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Manufacturing and physical properties of all-polyamide composites

Ying Gong · Guisheng Yang

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Abstract Based on the difference in melting points between polyamide 66 (PA66) fiber and polyamide 6 (PA6) matrix, all-polyamide composites were fabricated under various processing conditions. In these all-polyamide composites, the reinforcement and matrix share the same molecular structure unit (–CONH–$(CH_2)_5$–). Because of the chemical similarity of the two components, good bonding at the fiber/matrix interface could be expected. Effects of processing temperature and cooling rate on the structure and physical properties of composites were investigated by SEM, DMA, DSC analyses, and static tensile test. Fiber/matrix interface strength benefited from elevated processing temperature. The static tensile results showed that the maximum of tensile strength was observed in the processing temperature range of 225–245 °C. At different cooling rates, crystallization temperature of PA6 in the composites was increased compared to the pure PA6 because of the nucleation effect of PA66 fiber surface to the PA6 matrix. A study of the matrix microstructure in a single fiber-polymer composite gave proof of the transcrystalline growth at the fiber–matrix interface, the reason behind which was the similar chemical compositions and lattice structures between PA6 and PA66.

Y. Gong
Joint Laboratory of Polymer Science and Technology, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

G. Yang (✉)
Shanghai Genius Advanced Materials Co. Ltd, Shanghai 201109, China
e-mail: ygs20082008@gmail.com

Introduction

It is difficult for traditional fibers (such as glass or carbon fibers) reinforced polymer composites to satisfy the increasingly stringent environmental requirements because of the different composition between the fiber and the matrix. With the development of polymer fiber industry, there is a considerable incentive to explore the possibilities that high-performance polymer fiber can be used to reinforce the polymer matrix of identical or similar composition. This new kind of composites can be recycled after having been fully melted. A strong interface can be naturally produced since the reinforcement and matrix are of identical chemistry [1]. To make use of high-performance polyolefin fibers, research had mainly focused on the study of polyolefin fiber (polypropylene [2–8] and polyethylene [9–12]) reinforced polyolefin composites. Besides, other polymer fibers, including polyethylene terephthalate [13, 14], polymethyl methacrylate [15, 16], cellulose [17], and so on were also used to prepare the all-polymer composites.

Polyamide (PA) is a well-known high-performance engineering plastic with high strength and good fatigue resistance. Because of its good wearing durability, PA fiber is widely applied in the clothing industry. In the family of PA fibers, PA66 fiber possesses relatively better mechanical properties and is applied in the production of tire, air-bag, bullet-proof vest [18], and so on. Hine and Ward [19] used only PA66 fiber to successfully make a novel high fiber volume fraction polymer/polymer composites by a hot compaction process. During the hot compaction, the fiber surface was partly melted to form the matrix at precise temperature which resulted in the low temperature window.

In the present study, all-polyamide composites were manufactured firstly by a method of film stacking [20, 21]. PA66 plain weave was used as the reinforcement phase and

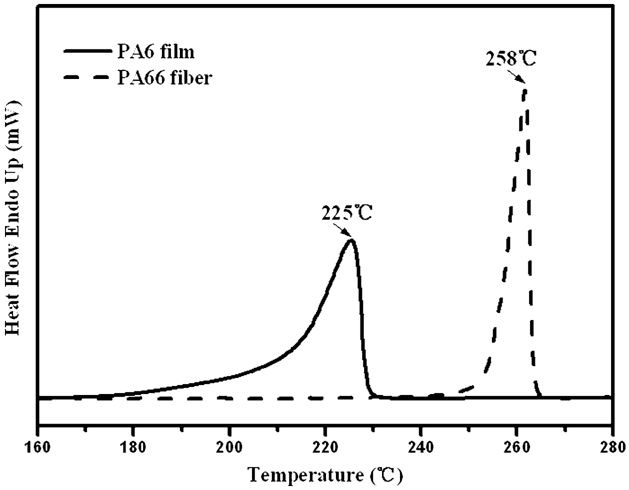

Fig. 1 Comparison in melting behaviors of PA66 fiber and pure PA6 film

PA6 as the matrix. Plain weave of PA66 was selected to balance the properties in both warp and weft directions of the final composites. The difference in the melting points of PA66 and PA6 (see Fig. 1) was essential for the successful preparation of the composites and guaranteed a wide temperature processing window. At a proper temperature (higher than the melting point of PA6 matrix and lower than that of PA66 fiber) PA6 film was melt to impregnate the PA66 fiber and crystallized to form the matrix after cooling. A stable and strong fiber/matrix bonding could be obtained because PA66 and PA6 are closely related from both chemical and physical standpoints [22]. The majority of this work was concentrated on studying the influence of the process conditions (processing temperature and cooling rate) on the structure and properties of composites.

Experimental

Materials

Pure PA6 pellets ($\bar{M}_n \approx 30000$, product code:YH-800) was purchased from Hunan Yueyang Baling petrochemical Co. Ltd. PA66 plain weave (40D 270T) was supplied by Shanghai Sanchuan Printing and Dyeing Co. The tensile strength and modulus of the PA66 fiber were 523 MPa and 9.3 GPa, respectively. To remove the sizing agent, PA66 fabric was washed by acetone for 24 h. After vacuum drying (50 °C, 24 h) PA66 cloth and PA6 pellets were both stored in a desiccator for later experiments.

Preparation of PA6 film

PA6 pellets were placed between two stainless steel plates in a hot press machine. The temperature of the hot press was set to 250 °C. At the initial stage, PA6 pellets were fully melted under a contact pressure for 5 min. Then a pressure of 5 MPa was applied to compress the melt into a film. After keeping the pressure for 5 min, the steel plates were removed from the hot press and cooled to the room temperature in the air to get the PA6 film, the size of which was 200 × 200 × 0.1 mm^3.

Preparation of all-polyamide composites

The prepared PA6 films and 10 layers of PA66 plain weave were plied together in sequence between two steel plates in the hot press. Proper processing temperature was needed to assure the fully melting of PA6 film and original high-orientation of PA66 fiber. Therefore, the hot press temperature was selected as 225, 235, and 245 °C, respectively, which were between the melting peaks of PA66 fiber and PA6 film (see Fig. 1). After some preliminary experiments, a pressure of 5 MPa was chosen and kept constant for all processing temperatures. This pressure forced the melting PA6 to impregnate the fabric and drove the redundant PA6 to flow out of the fabric and carry away air pockets. In addition, PA66 fiber was kept from relaxation by this pressure and the high orientation of fiber was then maintained, which preserved the original stiffness of PA66 fiber. After soaking the plates in the processing temperature for 30 min, the heating power was switched off and the whole system cooled slowly in the hot press machine. In this process, the pressure of 5 MPa was kept constant always. When the ambient temperature was achieved, the composites were removed out from the press.

Preparation of single fiber-polymer composites

Single PA66 fiber was stretched and two ends were fixed on a glass slide. PA6 film was plied on the single fiber and a cover glass was placed on the film. A weight of 50 g was used to press the film close to the fiber. PA6 was melted and the heat history was eliminated at 235 °C for 5 min in the hot press. For simulating the actual molding process as much as possible, three different cooling methods were used to get the final single fiber-polymer composites: slowly cooling in the hot press, moderately cooling in the air, and rapidly cooling in the water of room temperature.

Testing

The fiber weight content in the prepared composites was calculated by the following formula. Three samples were used to get the average value of fiber content.

$$\phi_f = \frac{10\rho_s S_C}{m_C} \times 100\% \qquad (1)$$

where ϕ_f (%) means the fiber weight content, ρ_s is the area density of single layer PA66 plain cloth (5.9×10^{-3}g/cm^2), S_C (cm^2), and m_C (g) are the area and the mass of the composite laminate, respectively. Void fraction of composites was measured according to ASTM D2734.

The crystal microstructure of the single fiber-polymer composite was observed by a polarizing microscope (BX51, Olympus). Interface morphology between fibers and matrix in composites after the cryogenically (liquid nitrogen) brittle fracture were observed by SEM (JEOL, Tokyo, Japan). Dynamic mechanical analyses were performed from 30 to 150 °C at 3 °C/min by tension mode at 1 Hz on a TA instrument Q800. The static tensile tests of the PA6 film and the prepared composites were performed on an universal testing machine (SANS, Shenzhen, P. R. China) according to ASTM D638 with a cross-head speed of 5 mm/min. Perkin–Elmer Pyris Diamond DSC instrument was used to study the non-isothermal crystallization of the pure PA6 film and the composites. Samples (about 5 mg) were heated from 50 to 235 °C at 50 °C/min and kept at 235 °C for 5 min to eliminate the heat history. Then the samples were cooled to 50 °C at different rates (1, 5, and 50 °C/min) to obtain the crystallization curves.

Results and discussion

Effect of processing temperature on the structure, interface bond, and mechanical properties of composites

The influence of processing temperature on the structure and properties of composites was investigated here. A direct effect of the processing temperature was the variation of the composites thickness (see Table 1). The viscosity of the melting PA6 decreased as the temperature increased. Without the restriction of the mold, more PA6 flew out of the plates as the temperature increased, which resulted in a higher fiber content in composites at the higher processing temperature. Decrease of PA6 melt viscosity was helpful to impregnate the fiber and repel the air. So the void fraction of composites reduced and the density was enhanced with the increase of temperature. From Table 1, the void content in composites was relatively low which assured the quality of composites.

Table 1 Effect of the processing temperature on the thickness, fiber weight content, density, and void fraction of composites

Processing temperature (°C)	Thickness (mm)	Fiber weight content (%)	Density (g/cm^3)	Void fraction (%)
225	0.65	67.6	1.152	1.16
235	0.60	69.2	1.157	0.73
245	0.54	69.4	1.160	0.47

PA66 is usually made from adipic acid and hexane diamine and PA6 is obtained by the ring-opening polymerization of caprolactam. Both polyamides share the same molecular structural unit (–CONH–(CH$_2$)$_5$–), which indicates that a strong interface can be formed between PA66 fiber and PA6 matrix. Effect of the processing temperature on the fiber/matrix interface bonding was investigated by the fiber surface morphology after cryogenically (liquid nitrogen) brittle fracture (see Fig. 2). At 225 °C, the fiber surface was clean and almost no PA6 matrix was bonded on it (see Fig. 2a). As the processing temperature increased, more PA6 adhered to the fiber surface after brittle fracture (see Fig. 2b, c). This difference indirectly suggested that a stronger interface was obtained as the temperature increased.

Molecular motions at the interfacial region of composites generally contribute to material damping. So estimation of the damping will enable to quantify the interface bonding [23]. Loss tangent (tan delta) of the composites which were produced at different temperatures is shown in Fig. 3. It is evident that the maximum loss tangent value of the composite prepared at 225 °C was bigger than the maximum value at higher temperatures. This also indicated that higher temperature was helpful to get a better interface bonding.

The effect of processing temperature on the interface bonding is related to physical and chemical reasons. First, the decrease of PA6 matrix viscosity as the temperature increased improved the wetting out of PA6 melt on the fiber surface and promoted the physical diffusion effect between fiber and matrix. Secondly, PA66 fiber and PA6 matrix both have plentiful –CONH– which could form the hydrogen bonds between them. Increase of temperature promoted the formation of the amide hydrogen bonds on the interface and strengthened the interface bonding.

Dynamic mechanical analysis was used to investigate the influence of processing temperature on the stiffness of composites. Figure 4 shows the storage modulus of composites which were prepared at different temperatures. There was a minor difference in storage modulus for three processing temperatures. The composites prepared at 235 °C possessed a slightly higher stiffness than the composites prepared at other two temperatures. In order to investigate the effect of the processing temperature on the mechanical property of the composites further, the tensile strength of three samples were shown in Fig. 5. The composite prepared at 235 °C possessed the maximum strength of 192 MPa which was about 280% of that of PA6 matrix (69 MPa). From above analysis, it is known that increase of processing temperature is helpful to decrease the void fraction and strengthen the interface bonding. But, higher processing temperature could cause the thermal degradation of PA6

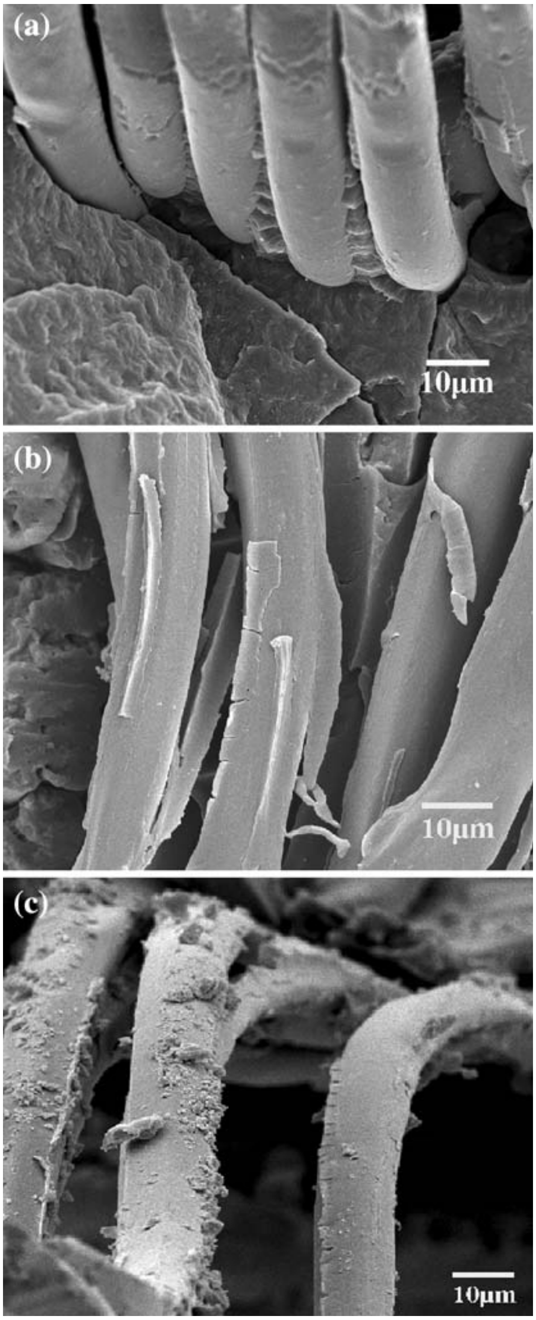

Fig. 2 Effect of processing temperature **a** 225 °C, **b** 235 °C, **c** 245 °C on the morphology of the PA66 fiber surface after cryogenically brittle fracture

matrix and the relaxation of PA66 fiber, which damaged the mechanical properties of composites. Therefore, an optimal processing temperature exists in this temperature range.

Effect of cooling rate on the crystallization behavior of composites

For PA, a semicrystalline polymer, the mechanical properties strongly depend on the crystalline structure and the

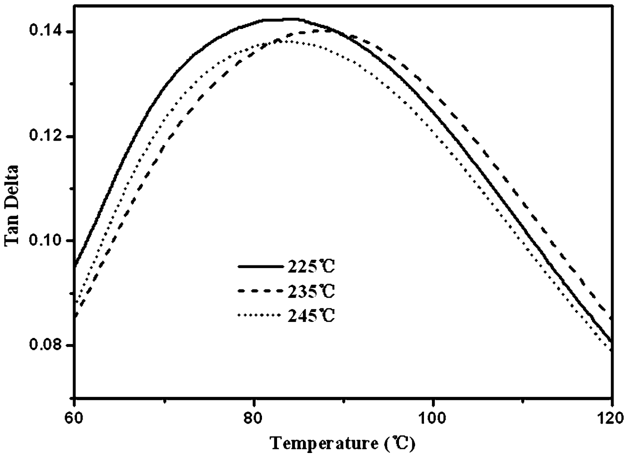

Fig. 3 Comparison in tan delta of composites prepared at different temperatures

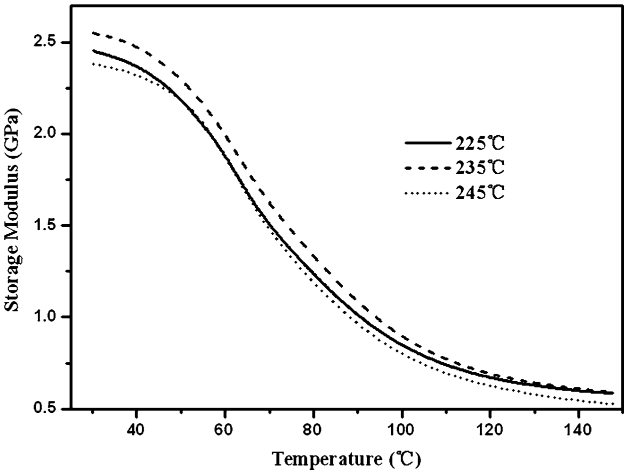

Fig. 4 Storage modulus of composites prepared at different temperatures

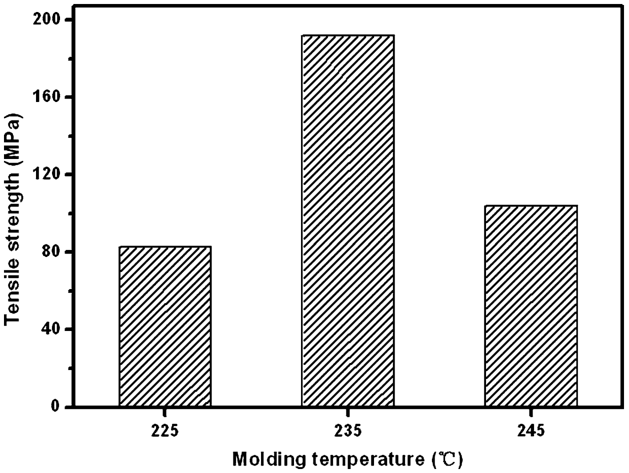

Fig. 5 Tensile strength of composites prepared at three temperatures

crystallinity. And the crystalline behavior is greatly influenced by the heat treatment in the molding process. Therefore, the heat treatment condition is essential to the high performance of all-polyamide composites. During the actual production, the non-isothermal crystallization process is suitable to industrial process. So effect of cooling rate on the crystallization property of PA6 matrix in composites was investigated by differential scanning calorimetry. Three different cooling rates were 1, 5, and 50 °C/min. The crystallization curves of PA6 matrix in composites and pure PA6 as control are shown in Fig. 6. The crystallization parameters (T_0—the initial crystallization temperature, T_p—the peak temperature, D—crystallization temperature range, and $t_{1/2}$—the crystallization half time) are listed in Table 2. Increasing the cooling rate decreased the crystallization temperatures of pure PA6 and composites. It is obvious that the crystallization temperatures of PA6 matrix in composites were higher than ones of pure PA6 at three cooling rates, which was due to the nucleation of PA66 fiber surface to PA6 matrix. Because of the densely packed fibers impeded the PA6 chain segment from regularly arrangement, the crystallization half time of composites was prolonged compared to the pure PA6.

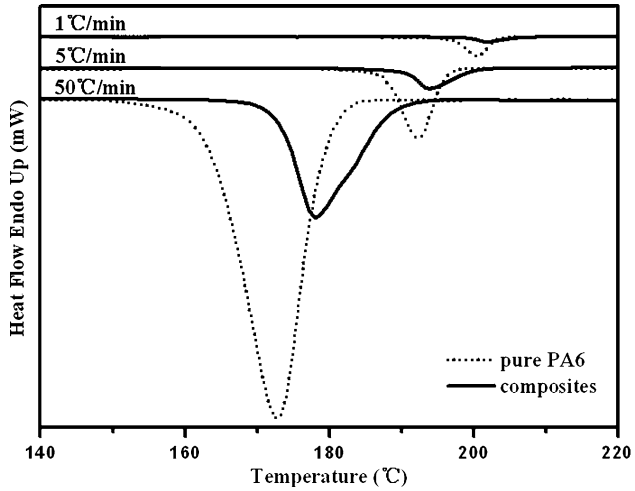

Fig. 6 Influence of PA66 fiber on the crystallization behavior of PA6 at different cooling rates

Table 2 Values of T_0, T_p, D, and $t_{1/2}$ at various cooling rates for PA6 and composites

	Cooling rate (°C/min)	T_0 (°C)	T_p (°C)	D (°C)	$t_{1/2}$ (min)
PA6	1	203.2	200.5	6.0	4.3
	5	196.1	192.2	8.3	1.3
	50	179.8	172.4	16.5	0.2
Composites	1	205.9	201.9	6.9	11.7
	5	200.3	193.9	9.8	1.7
	50	189.0	178.0	16.6	0.2

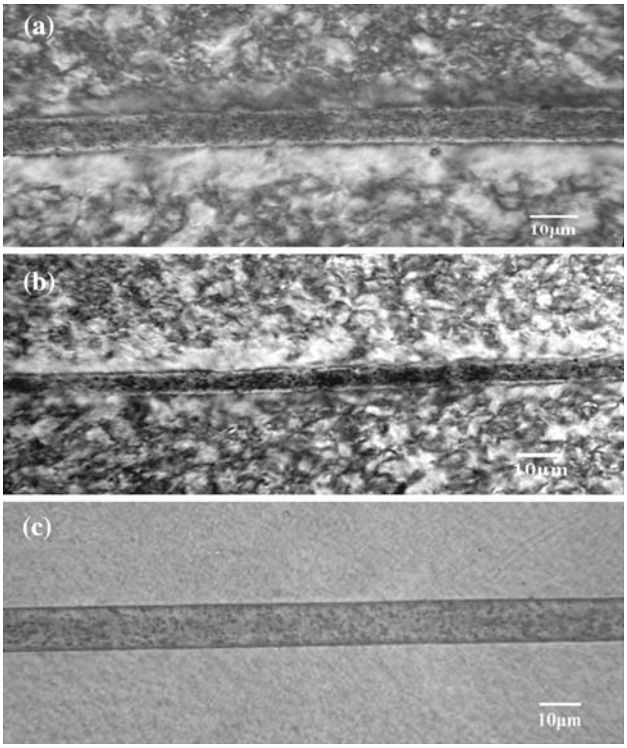

Fig. 7 Transcrystallization of PA6 matrix on the PA66 fiber surface after different cooling methods in the **a** hot press, **b** air, **c** water

In order to vividly investigate this nucleation effect, single PA66 fiber/PA6 composites were made by three different cooling methods (see section "Preparation of single fiber-polymer composites") and observed by polarizing microscope. The transcrystalline layers could be seen on the fiber surface in Fig. 7a, b. Due to the similar chemical composition and lattice structure between PA66 and PA6, PA6 matrix crystal nucleated epitaxially on the surface of PA66 fibers and grew radially relative to the fiber axis to form the transcrystalline layer [24]. Because of the fast cooling in water, there was no enough time for PA6 chain segment to regularly arrange. Therefore, neither apparent crystal of matrix nor transcrytallization on the fiber surface existed after cooling in water (see Fig. 7c). So cooling rate affected both the crystallization of matrix and the transcrystallization on the fiber surface and slowly cooling was helpful for the growth of matrix crystal and interface transcrystal. Influence of transcrystallization by incorporation of PA66 fibers on the interface strength and the mechanical properties of composites will be the emphasis in our future work.

Conclusions

All-polyamide composites were successfully manufactured based on the melting point difference of PA66 fiber and

PA6 matrix. At the optimal processing temperature of 235 °C, the tensile strength of the composites was 280% of that of the pure PA6. Because of the nucleation effect of PA66 fiber surface to PA6 matrix, crystallization temperature of PA6 in composites was increased comparing to the pure PA6 and transcrystalline layer of PA6 matrix was formed on the PA66 fiber surface after slowly cooling.

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