**Coupling effects of glass fiber treatment and matrix modification on the interfacial
microstructures and the enhanced mechanical properties of glass
fiber/polypropylene composites**

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Submitted to *Composites Part B: Engineering* to the editor

Abstract: High performance polypropylene/glass fiber (PP/GF) composites were prepared by treating GF with a film former (GFf) containing a certain ratio of maleic anhydride grafted polypropylene (MPP) and a kind of β -nucleating agent (TMB-5) via impregnation method, and meanwhile introducing different amount of MPP in the matrix. The coupling effects of GF treatment and the matrix modification on the mechanical properties and interfacial microstructures were investigated in detail. It is found that the film former can efficiently facilitate both the interfacial adhesion and β -transcrystallinity with the aid of appropriate MPP in the matrix. Addition of small amount of MPP (2 wt%) to the matrix in GFf system could significantly improve the mechanical properties with ca. 100% and 178% enhancements in tensile and impact strength, respectively, compared to the commercial GF reinforced PP (PP/GFc). With further increase of MPP content, the tensile strength of the composite increases slightly, accompanied by deterioration of the impact strength. The dramatically improved mechanical properties can be attributed to the simultaneously enhanced interfacial adhesion and β -form transcrystallinity through the coupling effects of nucleating agent locked by MPP on the surface of GFf and those MPP in both the film former and matrix. A schematic mechanism of interfacial microstructure formation is depicted, in which the diffusivity of MPP and PP, the nucleating agent and the molecular interactions are considered as key factors influencing the formation of β -transcrystallinity and interfacial adhesion.

Keywords: Polypropylene; Film former; Interfacial adhesion; β -transcrystallinity

1. Introduction

There has been a rapid growth in the development and application of fiber-reinforced polypropylene (PP) composites due to the commercial significance in recent years^[1,2]. Parallel to this growth has been the increasing recognition of the need to better control the microstructure and further understand the structure-property relationships in composites. It is well known that the addition of fibers including glass fiber (GF), carbon fiber, cellulose fiber, etc. into PP can result in changes in morphology and crystallization behavior at the interface^[3-7]. PP reinforced by GF has been widely used in pipes, automobile, and household appliances due to its high performance such as good corrosion resistance, excellent thermal resistance and, more importantly, low cost. Up to now, the common consensus is that the interfacial adhesion and crystallization as key factors could influence the properties of PP/GF composites. In order to improve the interfacial adhesion between PP and GF, several strategies were developed: one is the surface treatments of GF using binders^[4], nucleating agents^[8] or coupling agents^[9]; the other is introducing interfacial compatibilizer to the matrix including MPP^[10] (polypropylene-g-maleic anhydride), SEBS^[11] (styrene butadiene styrene block copolymer), SEBS-g-MA^[12] (styrene butadiene styrene block copolymer-g-maleic anhydride), DDP([(6-oxido-6H-dibenz[c,e][1,2]oxaphosphorin-6-yl)-methyl]-butanedioic acid)^[13]; and meanwhile the matrix treatment by oxygen plasma is sometimes adopted^[14]. On the other hand, crystallization at the

interface between PP and GF generally occurring as oriented columnar form crystal and defined as transcrystallinity has been extensively investigated to modulate the properties of PP/GF. However, how such peculiar transcrystallinity at the interface influences the interfacial and bulk properties is still in controversy^[15-18]. Most researchers agreed that the transcrystallinity could help to enhance the mechanical properties^[15,17] and the generation of β -transcrystalline might further toughen the materials^[19,20], but some others derived the opposite conclusions^[16,18]. Therefore, how to optimize the properties of the composites through tuning the interfacial microstructures and clarify the structure-property relationships are still challenging works.

Tremendous efforts have been concentrated on the mechanism of transcrystallinity formation. It is commonly recognized that under certain conditions^[21], the fibers could induce a relatively high density of crystal nuclei on their surface, therefore spherulites of the matrix grow from the fibers along the radial direction and then produce a columnar layer of crystalline structure. Gray^[22] found for the first time that slight mechanical stress at the interface of iPP/GF system could give rise to surface nucleation on which transcrystallinity will grow. Furthermore, Devaux et al.^[23] reported that the applied mechanical stress at iPP/GF interface during cooling could induce different crystalline superstructures (α - or β -transcrystalline), depending on the stress intensity and temperature. The classical explanation is that by pulling GF in single filament system, the sheared iPP melt near the surface of GF is more likely to form α -row nuclei and under certain conditions the β -crystal can be induced during crystal growth, leading

to the formation of β -transcrystallinity, but whether it can be applied to other systems and what is the specific forming condition are not well defined. Assouline et al.^[24] considered that α -crystal is more likely to occur on high modulus fibers such as Kevlar fiber, carbon fiber etc. based on studying the kinetics of α - and β -transcrystallinity. While the β -transcrystallinity is reported tending to form on GF under particular conditions or surface treatments. For example, Xie et al.^[19] obtained β -transcrystallinity through acid corrosion of GF and meanwhile applying pre-shear. Fu's group^[20] coated oxide graphene on the surface of GF, which, serving as wonderful nucleating agent, induced vivid β -transcrystallinity on GF. In all, there is no universal criterion to figure out the mechanism of transcrystallinity for different fiber reinforced PP composites and the transformation of the crystal types is not well understood.

Even though most researchers^[25-27] considered that the generation of transcrystallinity could lead to strong interfacial adhesion as evidenced by the enhancement of interfacial shearing strength (IFSS) or the improvements of interface situation observed by the SEM but exceptions also exist^[16,18]. Thus it is still ambiguous to distinguish transcrystallization and adhesion because the definition of adhesion is strongly dependent on the testing methods such as SEM, microdebonding test et al. and particular testing conditions like temperature, size etc.^[10,15-18,28,29]. More confusingly, similar to the chicken-and-egg paradox, for transcrystallinity and interfacial adhesion herein, it is still unclear which one is the prerequisite to the other. On one hand, the adhesion as one of the factors could facilitate the formation of transcrystallinity. For

example, Wang et al.^[30] found that chemical bonding, rather than the physical adhesion, between GF and PP could induce the transcrystallinity. But Fu's group obtained transcrystallinity between GF and PP only with physical adhesion^[31,32]. On the other hand, the transcrystallinity as a kind of microstructure will not only directly influence the adhesion^[26,27], but also contribute to the composites' performance which is often indirectly used to judge whether the adhesion is good or not^[10,31]. For example, as mentioned above the transcrystallinity could help to enhance the adhesion in most cases^[20,27] and β -transcrystallinity will make the materials tougher^[19]. Based on the above discussion, we consider that it is necessary to clarify what is the specifically defined interface and how the interrelation between adhesion and transcrystallinity and their coupling affect the performance of the composites.

In this study, the commercial GF was treated by a film former containing a certain ratio of compatibilizer MPP and β -nucleating agent TMB-5 and the PP matrix was further modified with different amount of MPP. The melt flow rate (MFR) of MPP is very high, which make the molecular chain move to the surface of GF more fleetly. TMB-5 is proven an excellent β -nucleating agent with high conversion rate of β - crystal ($\geq 90\%$)^[33-36] and low costs. Previous published literatures^[37,38] have applied TMB-5 in PP matrix for inducing β -nucleation and the crystallization kinetics was investigated. It was demonstrated that the addition of TMB-5 in PP is not only beneficial to the processability of the products^[39], but more importantly, could significantly enhance the impact strength with less or even not scarification of tensile strength by facilitating the

formation of β - crystal^[33]. Different from commonly used surface treatment, this film former could simultaneously facilitate the interfacial adhesion and β -transcrystallinity between GF and PP. Combining GF treatment and matrix modification, the mechanical properties of PP/GF composites were improved significantly (with 100% and 178% enhancements in tensile and impact strengths, respectively, as an example). The coupling effect of film former and compatibilizer MPP in the matrix on the microstructures particularly the transcrystallinity and the interfacial morphology will be discussed in detail. The positive impact of the film former on the mechanical properties and crystallization behavior of the composite is highlighted. The relationship between mechanical properties and the microstructures evolution will shed new light on the structure design of high performance composites.

2. Material and methods

2.1 Materials and sample preparation

The polypropylene (PP) with $M_w = 355,000$ g/mol, molecular weight distribution of 3.76 and MFR of 50g/10min was purchased from Exxonmobil (trade mark A501). The continuous glass fiber (GF) was supplied by Huayuan electronic materials company of Neijiang, China. Polypropylene-g-maleic anhydride (MPP) with $M_w = 169,000$ g/mol, molecular weight distribution of 18.21, graft ratio of 0.9wt%, and MFR of 83g/10min was supplied by Chenguang Co, China and used as compatibilizer. Aryl amide based β -nucleating agent (TMB-5) was purchased from Shanxi Provincial Institute of Chemical Industry, China. The Chemical structure presented as below has been

proven in the literatures^[33,36,39]:

The surface treatment of glass fiber with film former was realized by impregnation method as illustrated in scheme 1. A certain ratio of MPP and TMB-5 (100:1 by mass) were first dissolved in xylene at 120°C with 4 h stirring. After that, the hot solution was transferred into a larger flask containing 100 g GF and kept for 15 min dipping at the same temperature. The fully impregnated GF was subsequently precipitated and washed with large amount of cold methanol. To eliminate the redundant absorbed solvents, the treated GF covered with a layer of film former as illustrated in Scheme 1 was first dried in air for one day and further dried in vacuum oven at 80°C for 24 h until the constant weight reached. After drying, the total weight of film former containing MPP and TMB-5 coated on the surface of GF was about 6 wt%.

Composites with different formulations listed in Table 1 were first mixed in a HT-30 twin-screw extruder at 190°C with the rotational speed of 75 rpm. The extrudates were dried and kept in a vacuum oven at 80°C before injection molded in a NEX50 injection machine.

2.2 FTIR characterization

Fourier Transform Infrared Spectroscopy (FTIR) spectrums were recorded on a

NICOLET 6700 MAGNA IR spectrometer for GFc, GFf and GFc ablated by muffle as control. The GF samples were grinded into powder before use.

2.3 Mechanical tests

The electro-universal testing machine (Instron 5569) was used to measure the tensile strength of the composites, with crosshead speed of 50mm/min. For the notched Izod (2mm) impact strength, the injection molded parts were tested with a JXUD5.5 impact tester. The tensile and impact strength for each sample were both obtained as averages at least of 5 measurements.

2.4 Optical microscope observation

A single GF was placed between two PPthin films (about 25 μ m) and hot pressed at 200°C to form sandwiched composite. Isothermal crystallization of the sandwiched sample was observed by using polarized optical microscope (Olympus BX61) with Linkman hot stage at different temperatures, before which the samples were first melted at 200°C for 10min to eliminate the thermal history.

2.5SEMobservation

The interfacial adhesion and the crystal morphology between GF and PP was observed by scanning electron microscope (SEM) JSM-5900LV. The injection molded samples were cryo-fractured in liquid nitrogen. For the PP/2MPP/GFf sample, the cryo-fractured surfaces were further etched by xylene at room temperature for 72h to observe the crystal morphology. Before observation, all samples were coated with gold powder.

2.6 DSC measurements

Differential scanning calorimetry (DSC) analysis was carried out on a TA Q20 (USA) instrument with the sample weight of about 5.0mg under nitrogen purge. The samples were first heated to 200°C and held for 10min to eliminate the thermal history, and then cooled to 40°C with a rate of 10°C/min, after that the samples were subsequently heated to 200°C at the same rate for the second run.

2.7 XRD measurements

The samples for X-ray diffraction measurement with a XRD instrument Ultima IV (supply voltage: 20-60kv; goniometer radius: 185mm) were machined from the 10mm wide and 4mm thick chunk. The relative amount of β -crystal was calculated according to Turner-Jones equation^[40]:

$$K_{\beta} = \frac{I_{\beta 1}}{I_{\beta 1} + I_{\alpha 1} + I_{\alpha 2} + I_{\alpha 3}} \quad (1)$$

Where $I_{\beta 1}$ is the peak intensity of the β (300) plane, and $I_{\alpha 1}$, $I_{\alpha 2}$ and $I_{\alpha 3}$ are the peak intensity of (110), (040) and (130), respectively.

3. Results and Discussion

3.1 Analysis of the surface treatments on GF

Fig. 1 shows the FTIR spectra for GFc, GFf and GF-muffle as control. As seen in Fig. 1a, FTIR spectra of different glass fibers are nearly identical except they represent regions of 1300-1600 cm^{-1} and 2600-3100 cm^{-1} as marked in b and c squares. Fig. 1b and 1c are the corresponding enlarged spectra. As marked in Fig. 1b, compared with GFc and GF-muffle, the absorbance peaks observed at 1378 and 1460 cm^{-1} for GFf sample

represent the characteristic C-H symmetric and asymmetric bending vibration of $-\text{CH}_3$, respectively, indicating the existence of MPP on the surface of GF. As shown in Fig. 1c, there is none absorbance observed for the GF-muffle sample, while several strong absorbance peaks between 2800 cm^{-1} and 3000 cm^{-1} can be seen for GFf sample, which is ascribed to the C-H stretching vibrations of MPP backbone^[41]. This also suggests that MPP as the main component of the film former has been coated on the surface of GF. For GFc sample, absorbances at the wavenumber of 2854 , 2925 and 2957 cm^{-1} represent various C-H symmetric and asymmetric stretching vibrations of $-\text{CH}$, $-\text{CH}_2$, and $-\text{CH}_3$ and we speculate the commercial GF might be coated a layer of wax when it was produced.

3.2 Mechanical properties of the PP/GF composites

The tensile and the impact strength of PP/GF composites with different formulations are summarized in Table 2, and illustrated in Fig. 2. With the addition of 20 wt% commercial glass-fibers (GFc), the tensile strength slightly increased while the impact strength decreased remarkably. In sharp contrast to the PP/GFc sample, the PP/GFf composite showed drastic enhancement in tensile strength and intermediate increase in impact strength at the same GF content. Upon blending with 2 wt% MPP, the PP/2MPP/GFf composite showed comparable tensile strength to that of PP/GFf, the impact strength, on the other hand, was enhanced significantly. With increasing MPP content, the tensile strength increased modestly while the impact strength decreased significantly at more than 3 wt% of MPP. However, comparing with

PP/GFc samples as control, both the tensile and impact strengths of PP/MPP/GFf composites are simultaneously enhanced, by 100% and 178% enhancements, respectively, for the PP/2MPP/GFf composite. The observed simultaneous enhancement in both tensile and impact strength is surprising and different from the common trend of traditional polymer^[42]. From the mechanical properties of Samples #3-5, it seems that the optimal MPP content is about 1.8-3.0 wt% for the PP/GFf composites. Such fantastically improved performance can be attributed to the coupling effect of enhanced interfacial adhesion and the formation of β -crystals, more specifically the formation of β -transcrystallinity at the interface^[43-46]. The enhanced interfacial adhesion is ascribed to the interaction between the maleic anhydride group and the -OH group on the surface of GF, and the β -transcrystallinity is considered to be caused by the interaction between GFf and matrix, and most importantly, directed nucleation at GF surface due to the presence of nucleating agent in the film former.

3.3 SEM observation of interfacial adhesion

To verify the contribution of the interfacial adhesion between PP and GF to the mechanical properties of the composites, SEM was used to observe the fracture surfaces for PP/GFc, PP/GFf, PP/2MPP/GFf, PP/3MPP/GFf and PP/10MPP/GFf samples, and the corresponding micrographs are depicted in Fig. 3. For the PP/GFc sample as shown in Fig. 3a and 3a1, the debonding GF surface looks so smooth and poor interfacial adhesion is observed, which causes the poor mechanical properties especially the impact strength of the composite. When treated using the film former as described

in experimental section, the interfacial adhesion of the PP/GF composite is obviously improved and a layer of remnant polymer can be observed on the part of the GF surface as shown in Fig. 3b and 3b1. With the addition of 2 wt% MPP, the interfacial adhesion is further improved, more specifically, the covering polymer layer on the GF surface seems thicker and with a roughen fracture surface, as can be seen in Fig. 3c and 3c1. With the further increasing MPP to 3 wt% and 10 wt% in the matrix, the situation of the interface seems not change so much as shown in Fig. 3d and 3e. The SEM data suggest that the film former could enhance the interfacial adhesion and the small amount of MPP addition below 2 wt% in the matrix could further improve the interfacial interaction, but when the content of MPP increases to 3 wt% and 10 wt%, the interaction between film former and MPP in the matrix is saturated, thus the changes of interfacial adhesion in SEM is not so apparent. This synergistic coupling effect is hypothesized to arise from the strong interactions between the MPP molecules in the film former coated and anchored on to the surface of GF and those added in the matrix, which play a vital role on the improved mechanical properties of the composites. The nearly identical interface microstructures with the increasing MPP content in the matrix as shown in Fig. 3c, 3d and 3e seem not consistent with the variation of the mechanical properties of the composites illustrated in Fig. 2. This apparent inconsistency might be ascribed to the more elaborated microstructures at the interface such as the crystal form, transcrystallinity etc., which as key factors also influence the performance of composites significantly, especially on impact strength.

3.4 Crystallization behaviors of the composites

The DSC cooling and second heating scan curves of the PP/GFcomposites and the pure MPP and PP are shown in Fig. 4. Interestingly, as shown in Fig.4a, the introduction of GFc leads to lower crystallization temperature T_c than that of pure PP, which is consistent with Wagner's work^[8], indicating reduced nucleation. In contrast, addition of GFf slightly enhances nucleation as evidenced by the higher T_c . Note that in the film former, small amount of β -nucleating agent is involved, which induces nucleation. Upon blending with 2wt%MPP in the matrix, T_c evidently shifts to much higher values. With increasing MPP content, T_c shifts to lower values gradually, indicating reduced crystallization. This is because more MPP with lowernucleating ability involves the crystallization of PP matrix. One can see that there is an optimal MPPcontent in the matrix to induce the crystallization, which might be beneficial to the formation of β -transcrystallinity and helps to improve the performance of materials. In Fig.4b during the heating process, the melting peaks of β -form crystal at about 152°C can be obviously seen for the composites with GFf. This indicates that the β -nucleating agent in the film former could induce plentiful and preferentially the β -form crystals at the interface. With the appearance of β -crystal peaks upon addition of GFf and MPP, those peak heights ofthe α -form crystal decreases significantly compared tothe pure PP and PP/GFc samples.

For clarity, the thermal parameters including T_c , the melting temperature T_m of α - and β -form crystals, and the corresponding enthalpy values ΔH for composites and pure

PP are listed in Table 3. With increasing MPP content, the T_m values of both α -crystal and β -crystal decrease slightly due to the lower melting point of MPP. Addition of 2wt% MPP leads to obvious increase of melting enthalpy of β -crystal $\Delta H_{\beta m}$, while with the increase of MPP content $\Delta H_{\beta m}$ decreases evidently. The ratio of $\Delta H_{\beta m}/\Delta H_{\alpha m}$ reaches the maximum value of about 6 for the PP/2MPP/GF sample, which is a strong evidence to support the sharply enhanced mechanical properties, especially the impact strength.

Fig. 5 shows the changes of $T_{\beta m}$ and $\Delta H_{\beta m}$ with the content of MPP in the matrix. In this figure, the sharply increase of the $\Delta H_{\beta m}$ for PP/2MPP/GF sample and its drastic decrease with MPP content can also be clearly seen. The $\Delta H_{\beta m}$ is consistent with the observed impact strength of the composite materials in spite of potential variations in the practical processing conditions. The variation of $T_{\beta m}$ with MPP content reveals that MPP could be the defects of PP crystals and results in the lower melting point, especially at higher content of 10 wt%, which is disadvantageous to the thermal performance of materials and maybe to the mechanical performance. The optimum values of $T_{\beta m}$ and $\Delta H_{\beta m}$ are also located in 1.8~3.0 wt% MPP region, which is well consistent with the range of mechanical properties.

Fig. 6 shows the typical of XRD curves for the injection molded PP/GF composites and the pure PP sample of this study. The peaks located at $2\theta = 13.8^\circ, 16.5^\circ, 18.3^\circ$ are assigned to the reflection of (110), (040), (130) planes of PP crystals, respectively, based on the α -form monoclinic packing of PP^[47]. In Fig. 6a, it is worthy to be noticed that the pure PP possesses better defined peaks than those of its composites, especially at the

(040) plane, which implies that the loading of GF disturbed the defined crystalline structure of PP and decreased the portion of crystallinity in the samples. Fig.6b shows the enlarged diffraction peaks of the composite samples as marked in the dashed square in Fig.6a. Compared to the PP/GFc composite, the (040) diffraction peak of PP/GFf composite diminishes evidently, which might be due to poor completion degree of α -crystal which is ascribed to lots of nucleating agents in PP. Upon blending 2 wt% MPP in the matrix, an additional reflection at $2\theta = 15.7^\circ$ appears, which is an unique diffraction peak of the β -crystals corresponding to (300) plane reflection^[48]. The intensity of the β -crystal reflection decreases when MPP content increases to 3 wt%, and it almost disappears when MPP content increases further to 10 wt%. To quantify the content of β -crystals K_β in the composites, peak fitting of the XRD curves was performed and the β -crystals content was calculated using eq. (1). The obtained K_β values for the PP/2MPP/GFf and PP/3MPP/GFf composites are 23.6% and 20.4%, respectively. This is consistent with the DSC results (See Table 2 and Fig. 4b). The DSC and XRD data coherently indicate that the content of MPP has an optimal value facilitating the formation of β -crystal, and this occurs at about 2 wt% MPP for the injection molded samples. We thus consider that the nucleating agent in the film former can easily induce β -crystal of PP matrix and meanwhile the lower content of MPP will facilitates this crystallization.

3.5 Interfacial transcrystallinity

To further clarify whether the β -crystal appears at the interface between GF and PP

and whether the often reported transcrystallinity occurs in the current system, optical microscope was used to capture the crystallization process of the single fiber sandwiched samples. Fig.7 compares the development of isothermal crystallization near the GF surface prepared with different treatments at 135°C. As can be seen, the PP crystals nucleate randomly and grow into larger spherulites in the PP/GFc sample, in spite of the presence of GF. In sharp contrast, nuclei appear to grow concentrated near the surface of GF at the early stage of crystallization in the PP/GFf sample. After 600s, a layer of oriented crystalline lamellae surrounding GFf develops, accompanied with scattered crystal growth in the bulk PP matrix. This well-defined superstructure is identified as the transcrystalline interface and the uniform transcrystalline growth front indicates the high nucleating ability of the GFf toward the substrate. Further away from the GFf in the matrix, the PP spherulites can be observed. The impingement of the transcrystalline interface and bulk spherulites also occur at the late stage of crystallization. In addition, it was confirmed from the above XRD results that the transcrystal is a β -form crystallinity.

Fig. 8 shows a series of interfacial crystallization images taken at different temperatures for various time of the PP/GFf composite. Within the same crystallization time of 1080 s, transcrystals are all successfully induced at different temperatures of 138, 140 and 142°C, indicating the enhanced nucleation ability of GFf. However, at the higher temperature (142 °C) for shorter time of 600 s, transcrystallinity develops so slow that the nuclei on the surface of the GF can hardly be observed.

Fig. 9 shows the SEM micrograph of etched fractured surface of the injection molded PP/2MPP/GFf sample. The β -transcrystals are clearly shown at the PP/GF interface as spikes grown perpendicular to the GF surface. This observation suggests that the β -transcrystals could be formed in the injection-molded bar without special processing conditions^[32]. As revealed in Fig. 9, the β -transcrystals showed very good adhesion to the GFf surface, and this structure can contribute effectively to stress transfer between GF and the matrix. As a result of this unique fibrillar transcrystalline structure, and to the best of our knowledge, the PP/MPP/GFf composites of this study exhibited the highest mechanical property enhancement compared with the previously published data^[27].

3.6 Mechanism of interface formation

As discussed above in Fig. 3, small amount of MPP (2 wt%) in the matrix and combined with the film former on GF could provide good interfacial adhesion and hence the optimized mechanical properties. While increasing MPP content leads to the deteriorate impact strength, which is ascribed to the reduced β -transcrystallinity as evidenced in Fig. 6. To elucidate the coupling effects of the as-prepared film former and MPP dispersed in the matrix on the formation of interface between GF and PP from the molecular point of view, a schematic mechanism including molecular interaction and polymer chain motion is illustrated Fig. 10. On the surface of GF, a layer of film former containing MPP and small amount of nucleating agent (TMB-5) can be observed, in which a large portion of MPP are anchored on the surface of GF via hydrogen

bonding between -OH and -CO- as shown in Fig. 10, and meanwhile the anchored MPP chains lock the TMB-5 tightly on the surface of GF. When the resin is melted, the compatibilizer MPP chains with lower molecular weight in the PP matrix first move to the surface of GF because the shorter chains have shorter relaxation time and diffuse much faster than the longer ones. The diffusion of the shorter chains could drive the movement of the longer chains. The integrated movement of the polymer chains is originated from the thermodynamic driving force of the compatibilizer MPP^[10]. Due to the much wider polydispersity of MPP (18.21), those longer chains are far beyond the entanglement molecular weight ($M_{c1} = 15000$ g/mol) and tend to entangle with the matrix PP ($M_{c2} = 13800$ g/mol) chains^[49-51]. Thus the movement of MPP chains will promote the integrated diffusion of entangled PP chains to the surface of GF, where TMB-5 as β -nucleating agent subsequently initiate the formation of β -transcrystal of PP under cooling. However, upon loading more MPP in the matrix, large number of MPP chains with poor nucleating ability (demonstrated in Fig. 4a) diffusing to the surface of GF might form a protection layer of TMB-5 and hence weaken its nucleating efficiency to the PP chains, which is the main reason why redundant MPP (above 3 wt%) is negative to the performance of PP/GF composites. Besides the diffusion of polymer chains during the melting process, there is also a possibility of TMB-5 released from the surface of GF especially under shear, which also facilitate the formation of β -transcrystal of PP matrix when they met with each other. Nevertheless, there is an optimum amount of MPP required in the matrix (1.8~3.0 wt%), below which i.e. for the

formulation of PP/GFf, the nucleation of β -transcrystal is frustrated because of the absence of the driving MPP chains; while above which the redundant MPP will decrease the nucleating efficiency of β -transcrystal. In conclusion, as illustrated in Fig. 10, the nucleating ability of GFf, the diffusivity of polymer chains and the interaction between matrix and GFf are key factors for the formation of interface, which, in turn, has dominating effects on the mechanical properties of the composites.

4. Conclusions

This work aims to evaluate the influence of film former and MPP in the matrix on performance of PP/GF composites. The results indicate that the film former can nucleate the growth of β -transcrystal on the surface of GF and provide a strong interfacial adhesion between GF and PP. The content of MPP in the matrix has an optimum value to facilitate the formation of β -transcrystal at the interface and provide stronger interfacial binding between the fiber and matrix. Compared to the PP/GF composite, the PP/2MPP/GFf sample exhibited improvements of 100% and 178% in tensile and impact strength, respectively, which are the highest reported improvements to the best of our knowledge. Further increase in MPP content resulted in slight increase of tensile strength accompanied by deterioration in impact strength. Both the β -transcrystal and improved interfacial adhesion are related to contribute to the observed enhancement of the mechanical properties of the composites.

Acknowledgements Y.H. Niu thanks financial supports from the National Science Foundation of China with grant number 51573115 and the Technical Innovation Project

of National Institute of Clean and Low-Carbon Energy (No. 15H0543). G.X. Li thanks financial support from the National Science Foundation of China with grant number 51421061.

References

1. Suhara P, Mohini S. Injection-molded short hemp fiber/glass fiber reinforced polypropylene hybrid composites—mechanical, water absorption and thermal properties. *J Appl Poly Sci* 2007;103:2432-2441.
2. Duan SY, Mo FH, Yang XJ, Tao YR, Wu DS, Peng Y. Experimental and numerical investigations of strain rate effects on mechanical properties of LGFRP composite. *Compos Part B-Eng* 2016;88:101-107.
3. Arikan V, Sayman O. Comparative study on repeated impact response of E-glass fiber reinforced polypropylene & epoxy matrix composites. *Compos Part B-Eng* 2015;83:1-6.
4. Thomason JL, Schoolenberg GE. An investigation of glass fibre/polypropylene interface strength and its effect on composite properties. *Compos Part A-Appl Sci Manuf* 1994;25:197-203.
5. Zhang SJ, Kumar S, Minus ML, Zhu L, Wong CP. Polymer transcrystallinity induced by carbon nanotubes. *Polymer* 2008;49:1356-1364.
6. Gray DG. Transcrystallization of polypropylene at cellulose nanocrystal surfaces. *Cellulose* 2008;15:297-301.
7. Karsli NG, Yesil S, Aytac A. Effect of hybrid carbon nanotube/short glass fiber

- reinforcement on the properties of polypropylene composites. *Compos Part B-Eng* 2014;63:154-160.
8. Wagner HD, Lustiger A, Marzinsky CN, Mueller RR. Interlamellar failure at transcrystalline interfaces in glass/polypropylene composites. *Compos Sci Technol* 1993;48:81-84.
 9. Yue CY, Quek MY. The interfacial properties of fibrous composites. Part III. Effect of the thickness of the silane coupling agent. *J Mater Sci* 1994;29:2487-9240.
 10. Bikiaris D, Larena A, Flaris V, Panayiotou C. Use of silane agents and poly(propylene-g-maleic anhydride) copolymer as adhesion promoters in glass fiber/polypropylene composites. *J Appl Poly Sci* 2001;81:701-709.
 11. Tjong SC, Xu SA, Li KY, Mai YW. Mechanical behavior and fracture toughness evaluation of maleic anhydride compatibilized short glass fiber/SEBS/polypropylene hybrid composites. *Compos Sci Technol* 2002;62:831-840.
 12. Matjaz D, Vojko M, Ivan S. Polypropylene/talc/SEBS (SEBS-g-MA) composites. Part II. Mechanical properties. *Compos Part A-Appl Sci Manuf* 2005;36:1282-1290.
 13. Chen XX, Yuan L, Zhang ZY, Wang H, Liang GZ, Gu AJ. New glass fiber/bismaleimide composites with significantly improved flame retardancy, higher mechanical strength and lower dielectric loss. *Compos Part B-Eng* 2015;71:96-102.
 14. Sako N, Matsuoka T, Sakaguchi K. Proceedings of the international conference on fiber reinforced composites. In: *First International Conference on Composites in*

- Infrastructure. Tucson, April, 1998. p.15-17.
15. Chen EJH, Hsiao BS. The effects of transcrystalline interphase in advanced polymer composites. *Polym Eng Sci* 1992;32:280-286.
 16. Gati A, Wagner H. Stress transfer efficiency in semicrystalline based composites comprising transcrystalline interlayers. *Macromolecules* 1997;30:3933-3935.
 17. Stadlbauer M, Janeschitz-Kriegl H, Eder G, Ratajski E. New extensional rheometer for creep flow at high tensile stress. Part II. Flow induced nucleation for the crystallization of iPP. *J Rheol* 2004;48:631-639.
 18. Stern T, Teishev A, Marom G. Composites of polyethylene reinforced with chopped polyethylene fibers: effect of transcrystalline interphase. *Compos Sci Technol* 1997;57:1009-1015.
 19. Xie MC, Chang BB, Liu HL, Dai K, Zheng GQ, Liu CT, Shen CY, Chen JB. Enhanced β -crystal formation of isotactic polypropylene under the combined effects of acid-corroded glass fiber and preshearing. *Polym Compos* 2013;34:1250-1260.
 20. Ning NY, Zhang W, Yan JJ, Xu F, Wang TN, Su H, Tang CY, Fu Q. Largely enhanced crystallization of semi-crystalline polymer on the surface of glass fiber by using graphene oxide as a modifier. *Polymer* 2013;54:303-309.
 21. Quan H, Li ZM, Yang MB, Huang R. On transcrystallinity in semi-crystalline polymer composites. *Compos Sci Technol* 2005;65:999-1021.
 22. Gray DG. "Transcrystallization" induced by mechanical stress on a polypropylene melt. *Polym Lett Ed* 1974;12:645-650.

23. Devaux E, Chabert B. Nature and origin of the transcrystalline interphase of polypropylene/glass fibre composites after a shear stress. *J Mich State Med Soc* 1957;56:728-730.
24. Assouline E, Pohl S, Fulchiron R, Gerardd JF, Lustigere A, Wagner HD, Marom G. The kinetics of α - and β -transcrystallization in fibre-reinforced polypropylene. *Polymer* 2000;41:7843-7854.
25. Sorrentino L, Simeoli G, Iannace S, Russo P. Mechanical performance optimization through interface strength gradation in PP/glass fibre reinforced composites. *Compos Part B-Eng* 2015;76:201-208.
1. Yaara A, Gad M. On the β -transition in high density polyethylene: the effect of transcrystallinity. *Macromol Rapid Commun* 2004;25:1387-1391.
2. Ning NY, Fu SR, Zhang W, Chen F, Wang K, Deng H, Zhang Q, Fu Q. Realizing the enhancement of interfacial interaction in semicrystalline polymer/filler composites via interfacial crystallization. *Prog Poly Sci* 2012;37:1425-1455.
3. Thomason JL, Yang L. Temperature dependence of the interfacial shear strength in glass-fibre polypropylene composites, *Compos Sci Technol* 2011;71:1600-1605.
4. Simeoli G, Acierno D, Meola C, Sorrentino L, Iannace S, Russo P. The role of interface strength on the low velocity impact behaviour of PP/glass fibre laminates. *Compos Part B-Eng* 2014;62:88-96.
5. Wang H. Master's degree thesis of East China University of Science and Technology. p15, 1996 (in Chinese).

6. Guo M, Yang H, Tan H, Wang C, Zhang Q, Du RN, Fu Q. Shear enhanced fiber orientation and adhesion in PP/glass fiber composites. *Macromol Mater Eng* 2006;291:239-246.
7. Wang K, Guo M, Zhao DG, Zhang Q, Du RN, Fu Q, Dong X, Han CC. Facilitating transcrystallization of polypropylene/glass fiber composites by imposed shear during injection molding. *Polymer* 2006;47:8374-8379.
8. Zhang XL, Zhang PS, Zhu BC, Liu XY, Yang CL. Research progress in the β -nucleating agent for polypropylene. *China synthetic resin and plastics* 2015;32:68-76.
9. Zhang JH. Preparation of novel aromatic amide nucleating agent and its effect on the crystallization of polypropylene[D]. Zhejiang, China: Zhejiang University of Technology, 2013.
10. Shi YQ. Study on controlled crystallization of isotactic polypropylene based on α -/ β - compounded nucleating agents and nucleation mechanism of nucleating agents. Shanghai, China: East China University of Science, 2012.
11. Kang J, Weng GS, Chen ZF, Chen JY, Cao Y, Yang F, Xiang M. New understanding in the influence of melt structure and β -nucleating agents on the polymorphic behavior of isotactic polypropylene. *RSC Adv* 2014;2:181-186.
12. Li M, Li, Zhang ZS, Dai X, Mai KC. Enhanced β -crystallization in polypropylene random copolymer with a supported β -nucleating agent. *Thermochim Acta* 2014;598:36-44.

13. Han L, Li XX, Li YL, Huang T, Wang Y, Wu J, Xiang FM. Influence of annealing on microstructure and physical properties of isotactic polypropylene/calcium carbonate composites with β -phase nucleating agent. *Mat Sci Eng A* 2010;527:3176-3185.
14. Shui HY. Study on propylene copolymer modified by β -nucleating agents[D]. Dalian, China: Dalian University of Technology, 2011.
15. Turner JA, Aizlewood JM, Beckett DR. Crystalline forms of isotactic polypropylene. *Macromol Chem Phys* 1963;75:134-158.
16. Machado AV, Covas JA, Duin MV. Effect of polyolefin structure on maleic anhydride grafting. *Polymer* 2001;42:3649-3655.
17. Sheng Q, Zhang Y, Xia C, Mi DS, Xu X, Wang T, Zhang J. A new insight into the effect of β modification on the mechanical properties of iPP: The role of crystalline morphology. *Mater Des* 2016;95:247-255.
18. Ma Z, Balzano L, Erp TV, Portale G, Peters GWM. Short-term flow induced crystallization in isotactic polypropylene: how short is short?. *Macromolecules* 2013;46:9249-9258.
19. Tang XG, Yang W, Shan GF, Yang B, Xie BH, Yang MB. Effect of temperature gradient on the development of β -phase polypropylene in dynamically vulcanized PP/EPDM blends. *Colloid Polym Sci* 2009;287:1237-1242.
20. Li H, Yan S. Surface-induced polymer crystallization and the resultant structures and morphologies. *Macromolecules* 2011;44:417-428.

21. Dean DM, Rebenfeld L, Register RA. Matrix molecular orientation in fiber-reinforced polypropylene composites. *J Mater Sci* 1998;33:4797-4812.
22. Somani RH, Hsiao BS, Nogales A, Fruitwala H, Srinivas S, Tsou AH. Structure development during shear flow induced crystallization of iPP: In situ wide-angle X-ray diffraction study. *Macromolecules* 2001;34:5902-5909.
23. Han R, Nie M, Wang Q. Control over β -form hybrid shish-kebab crystals in polypropylene pipe via coupled effect of self-assembly β -nucleating agent and rotation extrusion. *J TaiWan Inst Chem Eng* 2015;52:158-164.
24. Eckstein A, Suhm J, Friedrich C, Maier RD, Sassmannshausen J, Bochmann M, Mulhaupt R. Determination of plateau moduli and entanglement molecular weights of isotactic, syndiotactic, and atactic polypropylenes synthesized with metallocene catalysts. *Macromolecular* 1998;31:1335-1340.
25. Zhao WY, Huang YZ, Liao X, Yang Q. The molecular structure characteristics of long chain branched polypropylene and its effects on non-isothermal crystallization and mechanical properties. *polymer* 2013;54:445-1462.
26. Stadler FJ, Piel C, Kaschta J, Rulhoff S, Kaminsky W, Münstedt H. Dependence of the zero shear-rate viscosity and the viscosity function of linear high-density polyethylenes on the mass-average molar mass and polydispersity. *Rheol Acta* 2006;45:755-764.

Figure captions

Scheme 1. Procedures of GF surface treatment with film former.

Fig. 1. FTIR bands of GFc, GFf and the muffle ablated GFc named as GF-muffle.

Fig. 2. Tensile and impact strength for GF/PP composites with different formulations.

Fig. 3. SEM micrographs representing the interfacial adhesion between GF and PP matrix for PP/GFc (a, a1), PP/GFf (b, b1), PP/2MPP/GFf (c, c1), PP/3MPP/GFf (d, d1) PP/10MPP/GFf (e, e1). (a1), (b1), (c1), (d1) and (e1) are enlarged areas marked by the dashed yellow squares in (a), (b), (c), (d) and (e) respectively.

Fig. 4. DSC cooling (a) and heating (b) scans for PP, MPP and GF/PP composites.

Fig. 5. Variations of the melting point $T_{\beta m}$ and the normalized enthalpy $\Delta H_{\beta m}$ of β -crystals for PP/GF composites with different formulations.

Fig. 6. XRD curves for PP and PP/GF composites (a) and the enlarged reflections for the composites (b).

Fig. 7. In-situ polarized optical micrographs for single fiber sandwiched PP/GFc and PP/GFf samples during isothermal crystallization at 135 °C.

Fig. 8. Polarized optical micrographs of single fiber sandwiched PP/GFf sample at different isothermal crystallization temperatures for 600s and 1080s.

Fig. 9. SEM micrographs of the etched fracture surface for PP/2MPP/GFf injection molded sample.

Fig. 10. Schematic illustration of the interface formation between PP and GFf.

Luo et al. Scheme 1

Luo et al. Fig. 1a

Luo et al. Fig. 1b

Luo et al. Fig. 1b

Luo et al. Fig. 2

Luo et al. Fig. 3

Luo et al. Fig. 4a

Luo et al. Fig. 4b

Luo et al. Fig. 5

Luo et al. Fig. 6a

Luo et al. Fig. 6a

Luo et al. Fig. 7

Luo et al. Fig. 8

Luo et al. Fig. 9

Luo et al. Fig. 10

Table captions

Table 1. Samples codes and the corresponding formulations for PP/GF composites.

Table 2. Mechanical properties for PP/GF composites.

Table 3. Melting and crystallization parameters for PP and GF/PP composites.

Code number	Sample Codes	Formulations
1	PP	PP
2	PP/GFc	PP + 20%GFc (commercial)
3	PP/GFf	PP + 20%GFf (film former)
4	PP/2MPP/GFf	PP + 2%MPP + 20%GFf (film former)
5	PP/3MPP/GFf	PP + 3%MPP + 20%GFf (film former)
6	PP/10MPP/GFf	PP +10%MPP + 20%GFf (film former)

Luo et al. Table 1

Code number	Sample Codes	Tensile strength (MPa)	Impact strength (KJ/m ²)
1	PP	27.1	10.4
2	PP/GFc	31.3	5.1
3	PP/GFf	61.8	7.4
4	PP/2MPP/GFf	59.6	14.2
5	PP/3MPP/GFf	61.6	12.8

6	PP/10MPP/GFf	67.3	10.2
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Luo et al. Table 2

Samples	$T_c(^{\circ}\text{C})$	Normalized ΔH_c (J/g)	$T_{\alpha m}(^{\circ}\text{C})$	$T_{\beta m}(^{\circ}\text{C})$	Normalized $\Delta H_{\alpha m}$ (J/g)	Normalized $\Delta H_{\beta m}$ (J/g)
PP	127.07	77.2	165.73	---	73.3	---
PP/GFc	125.43	82.4	165.59	---	80.2	---
PP/GFf	126.07	82.9	165.82	152.50	12.3	43.4
PP/2MPP/GFf	127.53	87.9	166.03	152.29	11.2	66.0
PP/3MPP/GFf	127.04	87.5	165.81	152.18	12.2	59.1
PP/10MPP/GFf	122.10	105.0	164.24	151.05	25.6	48.0

Luo et al. Table 3