INTERFACE SCIENCE

Interfacial crystalline behavior in glass-fiber/polypropylene composites modified by block copolymer coupling agents

Yin Li · Lingxia Chen · Xiaodong Zhou

Abstract A kind of di-block copolymer polystyrene-block-poly(γ-methacryloxy-propyltrimethoxysilane) (PS-b-PMPS) with different PS block length and a kind of tri-block copolymer polystyrene-block-poly(n-butylacrylate)-block-poly(γ-methacryloxypropyltrimethoxysilane) (PS-b-PnBA-b-PMPS) with different PnBA block length were synthesized by atom transfer radical polymerization (ATRP), in which PS was a 'hard' block and PnBA was a 'soft' block. The interfacial crystallization behaviors of glass fiber/polypropylene systems modified with different coupling agents MPS, PS-b-PMPS, and PS-b-PnBA-b-PMPS were investigated on different crystallization conditions. Transcrystallinity could not be induced on nonisothermal crystallization or without maleic anhydride (10%) in polypropylene, but it appeared when glass fibers were treated with common silane coupling agent γ-methacryloxypropyltrimethoxysilane (MPS) and di-block copolymer coupling agent PS-b-PMPS in 135 °C isothermal crystallization without shear and 150 °C isothermal crystallization with shear. However, it disappeared at the interface when the samples were treated with tri-block copolymer coupling agent (PS-b-PnBA-b-PMPS) either under static or shear-induced condition. It might be that the flexible interlayer formed by the flexible block PnBA of PS-b-PnBA-b-PMPS could relax not only the thermal stress resulted from interface temperature gradient arising from sample cooling for crystallization, but also the shear stress induced by fiber/matrix interface shear.

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Introduction

Isotactic polypropylene (PP) is often reinforced by glass fibers in order to improve their mechanical properties. In composites, polypropylene is often grafted with a polar unsaturated compound, such as maleic anhydride [1], or treated with oxygen plasma [2]. Glass fiber (GF) is often pretreated with a binder [3, 4], nucleating agents [5], or coupling agents [6]. Because stress transfer in the GF/PP composites is influenced by the interphase, optimization of the mechanical properties of composites requires an extensive knowledge of the crystalline behavior of the interphases, especially the effect of the treatment mentioned above.

Under certain conditions [7–12], the fibers induced a relatively high crystal nucleation density on their surface. Therefore the matrix spherulites grow from the fibers in the radial direction and then produced a columnar layer of crystalline structure, termed transcrystallinity. Thomason and Van Rooyen [8] observed that under isothermal and slow cooling conditions the glass fiber in GF/PP composites could not induce transcrystallization, while with a high cooling rate, the transcrystalline layer would form. The thermal stress arising from the interface temperature gradient induced transcrystallization. Varga and Karger-Kocsis [9] found that there was no transcrystallization in glass fiber/PP after isothermal crystallization at 138 °C. Transcrystallization could be induced by shear stress produced by pulling glass fiber slowly on the interface of glass fiber/PP. Honggan et al. [10, 11] found in experiments that transcrystallization would form if the glass fiber and polypropylene were chemically bonded, but it would not with the physical adhesion. Cai et al. [13] had put forth a comprehensively valid mechanism of transcrystallization. According to this mechanism, transcrystallization was

mainly induced by two factors: fiber/matrix interface shear and interface temperature gradient arising from sample cooling for crystallization. The structure and the size of transcrystalline layer were not only system-specific but also condition-specific. Some influences were known, for instance, the surface energy of fiber, the type of fiber, the sizing, and coupling agent [3, 14].

The strong orientation of the transcrystalline layer in glass-fiber/polypropylene composites has affected the mechanical properties of composite materials by the alteration of interfacial structure [15–20]. It has drawn much interest, because it implies the possibility of predicting and controlling the final structures and properties of glass fiber/semi-crystalline polymer composite in current manufacturing processes.

In fact, GF/PP composites are often produced by applied processing techniques such as injection molding and compression molding, which impose oscillatory shear on the melt during solidification stage. Shear has significant effects on molecular segmental orientation and chain conformation. In the end the mechanical properties of composite materials are influenced by the alteration of crystalline behavior. It is necessary to study the crystalline behavior under shearing.

However, the transcrystalline layer and its effects on the interfacial adhesion and the resulting mechanical properties caused by glass fibers modified with coupling agents of various structures are not yet systematically analyzed and understood. Tillie et al. and Pegoretti et al. reported that the introduction of flexible interlayer in polymer composites could reduce stress concentration, relax interface residual stress, and improve the impact toughness [21, 22], while the tensile, flexural strength and modulus would increase after the interface being treated by coupling agent. As seen in our previous works and other researchers' reports, the use of the tri-block coupling agents containing a middle flexible block could affect the fiber/matrix interlayer properties and the resulting mechanical properties of the composites [23, 24].

In this paper di-block copolymer coupling agent (PS-b-PMPS) and tri-block copolymer coupling agent (PS-b-PnBA-b-PMPS) were synthesized by atom transfer radical polymerization (ATRP). The middle flexible block PnBA acted as a flexible interlayer due to the poor compatibility with PP [25] and its low glass transition temperature ($T_g = -54$ °C), while the silicon ends of the block copolymer reacted with glass fiber and the PS block was compatible with polymer matrix. We studied the interfacial crystalline behaviors caused by glass fibers modified with three coupling agents, viz. γ-methacryloxypropyltrimethoxysilane (MPS), PS-b-PMPS, and PS-b-PnBA-b-PMPS, at different cooling rate under both static crystallization condition and shear-induced crystallization condition in glass fiber/polypropylene composites.

Experimental

Materials

Isotactic polypropylene (Y1600) was produced by Shanghai Petrochemical, China. Melt flow rate was 16 g/10 min. Glass fibers (GF) of average diameter of 12 μm were supplied by JUSHI Group Co. Ltd, China. Glass fibers were calcined in muffle at 500 °C for 6 h.

Maleic anhydride modified polypropylene (MPP) was produced from isotactic polypropylene by grafting with maleic anhydride (ratio of graft=1.21% wt/wt).

Styrene and *n*-butylacrylate was passed through a column filled with activated basic alumina (Al_2O_3, standard grade, 200–300 mesh) to remove the inhibitor, vacuum distilled before polymerization, and then stored in N_2. Copper (I) bromide (CuBr) was stirred with glacial acetic acid for 24 h under a nitrogen atmosphere, later washed consecutively with glacial acetic acid and ethanol, dried at 40 °C for 3 days, and stored under a nitrogen atmosphere. *N*,*N*,*N'*,*N'*,*N''*-pentamethlydiethylenetriamine (PMDETA), ethyl 2-bromoisobutyrate (EBrIB), anhydrous methanol, γ-methacryloxypropyltrimethoxysilane (MPS, Shanghai Yaohua Chemical Plant) and tetrahydrofuran (THF, 99%) were used without further purification. All other chemicals were purified by vacuum distillation before polymerization.

Synthesis of block copolymer coupling agent

All the block copolymers were synthesized using ATRP. The macroinitiator PS-Br was synthesized as follows: a 250-mL three-neck round-bottom flask was equipped with condenser, gas inlet/outlet, and a magnetic stirrer. Quantitative monomer PS and initiator EBrIB were added to the flask containing catalyst CuBr and ligand PMDETA, followed by bubbling for 30 min with nitrogen under stirring. Polymerization was conducted for 5 h at 90 °C in an oil bath. After polymerization, the crude product was dissolved in THF and passed through an alumina column to remove the catalyst. The polymer solution was concentrated, and precipitated in methanol, then was dried in vacuum at 60 °C, and used to initiate the polymerization of di-block copolymers.

The synthesis of di-block copolymers PS-b-PMPS and PS-b-PnBA(-Br) was carried out at 110 °C in a similar manner to that of macroinitiator PS-Br, but using xylene and cyclohexanone as the solvent in the synthesis procedure of PS-b-PMPS and PS-b-PnBA-Br, respectively.

After purification, PS-b-PnBA(-Br) was used as macroinitiator to further initiate the polymerization of tri-block copolymer PS-b-PnBA-b-PMPS in xylene at 110 °C under nitrogen for 20 h. All the copolymers were purified similar as the macroinitiator PS-Br.

Characterization of block copolymer coupling agent

The structure of copolymers is illustrated in Fig. 1 and characterized by FTIR using Thermo Electron Corporation Nicolet5700 and ^{1}H-NMR in CDCl$_3$ with a Bruker Avance 400 MHz spectrometer. Figure 2 shows the FTIR spectroscopy, in which an absorption band is seen at 1730.9 cm^{-1} which is a characteristic peak for stretching vibration mode of the carbonyl group(C=O) in PnBA. The ring vibration frequencies of aromatic groups of PS are at 1600.9, 1940.0, and 1451.9 cm^{-1} and the double peaks for the external plane of C–H ring of aromatic groups 756.1 and 696.7 cm^{-1} are the characteristic bands of PS. The 3,012–3,056 cm^{-1} band shows the vibrations of C–H stretching from the aromatic groups. Another characteristic absorption peak is at 1032.5 cm^{-1}, which is Si–O stretching adsorption of PMPS. These results show that the copolymer is composed of PS, PnBA, and PMPS.
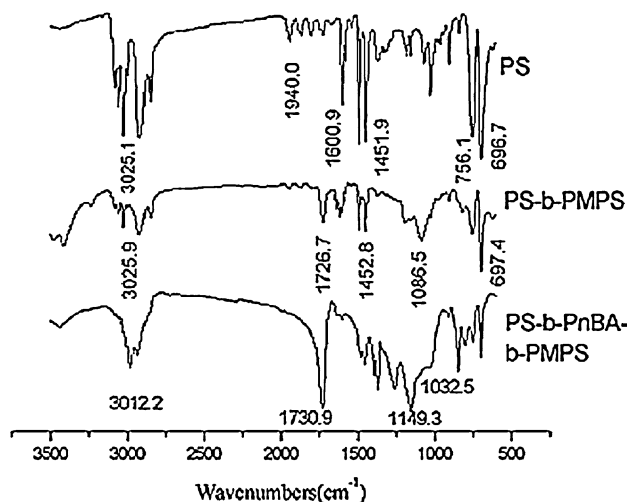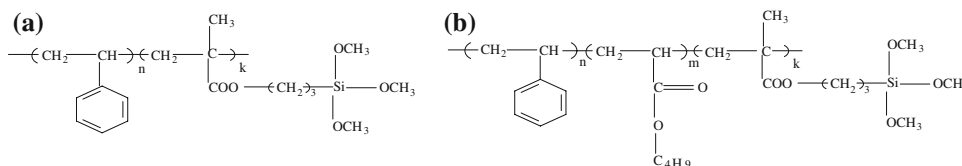
The ^{1}H-NMR spectrum of the PS-b-PnBA-b-PMPS tri-block copolymer is presented in Fig. 3: 7 ppm (phenyl protons, PS), 4.10 ppm (–COOCH*$_2$–, PnBA), 3.58 ppm (–Si (OCH*$_3$)$_3$, PMPS), 2.30 ppm (–CH$_2$CH*COOC$_4$H$_9$–, PnBA), 1.90 ppm (–CH$_2$CH*C$_6$H$_5$–, PS), 1.60 ppm (–COOCH$_2$ CH*$_2$–, PnBA), 1.60 ppm (–CH*$_2$CHCOOC$_4$H$_9$–, PnBA), 1.40 ppm (–CH*$_2$CHC$_6$H$_5$–, PS), 1.30 ppm (–COOCH$_2$ CH$_2$CH*$_2$–, PnBA), 0.95 ppm (–COOCH$_2$CH$_2$CH$_2$CH*$_3$, PnBA).

The absolute molecular weight and its distributions of the macroinitiator PS-Br, and PS-b-PnBA-Br, block copolymers PS-b-PMPS and PS-b-PnBA-b-PMPS were characterized with multi-detectors GPC equipped with a DAWN HELEOS static laser scattering detector and an Optilab Rex refractive index detector, which was produced by Wyatt Technology Corporation. GPC was performed using THF as eluent at a flow rate of 1 mL/min. Because of the narrow molecular weight distribution ($M_w/M_n < 1.2$), the degree of polymerization (DP$_n$) of each block could be calculated by the obtained number-average molecular weight M_n of the block stepwise. The GPC traces are shown in Fig. 4 and the data are summed up in Table 1.
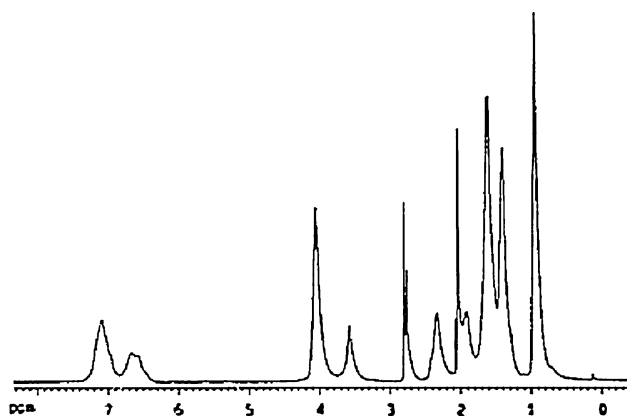
Surface treatment of glass fibers

Silane-coated glass fibers were prepared by exposing the fibers to aqueous solutions of MPS at a concentration of 0.1% (w/w) and reacted at 100 °C in a drying oven for 2 h.
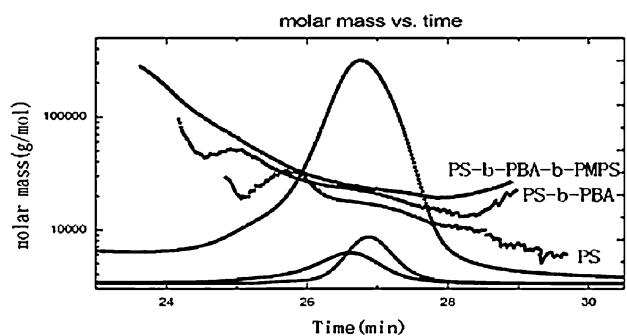

Fig. 2 IR spectra of PS-b-PMPS diblock and PS-b-PnBA-b-PMPS triblock copolymer

Fig. 3 ^{1}H NMR of PS-b-PnBA-b-PMPS triblock copolymer

Fig. 4 Molar mass of the block copolymers

Fig. 1 Molecular structure of PS-b-PMPS diblock (a) and PS-b-PnBA-b-PMPS triblock copolymer (b)

Table 1 Molar mass characteristics of copolymer coupling agent used in samples

Copolymer coupling agent	$\overline{M}_{n,GPC}$	$\overline{M}_{w,GPC}$	$\overline{M}_w/\overline{M}_n$
PS$_{57}$-b-PMPS$_{27}$	12870	14250	1.107
PS$_{149}$-b-PMPS$_{21}$	21830	24340	1.115
PS$_{119}$-b-PnBA$_{36}$-b-PMPS$_{25}$	22660	25470	1.124
PS$_{149}$-b-PnBA$_{55}$-b-PMPS$_{10}$	25150	28300	1.125
PS$_{149}$-b-PnBA$_{167}$-b-PMPS$_{21}$	40230	44070	1.193

Block copolymer-coated glass fibers were immersed overnight in the acetone solutions of PS-b-PMPS and PS-b-PnBA-b-PMPS at a concentration of 0.5 % (w/w), also reacted at 100 °C for 2 h.

All the treated glass fibers were eluted with THF for 2 days in order to remove the unreacted copolymer or silane and then were dried in vacuum at room temperature.

Observation under static crystallization condition

The crystallization behaviors of these samples were recorded by the Nikon LV100POL optical microscope (Japan). Samples were prepared as follows: one fiber with or without coating was placed on a glass slide. A piece of PP with or without MPP (10%) was placed on the fibers. After the polypropylene was heated by alcohol burner and melted, it surrounded the whole fiber and was pressed to a sheet. Then the temperature was raised up to 210 °C over a period of 10 min to erase the previous thermal history of the sample in a temperature-controlled oven, then down to the room temperature at various cooling rates.

Observation under shear-induced crystallization condition

Crystallization behavior under shear-induced condition was observed using a shearing stage (Linkam CSS450 optical shearing stage) under the optical microscope. A small piece of the GF/PP film, previously pressed at 200 °C between glass plates, was heated to 220 °C and maintained there for 5 min to erase any previous crystalline history. Then the sample was cooled at a constant rate of 20 °C /min and sheared with a fixed rate of 0.001 s^{-1} for 30 s when the temperature reached 160 °C. When the temperature was further cooled to 150 °C, the sample was allowed to crystallize isothermally for 1 h before being quenched to room temperature. The crystallization behaviors of these samples were recorded.

Testing of interfacial bond strength

The interfacial bond strength of the fiber/resin interface was usually determined by measuring the force needed to pull a single fiber axially out of the solid matrix. The interfacial bond strength, τ, between the fiber and the matrix resin from microbond tests was calculated as follows:

$$\tau = p/(\pi dl) \tag{1}$$

where p (in cN) was the rupture force, d (in mm) was the diameter of the fiber, and l (in mm) was the length of the embedded fiber [26].

To make such pull-out measurements, the length of the embedded fiber should be short enough so that the fiber does not break before it pulled free. It was difficult to achieve by the conventional methods for the glass fiber of small diameter. The approach in the present work was to dip the fiber into the polypropylene melt to form one or more discrete microdroplets and to make droplets take the shape of ellipsoid, located concentrically around the fiber.

After the resin had been solidified, each fiber was examined under an optical microscope (XTZ-E$_{TV}$). An image of each droplet was captured by a video camera. From these images it was possible to determine the embedded length of fiber in each droplet as well as the fiber length between both ends of the droplet. If a droplet was not axisymmetrical, it was not tested.

Similar as the single fiber/PP composites crystalline samples at isothermal crystallization, all the droplets were transferred to a temperature-controlled oven held at 210 °C for 10 min to erase the previous thermal history. Then they were cooled to 135 °C for isothermal times of 2 h, and then quenched to the room temperature.

An Electronic Single Fiber Strength Tester (Model YG004A) was attached with a chart recorder (Changzhou No.2 Textile Machinery Co. Ltd, China). The outcome of the test could be identified from the trace of the chart recorder and was discussed by Miller et al. [26].

About 30 specimens were tested for each condition. Each sample was examined by an optical microscope after mechanical testing to verify that debonding had occurred rather than cohesive failure of the matrix.

Results and discussion

Influence of cooling rate on interfacial crystallization behavior

The samples cooled in the air are referred to as "fast cooling course" and the samples cooled at 10 °C/min are referred to as "slow cooling course", while the samples crystallizing isothermally at 135 °C or 150 °C for 2 h are referred to as "isothermal crystallization course".

Table 2 indicates crystallization behaviors at different cooling rate in PP/glass fiber modified with different

Table 2 Survey of interfacial crystalline structure in GF/polypropylene system at different crystallization conditions

Sample	System	Fast cooling course	Slow cooling course	Isothermal crystallization under static condition		Isothermal crystallization under shear-induced condition
				at 135 °C	at 150 °C	at 150 °C
1	PP+uncoated glass fiber	No	No	No		No
2	PP+glass fiber modified by MPS	No	No	No		No
3	PP+MPP(10%)+ glass fiber modified by MPS	No	No	Yes	No	Yes
4	PP+glass fiber modified by PS_{57}-b-$PMPS_{27}$	No	No	No		No
5	PP+MPP(10%)+glass fiber modified by PS_{57}-b-$PMPS_{27}$	No	No	Yes	No	Yes
6	PP+MPP(10%)+glass fiber modified by PS_{149}-b-$PMPS_{21}$	No	No	Yes	No	Yes
7	PP+glass fiber modified by PS_{149}-b-$PnBA_{55}$-b-$PMPS_{10}$	No	No	No		No
8	PP+MPP(10%)+glass fiber modified by PS_{149}-b-$PnBA_{55}$-b-$PMPS_{10}$	No	No	No		No
9	PP+MPP(10%)+glass fiber modified by PS_{149}-b-$PnBA_{167}$-b-$PMPS_{21}$	No	No	No		No

surface treatment under different crystallization conditions. In common with the previous work of our research team and other studies of transcrystallization in fiber-reinforced polypropylene, [10–12, 27, 28] non-isothermal crystallization at any rate cannot induce transcrystallization. As seen in Fig. 5, the crystal nucleation and growth rates at the PP/modified glass fiber interface (sample 3) are found to be similar to those in the bulk on non-isothermal crystallization conditions. There is not sufficient high-density nucleation along the fiber surface to form transcrystalline layer, though the higher thermal stress is residual at the interface than isothermal crystallization course.

Moreover, transcrystallization does not happen without MPP in the PP matrix (samples 1, 2, 4, and 7) on any crystallization condition. MPP is maleic anhydride-grafted PP, it can significantly enhance the interfacial bonding strength between PP and glass fiber, because its anhydride group can react with the Si–OH of fiber surface, while the good compatibility between MPP and PP matrix leads to their firm chain entanglement [29]. Compared with MPS, block copolymers can form molecular entanglement to some extent because PS block is compatible with PP. However, the molecular entanglement between PS block and PP matrix is lower than that between MPP and PP matrix. As seen in Table 3, in the case of glass fiber modified by PS_{149}-b-$PnBA_{167}$-b-$PMPS_{21}$, the interfacial bond strength reaches 9.88 MPa when with 10% MPP, but only 2.56 MPa when without MPP. If good interfacial adhesion is not formed, the glass fiber is easily separated from matrix. As a result, when composites are cooled, stress can be released and therefore crystallization of resin is not disturbed by the fiber.

Fig. 5 Photographs of the border in GF/PP (sample 3) cooled at 10 °C/min (×100) (**a**) at 83.3 °C (**b**) at 82.1 °C (**c**) at 79.4 °C
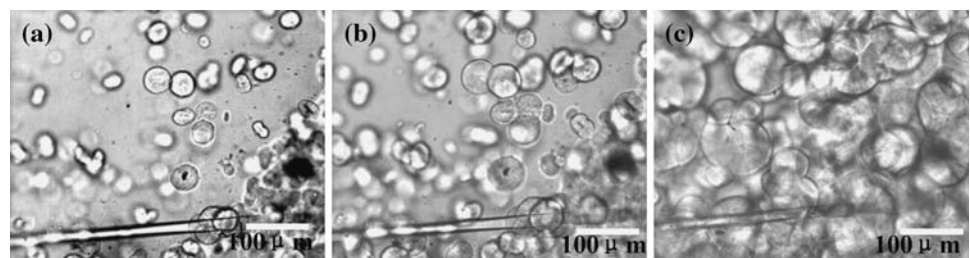
Table 3 Results of Microbond experiments after glass fiber modified by different coupling agent

System	τ (MPa)	Std dev. ($\pm$)
PP+MPP(10%)+glass fiber modified by MPS	7.53	0.29
PP+MPP(10%)+glass fiber modified by PS_{57}-b-$PMPS_{27}$	6.39	0.17
PP+glass fiber modified by PS_{149}-b-$PnBA_{167}$-b-$PMPS_{21}$	2.56	0.06
PP+MPP(10%)+glass fiber modified by PS_{149}-b-$PnBA_{167}$-b-$PMPS_{21}$	9.88	0.54

Fig. 6 Photographs of the border in GF/PP on isothermal crystallization condition at 135 °C (×500) (**a**) Sample 1(PP+GF) (**b**) Sample 2(PP+GF (MPS)) (**c**) Sample 3(PP+MPP (10%) +GF (MPS))
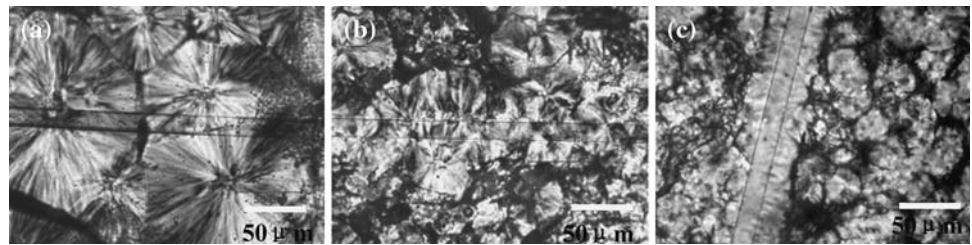
Figure 6 shows that there is transcrystallization with MPP in the PP matrix because MPP can form strong chemical bonding with glass fiber [30, 31]. In our experimental conditions, transcrystallization (samples 3, 5, and 6) forms only when there is strong interaction, i.e. chemical bonding between glass fiber and PP, which is the basic condition so that the stress can be effectively transferred from the matrix to reinforcement.

Influence of block copolymer coupling agent on interfacial crystallization behavior

To investigate the interfacial crystallization behavior of glass fiber modified by different block copolymer coupling agent reinforced polypropylene, we design and synthesize a kind of di-block copolymer PS-b-PMPS with different PS block length and a kind of tri-block copolymer PS-b-PnBA-b-PMPS with different PnBA block length, in which PS is a 'hard' block and PnBA is a 'soft' block.

As indicated in Table 2 and Fig. 7, MPS, PS_{57}-b-$PMPS_{27}$, and PS_{149}-b-$PMPS_{27}$ modified glass fibers in the polypropylene matrix with MPP (10%) induce transcrystalline layers during isothermal crystallization at 135 °C, while all the tri-block copolymers modified glass fibers fail to transcrystallize.

To find out whether or not the poor interfacial adhesion leads to such phenomena, we measure the mean interfacial bond strength for different coupling agent modified glass fiber reinforced PP. As seen in Table 3, in the case of glass fiber modified by PS_{149}-b-$PnBA_{167}$-b-$PMPS_{21}$, the interfacial bond strength reaches 9.88 MPa when with 10% MPP, which is larger than that without MPP by almost

4 times. Although the interfacial bond strength of glass fiber modified by MPS (7.53 MPa) is higher than that of the glass fiber coated with PS_{57}-b-$PMPS_{27}$ (6.39 MPa), transcrystallinity occurs not only in the former but also in the latter. As expected, the strong interfacial adhesion forms in the case of both di-block and tri-block copolymers when with 10% MPP. So the interfacial adhesion is not the reason for fail to transcrystallize.

From Table 2, there is a transcrystalline layer in PP/GF modified by block copolymer without PnBA block at 135 °C isothermal crystallization. The reason is perhaps that the thermal stress can be effectively transferred from matrix to fiber because the silicon ends of the block copolymer react with glass fiber and the PS block is compatible with polypropylene. However, even when the length of PS block corresponding to the degree of polymerization (DP_n) increases from 57 to 149, the thermal stress cannot be released by the deformation of PS block because the molecular flexibility of PS is lower than that of PnBA and PP, which is related to its higher glass transition temperature. Similar to MPS, di-block PS-b-PMPS can effectively transfers tress but not relax it.

The result is different when the fiber is modified by block copolymer with PnBA block. Compared with PS block, PnBA block has low glass transition temperature and its molecular chain presents high flexibility. It can distribute stress by the slippage of the chain segments. When glass fiber reinforced polypropylene composites are cooled from melting temperature, thermal stress abates slowly while encountering the flexible interlayer of PS-b-PnBA-b-PMPS and at the end it is not large enough to induce transcrystallization (samples 8 and 9). Even when

Fig. 7 Photographs of the border in PP/GF modified by different block copolymer coupling agent in isothermal crystallization at 135 °C (×500) (**a**) Sample 4(PP+GF (PS57-b-PMPS27)) (**b**) Sample 5(PP+MPP (10%)+GF (PS57-b-PMPS27)) (**c**) Sample 7(PP+MPP (10%)+GF (PS149-b-PnBA55-b-PMPS10))
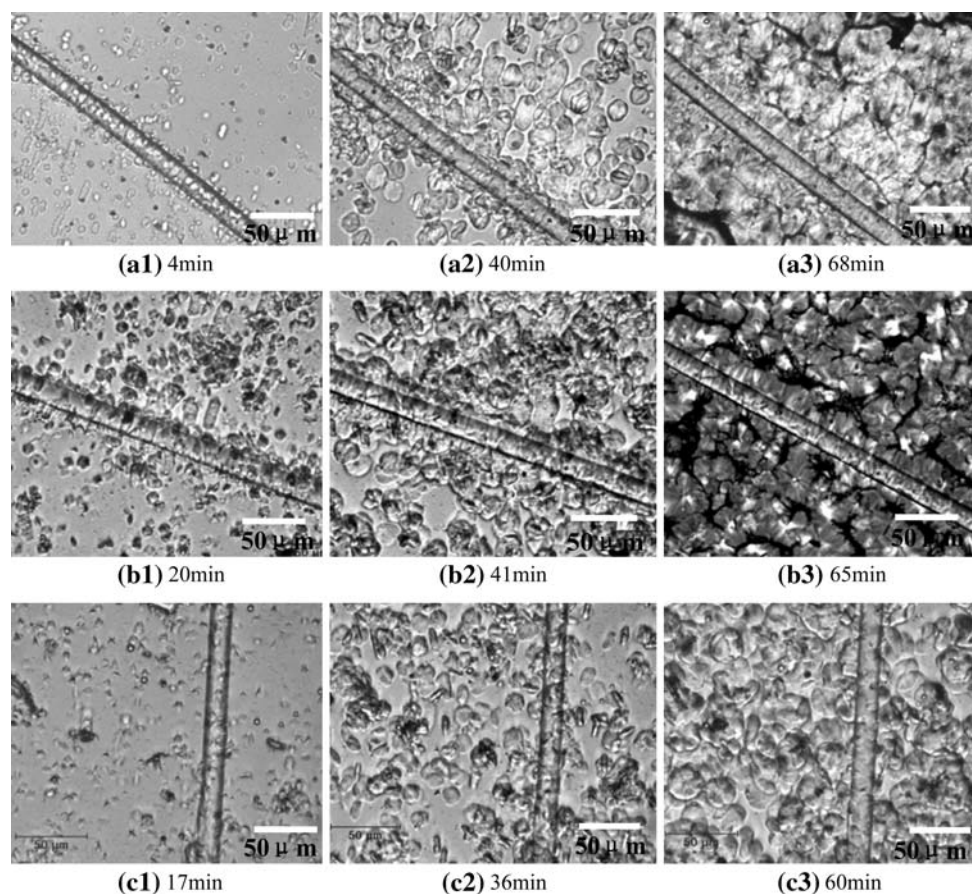
Fig. 8 Optical micrographs of isothermal crystallization at 150 °C under static condition (×500) (**a**) Sample 3(PP+MPP (10%)+GF (MPS)) (**b**) Sample 6(PP+MPP (10%)+GF (PS149-b-PMPS21))

(**a1**) 24min (**a2**) 35min (**a3**) 60min

(**b1**) 18min (**b2**) 33min (**b3**) 58min
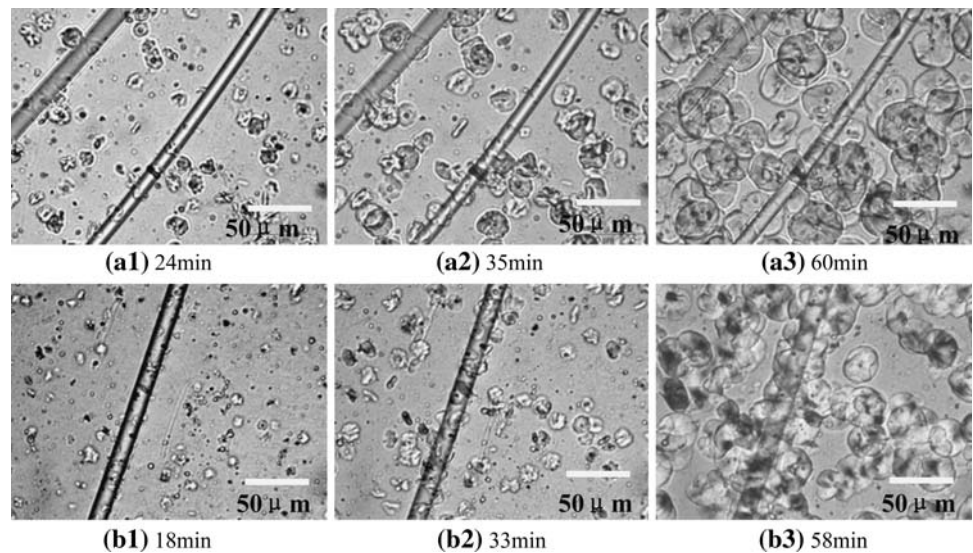
the DP_n of PnBA block is only 55 (sample 8), it can also relax the thermal stress by its larger deformation. As a result, when composites are cooled, no sufficiently high stress is present at the interface, and therefore there is no sufficient high-density nucleation along the fiber surface to form transcrystallization. From Fig. 7c, the crystal nucleation and growth rates in the bulk and at the PP/modified glass fiber interface are found to be similar.

Increasing the temperature of isothermal crystallization to 150 °C, transcrystallization that occurred at 135 °C isothermal crystallization cannot be observed in PP/GF treated by MPS and PS-b-PMPS (samples 3, 5 and 6). As revealed in Table 2 and Fig. 8a, b, the density of crystal nuclei along the interphase region is not higher than that in bulk matrix at the initial stage and the crystal in interphase region and in the bulk propagated with a similar rate. The

Fig. 9 Optical micrographs of isothermal crystallization at 150 °C after sheared (×500) (**a**) Sample 3(PP+MPP (10%)+GF (MPS)) (**b**) Sample 6(PP+MPP (10%)+GF (PS149-b-PMPS21)) (**c**) Sample 7(PP+MPP (10%)+GF (PS149-b-PnBA55-b-PMPS10))

(**a1**) 4min (**a2**) 40min (**a3**) 68min

(**b1**) 20min (**b2**) 41min (**b3**) 65min

(**c1**) 17min (**c2**) 36min (**c3**) 60min

reason is molecular chain segment movement is accelerated at 150 °C and then no primary crystal nuclei occurs along the fiber surface to form transcrystallization.

Our results agree with those of Thomason et al. [8] and Chatterjee et al. [32]. Thomason observed that for carbon, aramid and glass fibers used in the iPP matrix, transcrystallized regions are identical below 138 °C and no transcrystallization has been observed above 138 °C.

Influence of shear on crystallization behavior

However, transcrystallization occurred again in samples 3, 5, and 6 at 150 °C isothermal crystallization when they were sheared at a fixed shearing rate of 0.001 s^{-1} for 30 s using a Linkam CSS450 optical shearing stage. We can see that a large number of crystal nuclei start firstly around the glass fiber (Fig. 9a, b, left), and then grow gradually along the radial direction of fibers, as illustrated in Fig. 9a, b (middle). Fig. 9a, b (right) show the complete crystallization where the transcrystalline layer has been affected by the growth of the spherulites in the bulk matrix. Shear promotes reorganization of molecular chains and the pre-orientation of the polymer molecules in the interface of fiber/PP. High concentration of ordered clusters is promoted by the alignment of chain segments under the shearing at the fiber-melt interface [33, 34].

The interfacial crystallization behavior of GF/PP changes when glass fiber is modified by PS-b-PnBA-b-PMPS. PS-b-PnBA-b-PMPS modified glass fiber does not induce the transcrystalline layer (sample 8 and 9), as shown in Fig. 9c, in which only spherulite grows.

The results of tri-block copolymer on crystallization behavior of GF/PP are also concluded in Table 2 under sheared condition. It is obvious that no transcrystallization takes place in PS-b-PnBA-b-PMPS modified glass fiber reinforced polypropylene composites because the flexible interlayer deformation of PS-b-PnBA-b-PMPS can also relax the shear stress induced by fiber/matrix interface shear. When the shear stress encounters the flexible interlayer of PS-b-PnBA-b-PMPS, similar to the thermal stress, it abates slowly and at the end it is not large enough to induce the ordered clusters along the interface to form high-density nuclei.

Conclusion

A kind of di-block copolymer PS-b-PMPS with different PS block length and a kind of tri-block copolymer PS-b-PnBA-b-PMPS with different PnBA block length were synthesized by atom transfer radical polymerization, in which PS was a 'hard' block and PnBA was a 'soft' block.

They can be used as coupling agents to adjust the interfacial crystallization behaviors of PP/glass fiber systems.

The results show that non-isothermal crystallization at any rate cannot induce transcrystallinity in glass fibers reinforced polypropylene composites and transcrystallization does not happen in the system without MPP (10%) in PP matrix because there is not strong chemical bonding between PP and glass fibers.

Transcrystallization appears when glass fiber is treated with MPS and PS-b-PMPS under isothermal crystallization at 135 °C in a PP/MAH-PP matrix, but it cannot be seen at 150 °C isothermal crystallization. However, it appears again at 150 °C isothermal crystallization after sheared.

The interfacial crystallization behavior changes when glass fiber is modified by tri-block copolymer PS-b-PnBA-b-PMPS. Transcrystallization does not be observed either under a static crystallization condition or under a shear-induced crystallization condition because the flexible interlayer deformation of PS-b-PnBA-b-PMPS can relax the interfacial stress.

It is possible to control the interfacial crystallization behavior of glass fiber/PP systems by controlling the molecular structure of block copolymer coupling agent.

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