Strengthening and toughening mechanisms for polypropylene/glass fiber composite foams under three-phase coexistence[*)]

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Abstract: Composite foams were obtained through a two-step molding process in an injection molding machine. Gas phase was introduced into the mixture of molten polypropylene (PP) and solid glass fiber (GF). The interfacial behavior was investigated, and the strengthening and toughening mechanisms for PP/GF composites under three-phase coexistence were discussed. The incorporation of gas phase significantly increased the tensile strength by 112 % and impact toughness by 105 % in comparison to its unfoamed counterpart. The resulting mechanical properties of the PP/GF composite foams were found to depend considerably on the coexistence state of solid (GF) and gas (cells) phases and the cell structure of the foams.

Keywords: polypropylene, composite, foam, mechanical properties.

Mechanizmy wzmacniające i utwardzające pianki kompozytowe polipropylen/włókno szklane w warunkach współistnienia trzech faz

Streszczenie: Pianki kompozytowe otrzymano w dwustopniowym procesie formowania wtryskowego. Fazę gazową wprowadzano do mieszaniny stopionego polipropylenu (PP) ze stałymi włóknami szklanymi (GF). Badano właściwości mechaniczne otrzymanych pianek PP/GF oraz omówiono mechanizmy powodujące wzmacnianie i utwardzanie tych pianek w warunkach współistnienia trzech faz. Zaobserwowano, że wprowadzenie fazy gazowej znacznie zwiększa wytrzymałość na rozciąganie (o 112 %) i udarność pianki (o 105 %) w porównaniu z wartościami otrzymanymi w przypadku jej niespienionego odpowiednika. Stwierdzono, że właściwości mechaniczne pianek kompozytowych PP/GF w znacznym stopniu zależą od stanu współistnienia fazy stałej (GF) i gazowej (pory) oraz struktury komórkowej pianki.

Słowa kluczowe: polipropylen, kompozyt, pianka, właściwości mechaniczne.

Over the past several decades, the strengthening and toughening mechanisms of polymer composites have been consistently reported, and some relatively mature theories have been developed within the field [1—3]. Generally, when gas phase is introduced into polymer composites filled with solid fillers, producing the so-called microcellular foams, gas diffuses along the solid-melt interface. The poor compatibility between melt and solid phases thereby reduces the strengthening effect of fillers. When cells are formed in the composite, the cell size and cell size distribution have significant impact on the strengthening effect. It is thus vital to assess how the gas phase affects the structure of polymeric composite foams and their resulting properties.

Matuana *et al.* [4] reported the mechanical properties of microcellular foamed PVC/wood-fiber composites. Their results indicated that the tensile and impact properties of microcellular foamed PVC/wood-fiber composites were most sensitive to changes in the cell morphology and the surface modification of fibers. Doroudiani *et al.* [5, 6] reported the relationship between the relative tensile strength and cell size of polystyrene (PS) foams. It was found that the tensile strength was determined by the foam density and only slightly affected by the cell size. The transition of plane stress conditions to plane strain conditions was considered as a source of toughening of PS foams. However, these above mentioned foamed composite materials have shown only moderate enhancements in the tensile strength and impact toughness.

The main focus of this study is the effect of surface modification of glass fiber (GF) and cell structure on the mechanical properties of polypropylene (PP) composite

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foams. Microcellular PP composite foams were fabricated by a two-step injection molding process [7—10]. The interfacial behavior and solid phase strengthening mechanism under three-phase coexistence were discussed in detail. Significant improvements of the tensile strength and impact toughness were achieved by surface modification of GF and control of foam structure. This is of great significance for understanding of the strengthening and toughening mechanisms and broadening of the industrial application of PP composite foams.

EXPERIMENTAL PART

Materials

Polypropylene T30S, a commercial product from Sinopec, was selected for this study. Glass fibers (GF with length to diameter ratio = 11/1) was purchased from PPG Fiber Glass. As a cell-nucleating agent was used commercially available nano-SiO_2. Silane coupling agent (KH-5710) was used for surface modification of GF. The commercial maleic anhydride grafted polypropylene (MA-PP) was used as received as a compatibilizer.

Preparation of PP/GF composites

Foaming masterbatch and assistant masterbatch were prepared in a twin-screw extruder, following the procedure described in our previous reports [7—9]. In this study, PP/GF composites with various weight ratios were prepared. Firstly, MA-PP was blended with PP and the weight ratio of PP/MA-PP was 95:5. Then, 5 wt % of the nano-SiO_2 was mixed with PP in a twin-screw extruder.

Preparation of microcellular PP/GF composite foams

According to ISO 3167:2002, foamed bars for standard tensile test were molded through a two-step molding process in an injection molding machine. PP/GF composites were firstly melted and blended with the masterbatches of chemical blowing agent CBA and additive with the weight ratio of PP composite/CBA masterbatch/additive masterbatch equal to 85/10/5. The prepared mixture was then injected into the mold cavity at the melting temperature of 170 °C, and injection pressure of 45 MPa was applied by the injection molding machine.

Methods of testing

Scanning electron microscope (SEM) was used to examine the foam morphology. The samples were dipped in liquid nitrogen and then fractured to expose their cellular surfaces which were coated with gold before the characterization of foam structure. The SEM images of foamed samples were analyzed with Image-Pro Plus software (Media Cybernetic), which can quantify the area and number of cells in the SEM images and then calculate the average cell size. For each sample, at least 100 cells in the SEM micrographs were used to evaluate the mean cell size and size distribution. Average cell size ($\overline{D}$) can be calculated according to equation [11—13]:

$$\overline{D} = \frac{1}{n}\sum_{i}^{n} D_i \tag{1}$$

where: n — the number of counted cells, D_i — the single cell diameter.

Tensile strengths were determined according to Chinese standard GB/T1040.1-2006 using a tensile test machine Instron 8510. Tests were performed at 24 °C with a constant crosshead speed of 50 mm/min. Impact tests were conducted according to Chinese standard GB/T1843-2008 at 24 °C on foam samples with different cell sizes using a drop-weight impact test machine.

RESULTS AND DISCUSSION

Effects of the surface modification of GF on the mechanical properties of the microcellular foamed PP/GF composites

The influence of pristine and modified GF content on tensile and impact strengths of the microcellular foamed PP/GF composites is shown in Fig. 1. For both samples,

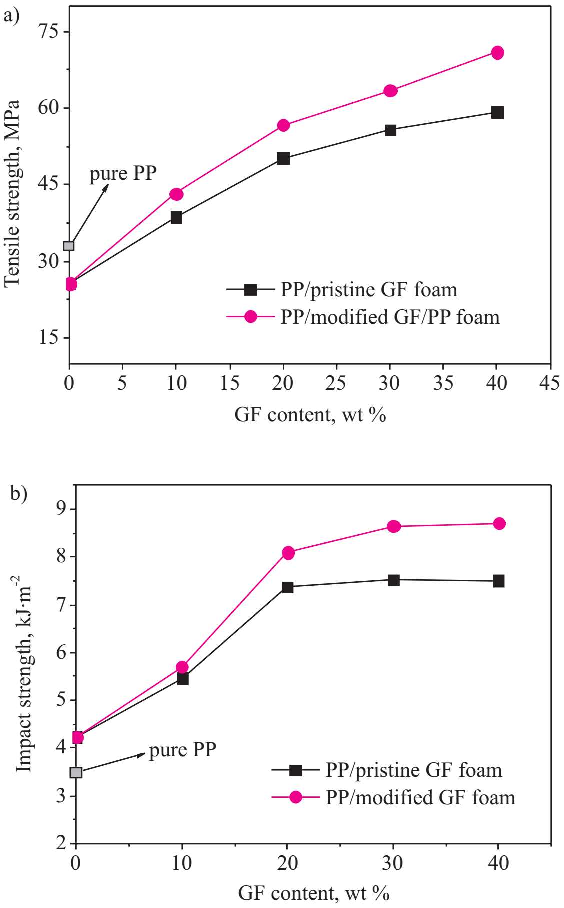

Fig. 1. The influence of pristine and modified GF content in microcellular foamed PP/GF composites on: a) tensile strength, b) impact strength

the tensile and impact strengths increased gradually with the increasing GF content. In comparison with solid pure PP, the microcellular foamed PP/modified GF composite achieved the increase by 112 and 105 %, respectively in tensile and impact strengths, which can be mainly attributed to the effects of GF. With the same GF content, the mechanical properties of the sample with modified GF were better than those of the sample with pristine GF, owing to the difference in interfacial bonding between PP and GF.

Structure of PP/GF composites under three-phase coexistence

The introduction of gas phase into the composites affected the mechanical properties due to the change in the composites structure. The SEM images of foamed PP/GF composites are presented in Fig. 2. It was found that the modified GF exhibited better interfacial compatibility with PP than the pristine GF. No significant difference was observed in the foam structures for the composites with pristine or modified GF. The increased GF content did not appear to significantly change the cell structure of the composite foams. The average cell size was around 60 μm with a broad size distribution.

SEM micrographs of foamed PP composites are shown in Fig. 3. In the PP/pristine GF composite foams, the GF seemed to penetrate through the cells (Fig. 3a), thus negating the stress transfer between GF and PP matrix. Moreover, the gas diffusion along the interface between GF and PP matrix could further reduce the strengthening effect of GF. On the contrary, in the PP/modified GF composite foams, cells were often seen around the GF or in the PP matrix, which did not affect the stress transfer between GF and PP matrix (Fig. 3b). Therefore, the foamed PP/modified GF composites exhibited better mechanical properties than the foamed PP/pristine GF composites with the same GF contents. A gas diffusion model was built to analyze how the interfacial behavior would affect the structure of PP/GF composite foams. As illustrated in Fig. 3c and 3d, the gas diffusion courses were quite different for the two composite systems, displayed by the black lines. In the PP/pristine GF composite foams, the gas preferred to diffuse along the interface between GF and PP matrix owing to the weak interfacial bonding between them, thus forming the cells with segmental GF in them (Fig. 3a). In the case of PP/modified GF composite foams, the gas diffused along intermolecular gaps between polymer chains and thus the cells nucleated and grew mainly in the PP matrix (Fig. 3b).

Relationship between the mechanical properties and composite foam structure

As a cell-nucleating agent, nano-SiO_2 particles were added into the composites to improve the foam quality

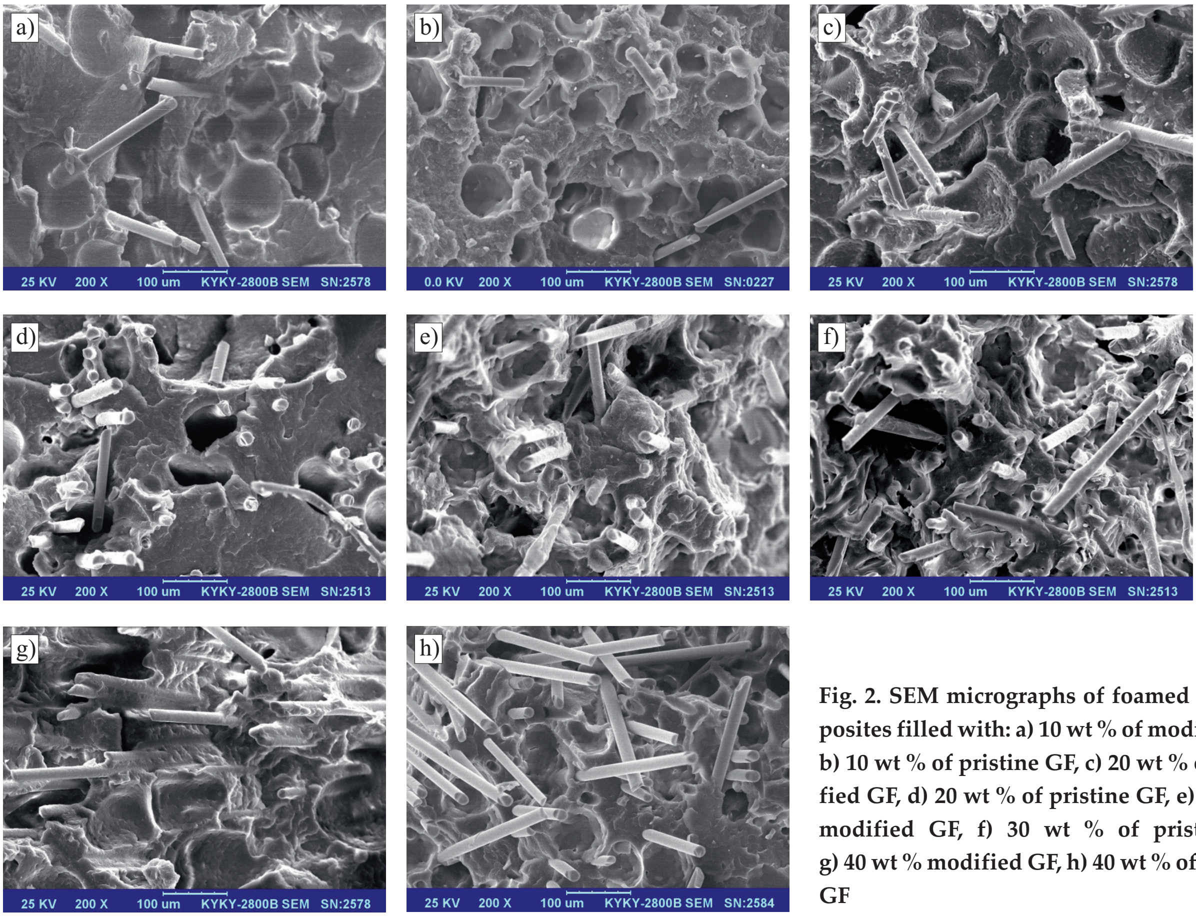

Fig. 2. SEM micrographs of foamed PP composites filled with: a) 10 wt % of modified GF, b) 10 wt % of pristine GF, c) 20 wt % of modified GF, d) 20 wt % of pristine GF, e) 30 wt % modified GF, f) 30 wt % of pristine GF, g) 40 wt % modified GF, h) 40 wt % of pristine GF

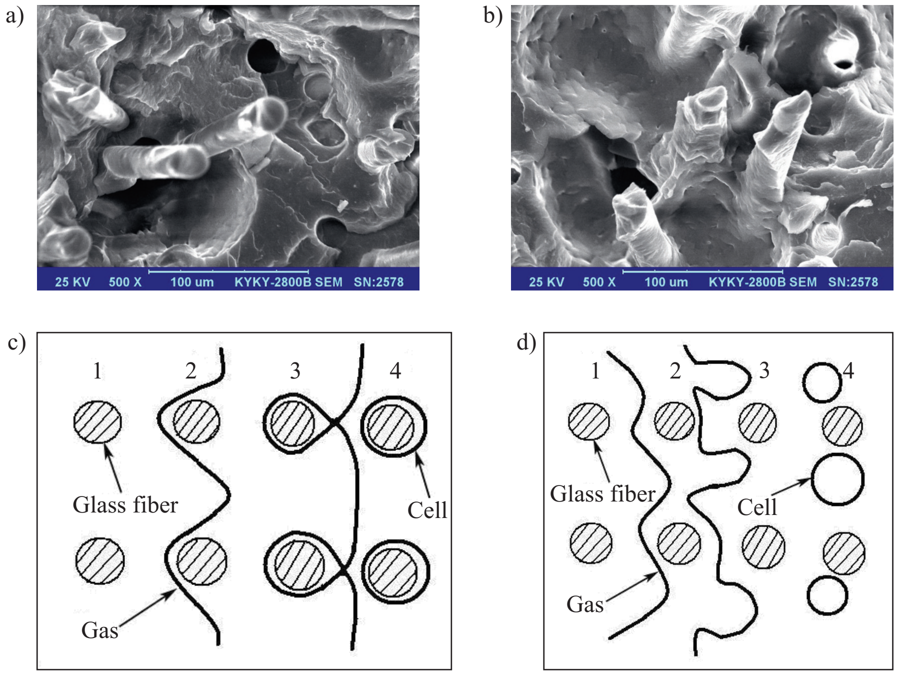

Fig. 3. SEM images of foamed PP composites filled with: a) pristine GF, b) modified GF, c) schematic diagrams of gas diffusion in the PP/pristine GF, d) PP/modified GF composites

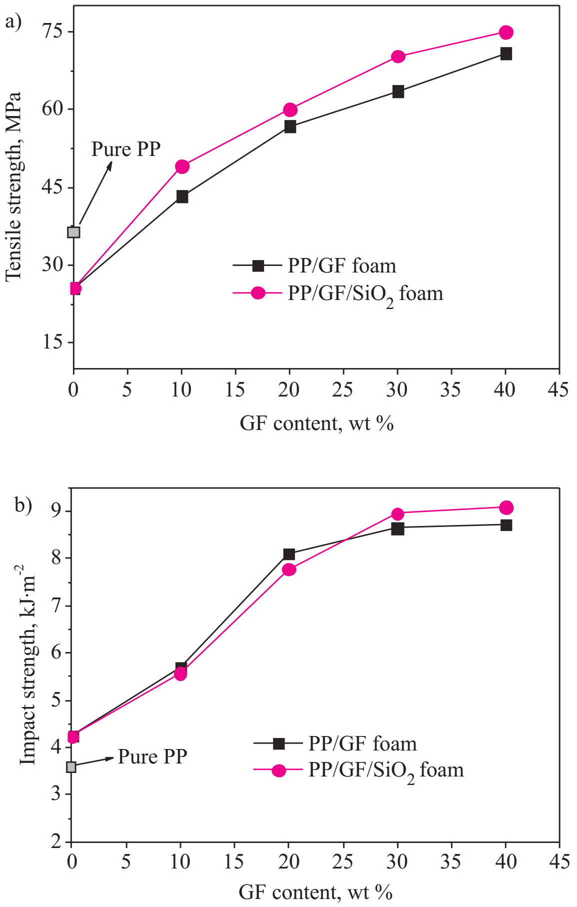

Fig. 4. Effect of the foam structure of microcellular PP/GF composite on: a) tensile strength, b) impact strength

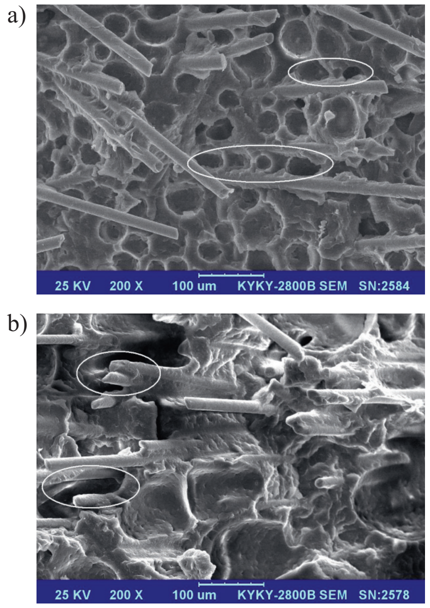

Fig. 5. SEM micrographs of the foam structure for: a) PP/GF/SiO$_2$, b) PP/GF

and assess the effect of the composite foam structure on the mechanical properties. The relationship between the mechanical properties of PP/GF/SiO$_2$ composites and the GF content is shown in Fig. 4. It can be seen that the tensile and impact strengths of the PP/GF/SiO$_2$ composite foams increased gradually with the GF content. Both strengths were superior to those of the PP/GF composite foams with the same GF content. Specifically, a 26 % of increment in tensile strength was observed for the PP/GF/SiO$_2$ composite foams at the GF content of 30 wt % when compared with that of the PP/GF composite foams. This may be attributed to the finer cells of the PP/GF/SiO$_2$ composite foams.

The fracture morphology of the PP/GF and PP/GF/SiO_2 composite foams is presented in Fig. 5. It can be seen that the nano-SiO_2 particles provided preferred heterogeneous nucleation sites and contributed to a sharp decrease in cell size and a much narrower cell size distribution for the PP/GF/SiO_2 composite foams. The fine and uniform cell structure helped to avoid stress concentration and thus improved the ability of the composite foams to withstand deformation when subjected to stress [14, 15]. It can be deduced that the resulting mechanical properties of the PP/GF composite foams depend considerably on the coexistence state of solid (GF) and gas (cells) phases and the cell structure of the foams.

CONCLUSIONS

In comparison with solid pure PP, the microcellular foamed PP/modified GF composites achieved the increase by 112 and 105 %, respectively, in tensile strength and impact strength, which can be mainly attributed to the effects of GF. The foamed PP/modified GF composites exhibited better mechanical properties than the foamed PP/pristine GF composites at the same GF contents, owing to the enhanced interfacial bonding between PP and GF. With the nano-SiO_2 particles, the fine and uniform cell structure was obtained which helped to avoid stress concentration and thus improved the ability of the composite foams to withstand deformation when subjected to stress. The resulting mechanical properties of the PP/GF composite foams were found to depend considerably on the coexistence state of solid (GF) and gas (cells) phases and the cell structure of the foams.

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