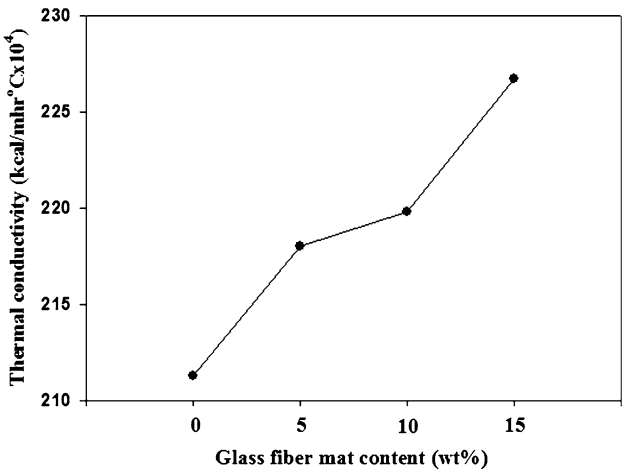

Fig. 6 Thermal conductivity of RPUF/glass fiber composites versus glass fiber content

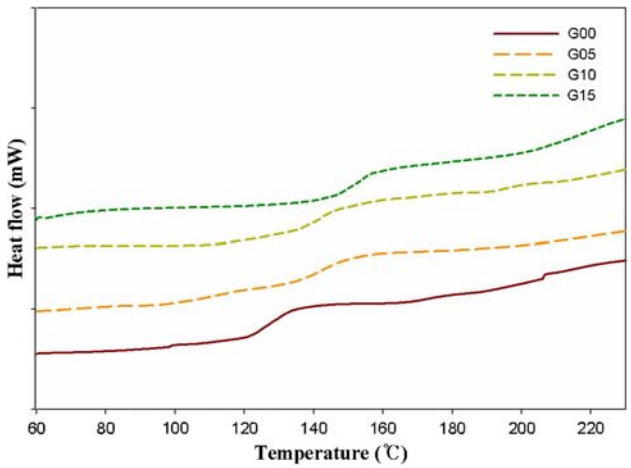

Fig. 7 DSC thermograms of RPUF/glass fiber composites versus glass fiber content

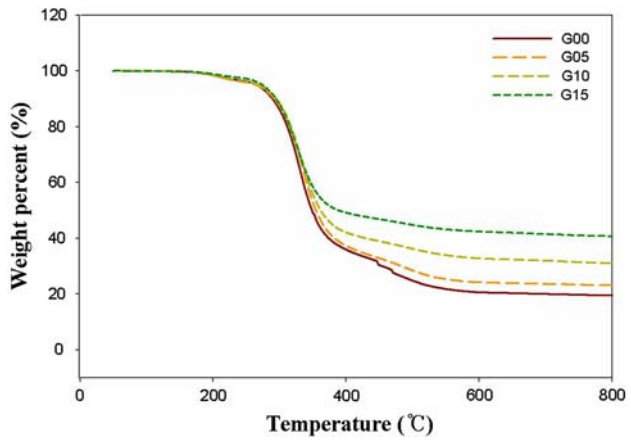

Fig. 8 TGA thermograms of RPUF/glass fiber composites versus glass fiber content

increases with the addition and increasing amount of glass fiber, and the increase is over 20 °C T_g with 15% glass fiber. This is an indication that the segmental motion of polymer is restricted by the presence of glass fibers, especially near the surface of fiber.

Figure 8 shows that the decomposition temperature of RPUF is increased with the addition of glass fiber. It can also be noticed that the final weight loss of the composites is decreased over about 20%. This beneficial effect can be explained by a decrease of the diffusion of oxygen and volatile products throughout the glass fibers.

Conclusions

Rigid polyurethane foam (RPUF)/glass fiber composites have been fabricated from glass fiber mat, polymeric MDI and polypropylene glycols (PPG) using an environmentally friendly blowing agent.

Foam density increased with the addition and increasing amount of glass fiber in accordance with the decreased cell size which is due to the decreased interface energy of the foam.

Compression strength, tensile modulus and strength increased with the addition of glass fiber implying that the glass fibers are properly incorporated into the polymer matrix. The increase was also in accordance with the increased foam density.

The increase of overall thermal conductivity with glass fiber showed that the increase of conductivity due to the high thermal conductivity of glass fiber is more pronounced than the increased thermal resistance due to the increased number of cell.

The significant increase of T_g and thermal stability of the RPUF in the presence of glass fiber imply that the chain motions of the polymer around the glass fiber and diffusion of gas are restricted by the fibers especially near the fibers.

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References

1. You M, Zhang XX, Wang JP, Wang XC (2009) J Mater Sci 44:3141. doi:10.1007/s10853-009-3418-7
2. Dweib MA, Vahlund CF, Bradaigh CM (2000) Compos A Appl Sci Manuf 31:235
3. Song B, Lu WY, Syn CJ, Chen W (2009) J Mater Sci 44(2):351. doi:10.1007/s10853-008-3105-0
4. Cao X, Lee LJ, Widya TC (2005) Polymer 46:775
5. Mondal P, Khakhar DV (2004) Macromol Symp 216:241
6. Li XB, Cao HB, Guan YT (2006) J Appl Polym Sci 102:4149
7. Antolini B, Bianchi F, Bottazzi M, Careri M, Musci M (2004) Chromatographia 60:323
8. Heintz AM, Duffy DJ, Hsu SL, Suen W, Chu W, Paul CW (2003) Macromolecules 36:2695
9. Seo WJ, Jung HC, Hyun JC, Kim WN, Lee YB, Choe KH, Kim SB (2003) J Appl Polym Sci 90:12
10. Lim H, Kim SH, Kim BK (2008) Polym Adv Tech 19:1729
11. Lim H, Kim SH, Kim BK (2008) J Appl Polym Sci 110:49
12. Lim H, Kim SH, Kim BK (2008) Macromol Res 16:467
13. Lim H, Kim SH, Kim BK (2008) Express Polym Lett 2:194
14. Kim SH, Lim H, Song JC, Kim BK (2008) J Macromol Sci P&AC 45:1
15. Karger-Kocsis J, Harmia T, Czigany T (1995) Compos Sci Technol 54:287
16. Wilberforce S, Hashemi S (2009) J Mater Sci 44(5):1333. doi:10.1007/s10853-008-3233-6
17. Seo WJ, Park JH, Sung YT, Hwang DH, Kim WN, Lee HS (2004) J Appl Polym Sci 93:2334
18. Xu Z, Tang X, Gu A, Fang Z (2007) J Appl Polym Sci 106:439
19. Oertel G (2004) Polyurethane handbook. Gardner Publications, New York

20. Harikrishnana G, Umasankar Patroa T, Khakhar DV (2007) Carbon 45(3):531
21. Szycher M (1999) Szycher's handbook of polyurethanes. CRC Press, New York
22. Bird RB, Stewart WE, Lightfoot EN (2006) Transport phenomena. Wiley, New York
23. Wang M, Pan N (2008) Int J Heat Mass Transf 51:1325