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All-polyamide composites prepared by resin transfer molding

Ying Gong · Guisheng Yang

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Abstract Resin transfer molding (RTM) was used to manufacture all-polyamide (all-PA) composites in which PA6 matrix was in situ formed by the anionic polymerization of ε-caprolactam (CL). Influence of molding temperature (T_M), a critical process parameter, on the structure and properties of all-PA composites was investigated using TGA, DSC, SEM, and tensile, flexural test. Increasing T_M resulted in the decrease of CL conversion and the enhancement of fiber/matrix interface bonding. By comparing the mechanical properties of all-PA composites prepared at different T_M (140–200 °C), an optimal T_M (180 °C) was found in this temperature range. As a whole, the complete consolidation of all-PA composites and the remarkable reinforcing effect of PA66 fibers on PA6 matrix were assured by low-void fraction, high-CL conversion and strong interface performance though in a wide T_M range.

Introduction

Recently, all-polymer composites (or single polymer composites) in which the fiber reinforcing phase and matrix are made from different morphologies of the same or similar polymer [1] are of considerable scientific interest. By virtue of the same composition between fiber and matrix, all-polymer composites possess better recyclability and stronger fiber/matrix interface performance in comparison with traditional glass or carbon fibers reinforced polymer composites. Therefore, all-polymer composites based on different kinds of polymer including polypropylene [2–7], polyethylene [8–11], polyethylene terephthalate [12, 13], polymethyl methacrylate [14, 15], cellulose [16], and so on, had been prepared by various methods(film stacking, solution impregnation, hot compaction, and co-extrusion, etc. [17–21]).

Polyamide (PA) is a widely applied general plastic due to its excellent physical properties [22]. However, a little work had been done on all-PA composites that comprised PA fibers reinforced PA matrix. Hine and Ward [23] introduced a process of hot compaction during which PA66 fibers surface were partly melt at precise temperature and PA66 matrix was formed after cooling and rescrystallization of this molten part, nevertheless this process possessed a low-temperature window (~2 °C). In our lab [24], we succeeded in manufacturing all-PA composites by the method of film stacking based on the difference in melting points of PA66 fiber and PA6 matrix. During this process, at a temperature higher than the melting point of PA6 film and lower than that of PA66 fibers, PA6 film was fully melt to impregnate the PA66 fibers and bonded them together after cooling. It was worth noting that this marked difference in melting points of two components was in favor of acquiring a wide temperature window (~30 °C) in this process. However, it was difficult for the PA melt to effectively impregnate the fibers and completely repel the air as a result of the high viscosity of PA melt during both the processes mentioned above for preparing all-PA composites.

In order to overcome this defect, resin transfer molding (RTM) technology [25, 26] combined with the anionic

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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

polymerization of ε-caprolactam (CL) was adopted to prepare all-PA composites consisting of PA66 fibers and PA6 matrix in this study. A reactive mixture (including CL, catalyst and activator) that exhibited a much lower viscosity than PA6 melt was infused into a matched mold and impregnated the PA66 fibers inside. Then, PA6 matrix was in situ formed by the anionic polymerization of CL. Low viscosity (close to water) of the reactive mixture made the whole impregnation process relatively easier. Besides, the wide anionic reactive temperature range of CL (~60 °C) [27] guaranteed a wide process temperature range in this method. This article gives a detailed description of this new preparation method for all-PA composites and focus on the influence of molding temperature (T_M), a critical process parameter, on the consolidation structure and the mechanical properties of all-PA composites.

Experimental

Materials

ε-Caprolactam of commercial grade was obtained from BASF Co. The sodium hydroxide (NaOH), acetone, and toluene 2,4-diisocyanate (TDI) (analysis purity) were purchased from Shanghai Chemical Reagents Company and used without further purification. Because of good strength and similar chemical composition with PA6 matrix, PA66 fiber was used as the reinforcement. PA66 plain cloth was supplied by Shanghai Sanchuan Printing and Dyeing Co. The structure of the cloth was shown in Fig. 1. The diameter of PA66 fibers from this cloth was 11.6 μm and the area density of the PA66 cloth was 60 g/m^2. The tensile strength, tensile modulus, and elongation at break of PA66 fibers were 560 MPa, 8.7 GPa, and 6.5%, respectively. PA66 cloth was stored in a desiccator for further use after extraction with acetone for 24 h and then vacuum drying at 50 °C for another 24 h.

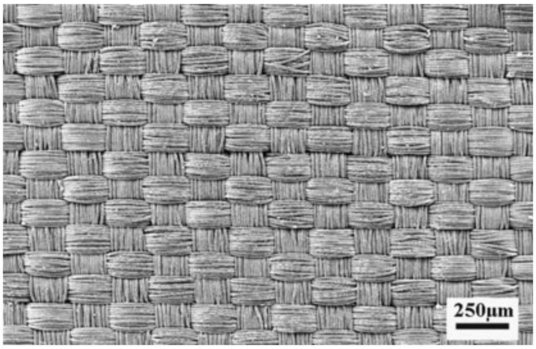


Fig. 1 Structure of PA66 plain cloth (40D 270T)

Preparation of reactive mixture

After melting in a flask, 100 g CL monomer was exposed to a vacuum at 140 °C for 15 min to remove water. Then, 0.4 g NaOH (catalyst) was added into the CL melt and this initial mixture was exposed to a vacuum for another 15 min. Subsequently, the initial mixture was cooled to 120 °C under dry nitrogen before 0.8 g TDI (activator) was added with stirring and then the reactive mixture was obtained.

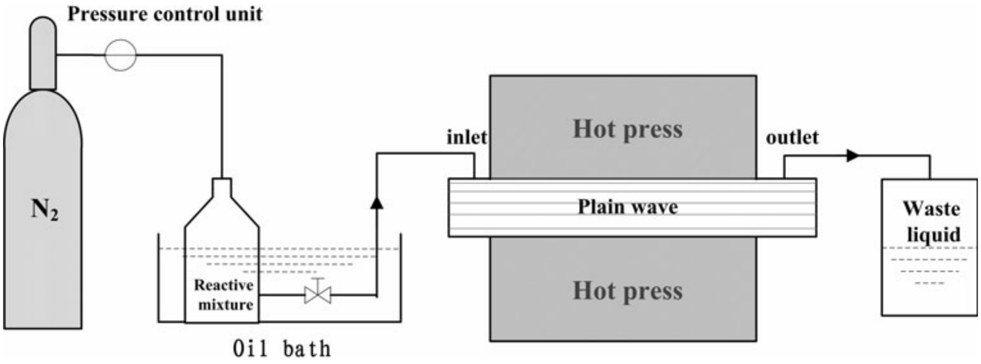
Preparation of all-PA composites

In our lab, a simple RTM equipment was set up as shown in Fig. 2. The prepared reactive mixture was poured into a stainless steel tank that was kept in an oil bath of 120 °C. At this temperature, the reactive mixture would not polymerize rapidly and could maintain a low viscosity (close to water) for a relatively long time. By a nitrogen pressure, the reactive mixture was infused into a matched stainless steel mold (200 × 100 × 0.6 mm) from the inlet and impregnated the 10 layers PA66 cloth placed inside. The steel mold was placed in a hot press the temperatures of which, named as the molding temperature (T_M), were set to 140, 160, 180, and 200 °C, respectively. For the purpose of preventing the fibers from relaxing at T_M, the stress of 10 MPa was applied to the mold by the press machine. As soon as the reactive mixture flew out from the outlet, the nitrogen pressure was removed and the inlet and outlet of the mold were both clamped immediately. In order to assure a complete reaction of anionic polymerization as possible, the set T_M was kept constant for 1 h. Then, the mold was cooled slowly to the ambient temperature in the press and all-PA composites were taken out. As control, pure PA6 (APCL) sheets were obtained by the anionic polymerization of CL at the same process conditions as above. All samples were preserved in a desiccator for further analysis.

Instrumentations and measurements

Void fraction of the composites was measured according to ASTM D2734. TGA measurements were performed at a Perkin-Elmer Pyris-1 apparatus. Melting curves were obtained by heating the samples from 50 to 280 °C at 10 °C/min under nitrogen on a Perkin-Elmer Pyris Diamond instrument. For tensile tests, samples of APCL sheet and all-PA composites were punched into the dumbbell specimen in which the width and length of narrow section, the width overall and length overall were 4 and 20 mm, 8 and 50 mm, respectively. The tensile tests were performed with a cross-head speed of 5 mm/min on a universal testing machine (SANS, Shenzhen, P. R. China). Flexural strength

Fig. 2 Structure diagram of the RTM equipment



was appraised according to ASTM D790 on the same testing machine. Fiber/matrix interface morphology of all-PA composites after tensile fracture was observed by SEM (JEOL, Tokyo, Japan).

Results and discussions

Consolidation structure of all-PA composites

In manufacturing all-PA composites by RTM, the reactive mixture was infused into the mold by nitrogen pressure and impregnated the PA66 plain cloth inside to eject the air out. However, the flow of the reactive mixture in the mold was complicated by the weave structure of PA66 fiber reinforcement phase (see Fig. 1) and various flow rates were formed. When the reactive mixture with different flow rates met each other, air could be entrapped [28] and void was retained in all-PA composites after PA6 matrix was in situ formed by the anionic polymerization. It is well known that existence of voids reduces the strength and surface quality of the composites. Therefore, low-void fraction is crucial to acquire high performance of composites.

As the temperature of reactive mixture (120 °C) was relatively lower before entering the mold, the reactive mixture needed time to absorb heat from the higher temperature ($\geq$140 °C) environment to begin the anionic polymerization after flowing into the mold. For this reason, a low viscosity of the reactive mixture could be maintained for a reasonable period in which the impregnation of PA66 plain cloth with reactive mixture would be completed. In addition, similar chemical composition and polar nature between PA66 fiber and reactive mixture decreased the difference of surface energy between them. Similar surface energy was beneficial to the wetting of PA66 fibers by the reactive mixture. Therefore, it was not difficult for the reactive mixture to effectively impregnate the PA66 fibers and for the all-PA composites to obtain a low-void fraction (see Fig. 3). The values of void fraction of all-PA composites were all about 1% except that the all-PA composites prepared at 200 °C possessed a value of 2.1%. Higher T_M resulted in a higher polymerization rate and more rapidly increase of the viscosity of reactive mixture, so impregnation of PA66 fibers with reactive mixture and discharge of air became more difficult. Thereby, more air was trapped in the all-PA composites prepared at 200 °C comparing with the other three lower T_M.

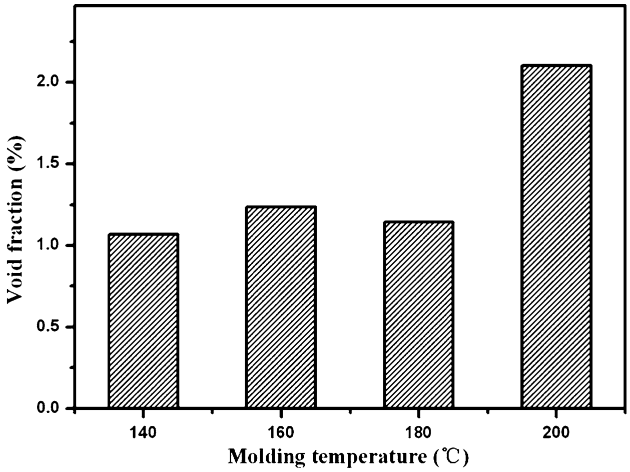


Fig. 3 Void fraction of all-PA composites prepared at different T_M

In order to achieve high-performance PA6 matrix by the anionic polymerization of CL to effectively bond PA66 fibers together, high-CL monomer conversion is prerequisite. In this study, TGA was used to investigate the effect of T_M on the CL conversion of APCL and all-PA composites. Samples were heated from 50 to 600 °C at 10 °C/min under nitrogen. A typical TGA curve is shown in Fig. 4. Based on the principle that the mass loss of samples heated from 100 to 300 °C is a result of residual CL evaporation [29], the CL conversion of APCL and all-PA composites were calculated by comparing this mass loss to the matrix content according to the formula in Fig. 4 and were shown in Fig. 5. For APCL and all-PA composites, the matrix weight content (φ) was 100 and 40%, respectively.

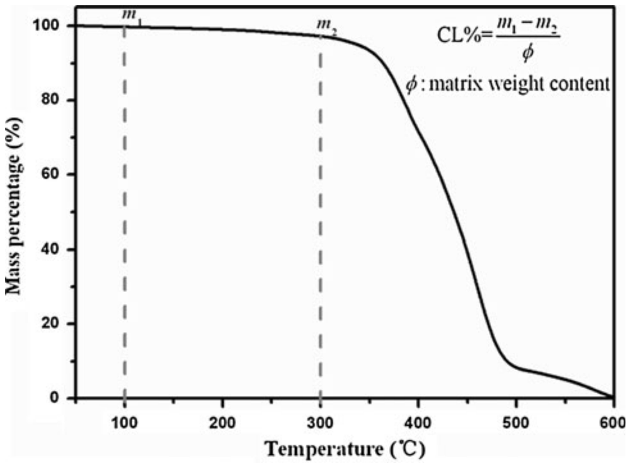


Fig. 4 TGA curve of all-PA composites prepared at 180 °C

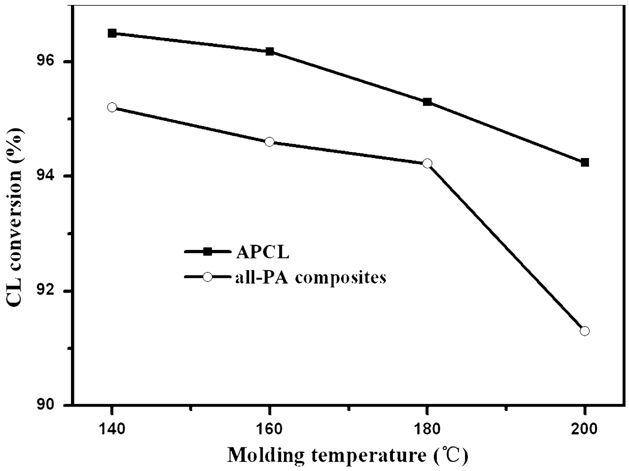


Fig. 5 Effect of T_M on the CL conversion of APCL and all-PA composites

From Fig. 5, it is easily found that CL conversion of APCL and all-PA composites decreased gradually with increasing T_M. This relation of CL conversion to T_M was attributed to the shift in the equilibrium of anionic polymerization toward the monomer side, increase of the amorphous phase and activator depletion by branching with polymerization temperature increasing [30]. It is also noteworthy that the CL conversion of APCL was obviously higher than that of all-PA composites when they were prepared at the same T_M. The main reason for this inhibited effect of PA66 fibers on the anionic polymerization of CL was that –COOH groups and residual H_2O molecules on the surface of PA66 fibers consumed some –NCO groups of TDI activator when the reactive mixture impregnated the PA66 fibers. Overall, high-CL conversion (>91%) assured the successful formation of PA6 matrix by in situ anionic polymerization of CL and the complete consolidation structure of all-PA composites though in a wide T_M range (140–200 °C).

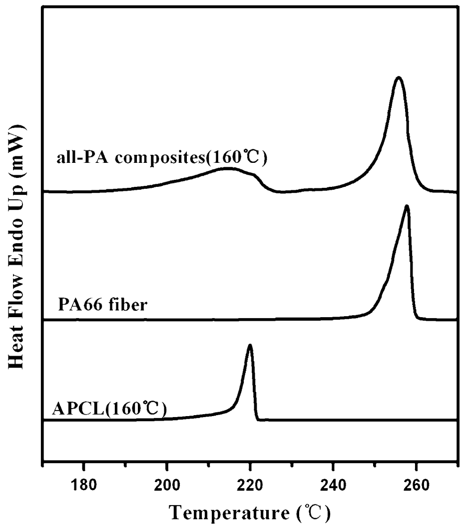


Fig. 6 Melting curves of PA66 fiber, APCL and all-PA composites prepared at 160 °C

Therefore, as to further illustrate the structure of PA66 fibers reinforced PA6 matrix in all-PA composites, three melting curves of PA66 fibers, APCL, and all-PA composites prepared at 160 °C are shown in Fig. 6. It is observed that all-PA composites prepared at 160 °C possessed two melting peaks (214 and 254 °C). Comparing with the melting behaviors of PA66 fibers and APCL prepared at 160 °C, it was not difficult to deduce that higher-melting-peak during heating all-PA composites was corresponding to the melting of PA66 fibers and lower-melting-peak corresponding to the melting of PA6 matrix formed by anionic polymerization of CL.

Mechanical properties of all-PA composites

Influence of T_M on the mechanical properties of all-PA composites was researched by tensile and flexural tests and the detailed data were shown in Figs. 7 and 8, respectively. When T_M was lower than 180 °C, increasing T_M had a positive influence on the tensile strength of all-PA composites. However, with increasing T_M further (higher than 180 °C), the tensile strength of all-PA composites decreased. At 180 °C, the maximal value of tensile strength of all-PA composites was 156 MPa that was about 220% as high as that of APCL (70 MPa) prepared at the same T_M. By this comparison, it is concluded that the presence of PA66 fibers had a marked reinforcing effect on the in situ formed PA6 matrix in all-PA composites. From Fig. 8, it is obvious that T_M had a similar effect on the flexural strength of all-PA composites.

For the purpose of quantificationally analyzing the reinforcing effect of PA66 fibers on PA6 matrix, a coefficient (ϕ) was calculated according to a parallel rule of

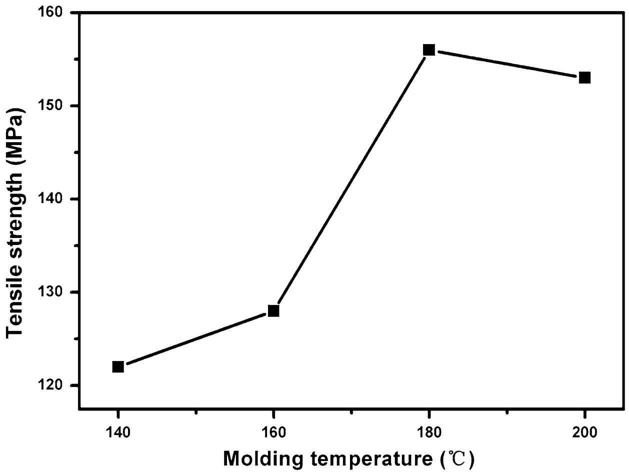


Fig. 7 Tensile strength of all-PA composites prepared at different T_M

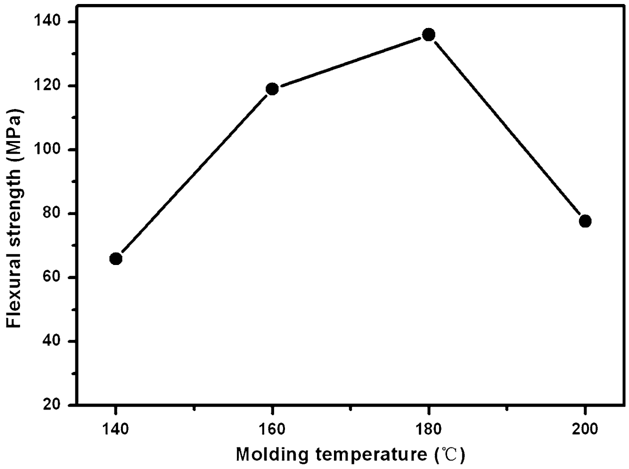


Fig. 8 Flexural strength of all-PA composites prepared at different T_M

mixtures for the tensile strength of the plain weave reinforced composites [31],

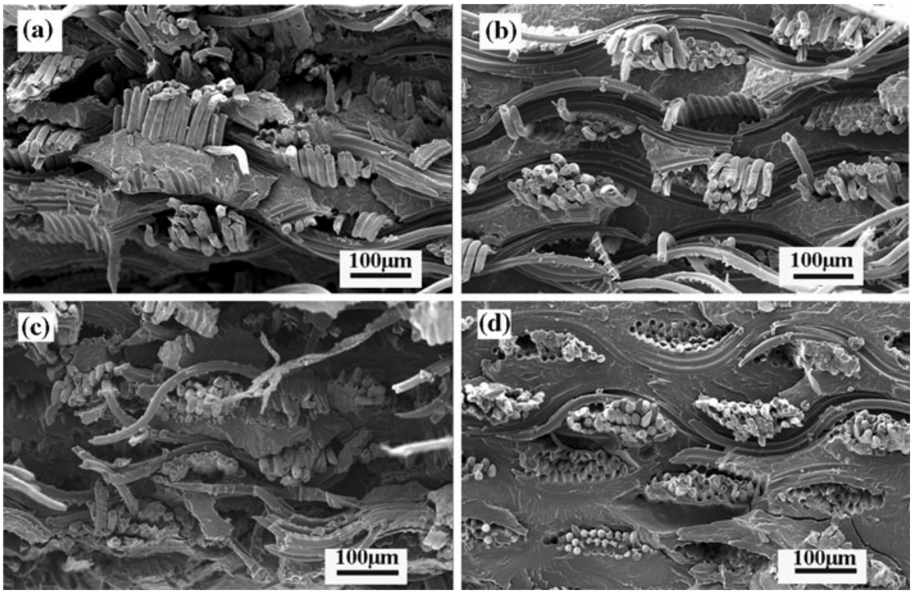
$$\phi = \delta_e / \delta_c, \tag{1}$$

$$\delta_c = \delta_f \frac{V_f}{2} + \delta_m \left(1 - \frac{V_f}{2}\right), \tag{2}$$

where δ_c and δ_e are the theoretical value and experimental value of tensile strength of composites, δ_f and δ_m the tensile strength of fibers and matrix, respectively, and V_f the volume fraction of fibers. Taking the all-PA composites prepared at 180 °C, for example, the value of δ_c is 217 MPa and that of ϕ is 0.72 after calculation. This relatively high coefficient further inflected that the presence of PA66 fibers in all-PA composites markedly increased the strength of PA6 matrix.

Tensile fracture morphology of all-PA composites was investigated by SEM and shown in Fig. 9. When T_M was lower than 200 °C, PA66 fibers stuck out of the fracture surface apparently and this morphology reflected the fiber pull-out and debonding failure mechanism. However, at 200 °C, PA66 fibers fractured almost in the cross-section, which indicated that the bond between fibers and matrix was better and failure mode changed into the fiber fracture. For the purpose of explaining the change of tensile fracture morphology with T_M increasing, it must be considered that PA66 can be dissolved in CL melt at high temperature and the solubility increases with temperature increasing [32]. Therefore, in this study, more molecules of PA66 fibers surface dissolved in the reactive mixture consisting of CL melt, catalyst, and activator and lost the original high orientation with T_M increasing. With the development of anionic polymerization, PA6 molecules were formed gradually and the dissolved PA66 molecules were likely to

Fig. 9 Te nsile fracture surface morphology of all-PA composites prepared at **a** 140 °C, **b** 160 °C, **c**180 °C, **d** 200 °C



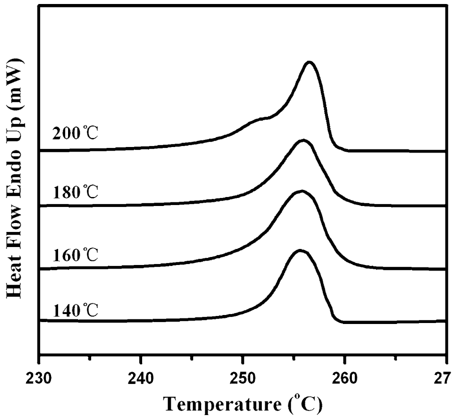


Fig. 10 Melting behaviors of PA66 part in all-PA composites prepared at different T_M

entangle with these newly generated PA6 molecules. After the polymerization, a continuous fiber/matrix interface comprised PA66 molecules entangling with PA6 molecules could be formed by virtue of the solubility of PA66 in CL melt.

In order to prove this standpoint, melting behaviors of PA66 part in four all-PA composites were investigated (see Fig. 10). Different from the other three melting curves, a shoulder melting peak appeared in the melting range of PA66 in all-PA composites prepared at 200 °C. This shoulder melting peak was contributed to that an obvious part of PA66 fibers surface dissolved in CL melt at 200 °C and lost the original high orientation of PA66 fibers and rescrytallized into a new form. As a result of lost of high orientation, the newly formed PA66 crystal appeared a lower-melting-point by DSC. Moreover, the intact PA66 fibers preserved the high orientation and could be melted at a higher temperature. Therefore, it was further proved that a continuous fiber/matrix interface was likely formed by the partly dissolution of PA66 fibers into the reactive mixture by means of comparing the melting behaviors of PA66 part in four all-PA composites. The difference of melting behaviors also explained the change of tensile fracture morphology of all-PA composites in the studied temperature range.

From above analysis, it is well known that CL conversion decreases with T_M increasing and residual CL monomers in all-PA composites harm the strength properties of the composites. In addition, more molecules of PA66 fibers surface lose the high orientation and tangle with PA6 matrix when T_M increases. Lost of high orientation causes a decrease of the strength of PA66 fibers along the fibers direction and also an improvement of interface bonding. Taking these factors into account, it is educible that the strength properties of all-PA composites display a peak value in the studied T_M range, as shown in Figs. 7 and 8.

Conclusions

Resin transfer molding technology combined with the anionic polymerization of CL was successfully applied to manufacture all-PA composites comprised PA66 fibers reinforced PA6 matrix. Comparing with the other methods to prepare all-polymer composites, this novel method possesses an easier impregnation process and a wider T_M range. In a word, low-void fraction, high-CL conversion, and strong interface bonding guaranteed the integrated structure and high performance of all-PA composites by RTM. More important, this kind of all-PA composites could be recycled only by fully melting, which was a great advantage than glass or carbon fibers reinforced polymer composites.

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