



Thermoplastics reinforced by self-welded glass fibers: Effect of interfacial affinity on preferential segregation

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ABSTRACT

The aim of this study is to clarify the effect of relative interfacial affinity on the formation of glass fiber–polyamide 6 (GF–PA6) networks in different polymer matrices. The fiber–polymer interaction was estimated by the contact angle of the *in situ* formed micro-drops on the GF surface and by the interfacial shear strength (IFSS) between the glass fiber and the polymer. The self-welded GF–PA6 network in the ternary composites was examined via the scanning electron microscopy (SEM) and dynamic mechanical analysis. It was found that a relatively high interfacial affinity between GF and PA6 (a positive ΔW_A^*) is essential for the preferential adsorption of PA6 on the GF surface. However, the encapsulation ratio, N_{PA6} , a parameter for the percentage of the PA6 phase that encapsulates the fiber, depends on the interfacial tension between PA6 and the polymer matrix. A simplified theoretical analysis elucidated that a lower interfacial tension between PA6 and the polymer matrix is effective to minimize the total free energy in the ternary system by increasing N_{PA6} for the construction of a stronger GF–PA6 network throughout the polymer. Polymer viscosity affects the kinetic process of the preferential segregation and the PA6 domain size, which is another factor that causes the variation in N_{PA6} .

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1. Introduction

The incorporation of an inorganic fiber improves the stiffness, strength, and high-temperature performance of thermoplastic materials [1–4]. The addition of a second polymer in fiber-reinforced thermoplastics may result in the formation of an effective continuous reinforcing network. In this network, the second polymer component bridges the fibers, thereby enhancing the properties of the final products. For example, a very low percolation threshold was achieved by blending a small amount of polyethylene (PE) to the poly(methyl methacrylate) (PMMA)/vapor-grown carbon fiber (VGCF) composite because of the formation of a self-assembled VGCF–PE network in the PMMA matrix [5,6]. Malchev et al. [7] reported that the addition of a minor phase [polyamide 6 (PA6)] to the PE/glass fiber (GF) composite could improve the elasticity modulus in the high temperature region (above the melting point of the PE matrix). They ascribed this occurrence to the formation of a fiber network (GF–PA6) within the PE matrix.

The effect of viscosity ratio, mixing time, and thermal treatment on the preferential encapsulation of polymers on the GF surface and the mechanical property of ternary polystyrene (PS)/PA6/GF

composites were investigated [8]. Many short GFs are “self-welded” together by the minor PA6 phase, and a continuous GF–PA6 network is formed throughout the PS matrix. As a result, the elastic modulus is markedly enhanced over a wide temperature region from T_g of PS to T_m of PA6. Moreover, the heat distortion temperature of the composites significantly increases up to 201 °C. The bulk strength of the GF–PA6 network depends on the encapsulation ratio, N_{PA6} , which corresponds to the percentage of the PA6 phase that encapsulates the fibers. As the mixing time increases, N_{PA6} gradually increases and remains constant thereafter. The PA6 with a lower viscosity shows a rapid increase in N_{PA6} , but a large difference in viscosity between PA6 and PS results in a high saturating value. A marked increase in N_{PA6} was noted for the samples after isothermal post-treatments. Based on these results, the formation of the GF–PA6 networks is kinetic. Moreover, the strength of the GF–PA6 networks is kinetically determined by the preferential segregation of these PA6 domains to the junction point of fibers because of the driving force of capillarity.

The aim of this study is to clarify the effect of interfacial affinity on the formation of the self-welded GF network. Four kinds of polymers with different polarities were used as polymer matrices. PA6-compatible and unsized GFs were used as reinforcements. To emphasize the competitive encapsulation of GF by the polymer components, an unfavorable mixing procedure was performed to prepare the ternary composites, i.e., GF was pre-impregnated with the polymer matrix and the minor phase, PA6, was then added.

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Thus, the preferential segregation of PA6 on GF only occurs when the polymer matrix is depletable from the GF surface. The fiber–polymer interaction was estimated by the contact angle of the *in situ* formed micro-beads on the GF surface and by the ultimate interfacial shear strength between GF and the polymers. Theoretical prediction was also performed using the difference in the work of adhesion between GF and the polymers. The correlation between the interfacial affinity and the strength of GF–PA6 networks was investigated.

2. Experimental

2.1. Sample preparation

The materials used in this study are described in Table 1. Acrylonitrile–butadiene–styrene (ABS), polystyrene (PS), polypropylene (PP), and polyethylene (PE) were used as the matrices and PA6 as the minor phase. The short GF was surface-treated using a silane coupling agent (γ -aminopropyltriethoxysilane, γ -APS) for better compatibility with PA6, which was denoted as “ γ -APS treated GF”. The thermogravimetric test result showed that the treated GF had approximately 0.5 wt% of the silane coupling agent on the surface. For comparison, an untreated GF obtained by burning off the original form in a furnace for 30 min at 500 °C was also used, which was denoted as “unsized GF”. The short glass fiber used in this work was 3.2 mm in length and 10 μ m in diameter.

All components were vacuum-dried prior to compounding at 80 °C for approximately 24 h. First, the matrix was blended in a Haake Rheomixer (Rheotress 600, Haake) at 240 °C and 60 rpm for 3 min, and GF was then added and mixed for 2 min. Finally, PA6 was added and mixed for another 10 min. The binary polymer blends (80/20) were mixed at the same conditions for 10 min. The mixtures were quenched in cool water. The weight fraction of all ternary composites was set at 49/12/39. The Irganox 1076 FD antioxidant (0.3 phr) obtained from Ciba–Geigy was added to all formulations. The mixtures were dried for another 24 h for various measurement determinations.

The polymer drops were formed *in situ* on GF in the polymer solutions for contact angle measurement to estimate the fiber–polymer interaction. The polymers were dissolved in their corresponding solvents in Table 1 to form 5 wt% solutions. The operating temperatures of the PP and PE solutions were 100 °C and 150 °C, respectively, and the others were performed at 20 °C. The surface-treated glass filament was then dipped into the polymer solutions for 3 h. Finally, GF was annealed at 240 °C for 10 min.

2.2. Characterization

The viscosity of the materials was determined using a rheometer (RS600, Thermo Hakke) at 240 °C in a plate–plate configuration with a 25 mm plate diameter and a 1 mm setting gap.

Scanning electron microscopy (SEM) (JEOL JSM-6360) was performed to observe the morphology of the GF–PA6 network at an accelerating voltage of 15 kV. The specimens of the ternary composites were polished, and then etched with the corresponding solvents to dissolve the matrix. The etched surface was then coated with gold.

The microbond pull-out technique was carried out using a pull-out apparatus which allows high-precision fiber displacement, force measurements, and data management. GF was embedded in the polymers melts and then annealed at 240 °C for 10 min. Before the test, each specimen was observed using an optical microscope (OM) to determine the geometry of the specimen, namely, the fiber diameter, microdrop diameter, and bond length, and to confirm that the drop was symmetrical and without defects. The pull-out test was performed at a crosshead displacement rate of 1.2×10^{-2} mm/min, as shown in Fig. 1. Approximately 15–20 separate tests were performed for each GF–polymer combination. From each force–displacement curve, the debonding force, F , the embedded fiber length, l , and the fiber radius, r , were determined and the interfacial shear strength (IFSS), τ_{app} , can be calculated as follows [10]:

$$\tau_{app} = \frac{F}{2\pi rl} \quad (1)$$

Dynamic mechanical analysis was performed using Rheogel-E-4000 (UBM, Japan) in a stretching mode. The dynamic storage and loss modulus were determined at a frequency of 10 Hz and a heating rate of 5 °C/min in a temperature region of 50 °C–220 °C. The storage modulus was monitored by small oscillations with an amplitude of 0.01%. The compounded mixtures were polished into a size of 30 mm \times 3 mm \times 1 mm as specimens for the DMA tests. Two separate determinations were carried out to check the variation between specimens. The heat distortion temperature of the composites was determined according to ASTM D648 at a bending stress of 0.46 MPa by using the samples after compression molding at 240 °C and 10 MPa for 10 min.

3. Results and discussion

3.1. Contact angle between GF and polymers

From a thermodynamic viewpoint, the fiber–polymer interaction is specified by the reversible work of adhesion, W_A , to break a unit area of an adhesive contact. This interaction is defined in terms of surface free energies. For the practical determination of the surface free energy, techniques based on the wetting of solid surfaces by liquids are commonly used. The work of adhesion is determined by this approach from the Dupré–Young equation [11]:

$$W_A = \gamma_L(1 + \cos \theta) \quad (2)$$

Table 1
Materials used in the study.

Materials designation	Source	Grade name	E' (GPa) ^a	α ($\times 10^{-5}/K$) ^b	Solvent	Solubility parameter ($J^{1/2} cm^{-3/2}$) ^c
PA6	Mitsubishi Engineering-Plastic	1020J	2.5	11	Formic acid	20.72
ABS	Ningbo Yongxing Chemical	HI-140	2.1	12	Tetrahydrofuran	17.98
PS	Shanghai Secco petrochemical	251	3.2	8	Toluene	23.41
PP	Yanshan Petrochemical	K8303	1.3	13	Xylene	18.09
PE	Honam Petrochemical	2200J	1.9	10	Decalin	16.26
GF	PPG	3540	72	0.5	–	–

^a The storage modulus, E' , was measured at 20 °C at a frequency of 10 Hz.

^b α is the coefficient of linear thermal expansion.

^c The solubility parameter of polymers, data from Ref. [9].

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