Physical and Rheological Properties of Maleic Anhydride-Incorporated PVDF: Does MAH Act as a Physical Crosslinking Point for PVDF Molecular Chains?

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ABSTRACT: The miscibility and physical and rheological properties of binary poly(vinylidene fluoride)/maleic anhydride (PVDF/MAH) blends have been systematically investigated. MAH was found to be miscible with PVDF by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). Fourier transform infrared (FTIR) investigations provided positive evidence for the specific interaction between the carbonyl groups of MAH and the methylene groups of PVDF. Rheological measurements showed that both the storage modulus and the melt viscosity of PVDF increase with the addition of MAH, followed by a decrease with excess MAH. In addition, the elongation of the PVDF/MAH blend with 10 wt % MAH is 589.7%, which is almost 5 times that of neat PVDF. It is concluded that MAH small molecules act as physical “crosslinking” points for the neighboring PVDF molecule chains due to this specific interaction between PVDF and MAH. Such a physical crosslinking function enhances the storage modulus, viscosity, and mechanical properties of PVDF.

1. INTRODUCTION

Poly(vinylidene fluoride) (PVDF) is an important semicrystalline fluoropolymer. Due to its excellent heat resistance, climate resistance, processability, and irradiation resistance, PVDF has attracted both academic and industrial attention. It is an economic and easy strategy to obtain high-performance PVDF composites by blending PVDF with other polymers.1−3 However, the overall improvement is limited due to the poor miscibility between PVDF and these polymers. Generally speaking, the final properties of the material are closely related to the compatibility of the two components in the blend. Besides, the intermolecular interactions between the two components in the blend play an important role in their miscibility. The four most common interactions include the acid–base type,4 hydrogen bonding, dipole–dipole,5 and charge-transfer6 interactions. In particular, hydrogen bonding often acts as a miscibility enhancer, which has been proved in several studies.8,9 A vast majority of the studies have emphasized that PVDF/poly(methyl methacrylate) (PMMA) are completely miscible because of the hydrogen-bonding interactions between the carbonyl group of PMMA and the acidic hydrogen of PVDF.5,10 Additionally, various nanofillers have been used to modify the PVDF matrix, leading to the improvement of the mechanical and ferroelectric properties of PVDF.11−13 Tiwari11 reported the preparation of polar PVDF by amine-modified porous silica nanofillers. The PVDF film with porous silica exhibited a high relative intensity of the β-phase and strong adhesive strength over different metallic substrates.

Maleic anhydride (MAH) is a polar compound containing many functional groups, especially the unsaturated double bonds, which is easy to polymerize with other polymers by

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adding some agents or by irradiation. Moreover, the anhydride groups can also react with hydroxyl, carboxyl, amine, and other functional groups. Therefore, MAH functionalization of some nonpolar polymers is beneficial to increase their compatibility with polar polymers and improve the adhesion of materials and the interaction between fillers and polymers. Dang and co-workers reported PVDF/PP composites with high dielectric properties. Polypropylene grafted maleic anhydride (PP-g-MAH) acts as a suitable compatibilizer, which can efficiently increase the dielectric permittivity of composites. Iqbal and co-workers reported the chemical modification of low density polyethylene (LDPE) with MAH in a twin-screw extruder, using BPO as an initiator. The grafting degree first increased with the increasing content of BPO and MAH, and then decreased continuously on further increasing the BPO and MAH content. Ismail and co-workers also fabricated ethylene-propylene-diene monomer (EPDM)-g-MAH through melt-blending. They believed that the enhancement of interfacial interaction in compatibilized EPDM/bentonite (Bt) composites was due to the presence of the EPDM-g-MAH compatibilizer promoting the dispersion of Bt particles in the EPDM matrix. It is an effective strategy to modify polymers using MAH, although the modification of PVDF with MAH is rarely reported in the past decades. Meanwhile, the functionality of PVDF by reactive groups is another effective method to improve the miscibility between PVDF and other polymers.

In this work, MAH was introduced to modify PVDF owing to the reactivity of the anhydride group on the MAH monomer, which makes it possible to expand the applications of PVDF. Besides, the immobilization of the MAH monomer onto PVDF chains can be achieved by adding some agents or by irradiation, due to the unsaturated double bonds on the MAH monomer. The miscibility, properties, and specific interaction of PVDF/MAH binary blends have been investigated systematically. The physical and rheological properties of PVDF/MAH blends are significantly different from those of other PVDF blends with other small molecules due to the specific interactions between carboxyl groups of MAH and methylene groups of PVDF. Such interactions make the MAH play the role of physically bridging the molecular chains of PVDF.

2. RESULTS

2.1. Morphology of the PVDF/MAH Blends. The cross-sectional surfaces of PVDF and PVDF/MAH blends with different MAH contents (1, 5, and 10 wt %) before and after acetone etching are shown in Figure 1. Similar to the homogeneous phase of neat PVDF, after adding MAH (1–10 wt %), no apparent phase separation was observed in PVDF/MAH binary blends. To confirm the dispersion of MAH in the PVDF matrix, all of the PVDF/MAH blends were etched by acetone, which is a good solvent for MAH but a nonsolvent for PVDF, and then dried at 50 °C under a vacuum atmosphere for 3 h before SEM observation. The morphologies of etched PVDF/MAH blends are similar to the blends before etching, indicating the good miscibility between PVDF and MAH.

2.2. Physical Properties of the PVDF/MAH Blends. Figure 2a shows the stress–elongation curves of PVDF and PVDF/MAH blends with different MAH contents. The yielding strength and elongation as functions of MAH contents are shown in Figure 2b. Compared with the neat PVDF, the yielding strength and modulus of the blends are reduced slightly with the incorporation of MAH due to the plasticization effect of MAH. Besides, the elongation of samples greatly increases with the increasing MAH content, which indicates that the addition of MAH improves the ductility of PVDF. The elongation of the sample with 10 wt % MAH is 589.7%, which is almost five times that of neat PVDF. Moreover, the fracture strength at the break of blend is significantly increased from 36.4 MPa (neat PVDF) to 63.6 MPa (blend with 10 wt % MAH), an increase of nearly 1.75 times.

2.3. Rheological Properties of PVDF and the PVDF/MAH Blends. Small-amplitude oscillatory shear (SAOS) is an effective method to determine the structure/phase behavior of the blend system. The frequency dependencies of the storage modulus \(G'\), loss modulus \(G''\), complex viscosity \(\eta^*\), and damping factor (Tan \(\delta\)) of neat PVDF and PVDF/MAH blends with different constituents are plotted in Figure 3a–d, respectively. It is found that the \(G'\) and \(G''\) values of PVDF/MAH blends with different MAH contents.
various PVDF/MAH blends were higher than those of neat PVDF at the high detection frequency, reaches the maximum when the MAH content is 5 wt %, and then decreases slightly at a high MAH content (8–10 wt %). It is generally believed that small molecules often act as the diluents or plasticizers of polymers; therefore, the modulus of the blend system will be decreased with the incorporation of small molecules. However, the modulus of PVDF/MAH blends significantly increases with the addition of MAH compared to that of neat PVDF, indicating the presence of strong intermolecular interactions in PVDF/MAH blends. These intermolecular interactions may exist between two MAH molecules or between PVDF and MAH molecules, which are much stronger than those between two PVDF molecules. In other words, the intermolecular interactions between PVDF and MAH induce the enhancement of $G'$ and $G''$ values. Moreover, it is worth noting that there is a transition in $G'$ and $G''$ values, which is strongly related to the competition between plasticization and interaction. With a small amount of MAH, the effect of interaction is dominant, which enhances the $G'$ and $G''$ values. However, with further increase in the MAH content, the effect of plasticization will be much stronger than that of the interaction and results in the decrease of $G'$ and $G''$ values. In addition, no modulus plateau is found in the $G'$ and $G''$ curves, which means that there are only physical “crosslinking” points caused by hydrogen bonding in the PVDF/MAH blends, but not a crosslinking network.

**Figure 3c** shows the complex viscosity curves of neat PVDF and PVDF/MAH blends. Similar to the changes of the $G'$ and $G''$ values, the $\eta^{\prime\prime}$ values of PVDF/MAH blends first increase with the incorporation of MAH (0.5–5 wt %) and then decrease with further increase in the MAH content (8–10 wt %). The $\eta^{\prime\prime}$ values of all PVDF/MAH blends are always higher than that of neat PVDF in the whole range of frequency ($\omega$) investigated, even if the MAH content reaches 10 wt %. This is also due to the stronger interaction in PVDF/MAH blends, which restricts the motion of PVDF molecular chains. Besides, the $\eta^{\prime\prime}$ values of neat PVDF and the PVDF/MAH blends decrease gradually with the increase of the angular frequency, especially in the high-frequency region, which is consistent with the shear-thinning phenomenon of non-Newtonian fluids.

The $\tan \delta$ values against angular frequency curves of PVDF and PVDF/MAH blends are exhibited in Figure 3d. It is reported that the $\tan \delta$ curve is an effective way to detect irreversible changes in polymers.22 The curve crest value of neat PVDF appeared at the vicinity of 0.02 rad s$^{-1}$, which shifts to relatively lower frequencies with the incorporation of MAH. This result indicates the existence of stronger intermolecular interactions and greater obstruction of molecular movement. Similar to the variation of modulus and viscosity, the $\tan \delta$ first increases with the increasing MAH content, and then decreases significantly with further increase in the MAH content, especially in the low-frequency region. This result also indicates that there is a competitive relation between plasticization and interaction.

The Cole–Cole plot is an effective method to detect the phase-separation behavior of two-phase blends by characterizing the relaxation behavior of polymers, which can eliminate the frequency dependence of viscosity.23 Generally speaking, if the two-phase polymer has good compatibility, the Cole–Cole curve will have a smooth semicircle shape, corresponding to a long relaxation process. The Cole–Cole plots of neat PVDF and various PVDF/MAH blends are shown in Figure 3e. Almost all samples are fitted well to a semicircle, indicating that the PVDF/MAH blend is a homogeneous system. The radius of the semicircle increases with the incorporation of MAH and reaches a maximum when the MAH content is 5 wt %, and then decreases with further increase in the MAH content (8–10 wt %). The radius of blends is always larger than that of neat PVDF. These results are in good agreement with the results of modulus and viscosity. It can be inferred that the relaxation time is related to the molecular weight and the intermolecular interactions. With the incorporation of MAH, a small amount of MAH (0.5–5 wt %) acts as a physical “crosslinking” point between PVDF molecular chains, leading to a longer relaxation time, which induces an enlarged radius of Cole–Cole plots. Once the MAH content reaches more than 8 wt %, the excess MAH acts as the plasticizer, promoting the motion of PVDF molecular chains, and results in a shorter relaxation time.

The compatibility of polymer–polymer or polymer–nanofiller is often confirmed by a Han plot, which is drawn from log $G'$ to log $G''$. For compatible blends, the Han plot usually shows an independent dependence on components, while for incompatible blends, there is a significant dependence on the content of components.24 As shown in Figure 3f, compared to neat PVDF, it is worth noting that the Han plot curves of PVDF/MAH blends do not change significantly with the incorporation of MAH, indicating that PVDF and MAH have good compatibility.
2.4. Thermal Behaviors of the PVDF/MAH Blends.

2.4.1. Glass-Transition Behaviors. The glass-transition behaviors of the blends can be used to infer the compatibility of the two substances. Generally speaking, the two components are considered to be thermodynamically miscible with only one glass-transition temperature in their blends. As shown in Figure 4a, the loss tangent (\(\tan \delta\)) and storage modulus (\(G'\)) of neat PVDF and the PVDF/MAH blends were measured by the dynamic mechanical analysis (DMA) as functions of temperature. The microstructure of crystalline polymers (taking PVDF as an example) consists of a crystalline lamellar phase, an amorphous phase, and a crystal–amorphous interface, which correspond to three distinct relaxations of neat PVDF in DMA, respectively. First, the relaxation resulting from the motion of the molecular segments in the amorphous region at low temperature (\(-35 \, ^\circ\text{C}\)) is corresponding to the \(T_g\) of PVDF. Second, the intermediate relaxation is usually relatively weaker than the other two relaxations, which is caused by the motion of the molecular chains at the amorphous–crystal interface. Lastly, Mijovic et al. believed that various defects in PVDF crystals result in the relaxation at high temperatures (between 90 and 110 °C). Figure 4a shows that the \(T_g\) of neat PVDF is \(-38.4 \, ^\circ\text{C}\), which initially increases with the addition of MAH (less than 5 wt % MAH) to \(-28.2 \, ^\circ\text{C}\) for the sample with 5 wt % MAH, and then decreases drastically to \(-33.2 \, ^\circ\text{C}\) with 10 wt % MAH. The corresponding \(T_g\) as a function of the MAH content is shown in Figure 4c. According to SEM observations and SAOS results, MAH shows good miscibility with the PVDF matrix. It can be inferred that the increase of \(T_g\) may be a result of the strong interactions between the PVDF matrix and MAH, which restrict the motion of the PVDF chain segment, while a large amount of MAH has a plasticizing effect on the PVDF matrix, leading to the decrease of \(T_g\). With the incorporation of a small amount of MAH, the relaxation temperature of the amorphous–crystal interface shifts to a lower temperature gradually; meanwhile, the intensity increases significantly compared to that of the neat PVDF. This means that MAH is expelled out from the gallery of PVDF lamellae and located in the amorphous regions during the crystallization of PVDF. As depicted in Figure 4b, the storage modulus (\(G'\)) increases first and then decreases rapidly; the strong interaction between the PVDF matrix and MAH and the plasticizing effect of MAH on the PVDF can be proven again.

2.4.2. Thermal Stability of the PVDF/MAH Blends. The thermal stability of PVDF and PVDF/MAH blends with different MAH contents is measured by thermogravimetric analysis (TGA), as shown in Figure 5. It is well-known that MAH is a volatile monomer with poor thermal stability, and the initial degradation temperature (\(T_{5\%}\)) is 67.0 °C. The thermal stability of neat PVDF is much better than that of MAH, according to the higher \(T_{5\%}\) (470.5 °C) of neat PVDF as shown in Figure 5 and Table 1. The blends have two separate degradation steps, corresponding to the thermal degradations of MAH and PVDF, respectively. MAH shows a low thermal stability and degrades at lower temperatures, while the degradation of PVDF occurs at a relatively higher temperature. The DTG curves show that when the MAH content in the blend is less than 2 wt %, the MAH degradation can be negligible. This demonstrates again that the PVDF matrix shows good compatibility with MAH. On further increasing the MAH content, the degradation process of MAH can be observed. The weight loss percentage of MAH in the blends is slightly lower than the amount we added. Besides, due to the good compatibility of PVDF and MAH and the strong interaction between them, the thermal stability of MAH in the blend increased significantly. The detailed TGA parameters are summarized in Table 1.

2.4.3. Crystallization and Melting Behaviors. Enthalpy of melting in the first heating scan and the nonisothermal crystallization exotherm in the first cooling scan of PVDF and PVDF/MAH blends are recorded in Figure 6. The crystallization temperature (\(T_c\)) and melting temperature (\(T_m\)) of PVDF used in this study are 140.9 °C and 175.2 °C, respectively. It is obvious that the MAH has a significant effect on the PVDF.
 impact on the crystallization and melting behaviors of PVDF. First, we can find that the $T_m$ of PVDF decreases remarkably with the increase of the MAH content, indicating that PVDF and MAH have a good compatibility. This result is consistent with the SEM observations and SAOS results. Second, a multiple melting behavior is present in all samples, which can be attributed to the thickness of the lamella, the crystal form, and the regularity of the crystal. The incorporation of MAH will not change the crystal form of PVDF (which will be proved in the following X-ray diffraction (XRD) studies); it can be assumed that the multiple melting behaviors result from crystal lamellae with different thicknesses due to the quick cooling process of PVDF. Third, the $T_c$ decreases with increasing MAH content in PVDF/MAH blends. The $T_c$ of PVDF/MAH blends with a small amount of MAH (0.5–2 wt %) is higher than the $T_c$ of the neat PVDF, which might be attributed to MAH’s nucleation of PVDF crystallization. However, the $T_c$ decreases drastically with a large amount of MAH (5–10 wt %) in the PVDF matrix, which might result from the diluting effects of a large amount of MAH on the PVDF molecular chain and the plasticizing effect of MAH might be another reason. The crystallinity of PVDF in all of the samples ($\chi_c$) was determined by eq 1 as follows:

$$\chi_c = \frac{\Delta H_\text{m}}{\Delta H_\text{m}^0} \times 100\%$$

\(\Delta H_\text{m}^0\) is the theoretical enthalpy value of the 100% crystalline polymer matrix. (the $\Delta H_\text{m}$ of PVDF is 104.7 J g$^{-1}$) and $\Delta H_\text{m}$ is the weight fraction of the PVDF matrix (Table 2).

Table 2. Detailed Thermal Properties of PVDF and the PVDF/MAH Blends with Different MAH Contents

| Sample          | $T_m$ (°C) | $T_c$ (°C) | $\Delta H_\text{m}$ (J g$^{-1}$) | $\chi_c$ (%) |
|-----------------|------------|------------|---------------------------------|--------------|
| Neat PVDF       | 175.2      | 140.9      | 53.6                            | 51.2         |
| PVDF/MAH, 99.5-0.5 | 175.0      | 145.4      | 54.1                            | 51.9         |
| PVDF/MAH, 99.1  | 174.1      | 143.9      | 53.4                            | 51.5         |
| PVDF/MAH, 98-2  | 173.5      | 142.7      | 52.2                            | 50.9         |
| PVDF/MAH, 95-5  | 171.3      | 140.8      | 50.0                            | 50.3         |
| PVDF/MAH, 92-8  | 170.8      | 140.7      | 46.2                            | 48.0         |
| PVDF/MAH, 90-10 | 168.5      | 136.1      | 45.1                            | 47.9         |

2.5. Crystal Form of PVDF, MAH, and the PVDF/MAH Blends. PVDF is a typical semicrystalline polymer with three major crystal forms, which are the $\alpha$, $\beta$, and $\gamma$-phases. $\alpha$-PVDF is more common and stable and usually arises when PVDF crystallizes under motionless conditions from the melt. $\beta$-PVDF and $\gamma$-PVDF exhibit excellent piezoelectric and pyroelectric properties and ferroelectric activity because of their high polarity. To verify the impact of MAH on the crystal form of PVDF, the XRD spectra of PVDF and PVDF/MAH binary blends are shown in Figure 7. It is clear that four characteristic diffraction peaks can be observed in neat PVDF at 2$\theta = 17.5, 18.1, 19.8,$ and 26.4°, corresponding to the (100), (020), (110), and (021) reflections of the $\alpha$-phase crystal, respectively. This means that the $\alpha$-phase crystal plays a dominant role in neat PVDF. With the incorporation of MAH, no crystal form transformation occurs in PVDF/MAH binary blends, indicating that MAH has no effect on the PVDF crystal form. It is reported that if two materials have low compatibility, each material would have its own crystal regions in the blends. From Figure 7, this case did not occur in the PVDF/MAH blends. After incorporating MAH (0.5–10 wt %) into the PVDF matrix, no characteristic MAH peaks were observed in the patterns of PVDF/MAH blends.

3. DISCUSSION

3.1. Interactions between PVDF and MAH. MAH usually acts as a plasticizer, a diluent for polymers, which has been reported in various studies. The decrease of the modulus, viscosity, $T_g$, and strength would be carried out with the incorporation of MAH into the polymer matrix. However, it is interesting that the incorporation of MAH can greatly enhance the modulus, viscosity, and mechanical properties of PVDF. We consider that MAH plays the role of physically connecting the PVDF molecular chains in the melt or the amorphous region. Fourier transform infrared (FTIR) spectroscopy is an effective method to detect the detailed crystal forms and the possible interactions between components. The FTIR spectroscopy results of neat PVDF, MAH, and PVDF/MAH blends with different MAH contents are shown in Figure 8. The characteristic absorption bands of the nonpolar $\alpha$-phase PVDF are observed at 409, 532, 615, 763, 855, 975, and 1382 cm$^{-1}$, as shown in Figure 8a. Besides, the absorption peak positions and absorption intensity of PVDF in PVDF/MAH with different compositions are similar to those of neat PVDF, indicating that the incorporation of MAH has no significant effect on the crystal structure of PVDF. To define the possible interactions between PVDF and MAH, more detailed analyses have been carried out. The absorption peaks observed at 481 and 512 cm$^{-1}$ are related to the bending and wagging vibrations of CF$_2$ respectively, and the 840 cm$^{-1}$ bend corresponds to the CF$_3$ asymmetric stretching vibration. The vibrational bend near 845 cm$^{-1}$ is related to the CH$_2$ rocking vibration of PVDF, which shifts to lower wavelengths in all PVDF blends, as shown in Figure 8b. Compared with

![Figure 6. Differential scanning calorimetry (DSC) curves of the (a) first heating and (b) first cooling of PVDF and the PVDF/MAH blends with different MAH contents.](image)

![Figure 7. XRD patterns of neat PVDF, MAH, and the PVDF/MAH blends.](image)
neat PVDF, several new absorption peaks are observed in the FTIR spectrum of the PVDF/MAH blend, such as the bands at 1857 and 1783 cm$^{-1}$, which are related to the asymmetric stretching and symmetric stretching of the carbonyl group (C=O) in MAH, respectively. In particular, Figure 8c shows that the asymmetric stretching of the carbonyl group (C=O) shifts to the lower-wavelength side in all PVDF/MAH blends, in comparison with neat MAH. According to these results, it can be inferred that the shift is a result of the intermolecular interaction between the carbonyl group of MAH and the CH$_2$ group of PVDF; in other words, this specific interaction is mainly attributed to hydrogen bonding between the MAH carbonyl oxygen and the PVDF protons.

According to the FTIR results, the effects of MAH on the miscibility and physical and rheological properties of PVDF/MAH blends can be assigned to the specific interactions between the carbonyl group of MAH and the CH$_2$ group of PVDF. When the MAH content is in the range of 0.5–5 wt %, the CH$_2$ groups of PVDF interact with the carbonyl groups of MAH in the melt state. One MAH molecule contains two carbonyl groups and can act as a physical crosslinking point between neighboring PVDF molecular chains, as shown in Figure 9. This not only leads to the good compatibility between PVDF and MAH, but also enhances the modulus, viscosity, and mechanical properties of the PVDF matrix.

According to the FTIR results, the specific interaction relates to the hydrogen bonding involving the carbonyl group of MAH and the CH$_2$ group of PVDF. This strong interaction has a significant effect on the structure and properties of the binary PVDF/MAH blends. We conclude that hydrogen bonding is the major driving force for the compatibility of PVDF and MAH. On the other hand, the storage modulus and viscosity of PVDF increase with the incorporation of a small amount of MAH and decrease with further increase in the MAH content. The enhancement of the modulus and viscosity is due to the two carbonyl groups of one MAH, which interact with the free CH$_2$ group of neighboring PVDF molecular chains. In other words, MAH acts as a physical crosslinking point between neighboring PVDF molecular chains, improving the mechanical properties of PVDF.

4. CONCLUSIONS

In this work, PVDF/MAH blends were prepared by a simple melt-blending. The miscibility, physical properties, and specific hydrogen-bonding interaction were systematically studied. According to FTIR results, it can be concluded that the strong specific interaction relates to the hydrogen bonding involving the carbonyl group of MAH and the CH$_2$ group of PVDF. This strong interaction has a significant effect on the structure and properties of the binary PVDF/MAH blends. We conclude that hydrogen bonding is the major driving force for the compatibility of PVDF and MAH. On the other hand, the storage modulus and viscosity of PVDF increase with the incorporation of a small amount of MAH and decrease with further increase in the MAH content. The enhancement of the modulus and viscosity is due to the two carbonyl groups of one MAH, which interact with the free CH$_2$ group of neighboring PVDF molecular chains. In other words, MAH acts as a physical crosslinking point between neighboring PVDF molecular chains, improving the mechanical properties of PVDF.

5. EXPERIMENTAL SECTION

5.1. Materials. The PVDF used in this work was supplied by Hangzhou Fumo new materials technology Co., Ltd., China, with an $M_n$ of 98,000 g mol$^{-1}$. MAH was purchased from Shanghai Zhanyun Chemical Co., Ltd., China, with the A.R. level, and used as received.

5.2. Preparation of the PVDF/MAH Binary Blends. PVDF and MAH were dried in a vacuum oven at 80 °C for 12 h to remove excrescent water before melt-blending. The melt-blending of PVDF and MAH was carried out at 190 °C using a batch mixer (Haake PolyLab QC) with an initial rotation speed...
of 20 rpm (2 min) and subsequently increased to 50 rpm (5 min).

5.3. Characterization. Scanning electron microscopy- (SEM, Hitachi S-4800) was applied to observe the microstructure of the fractured surface of samples at the acceleration voltage of 3 kV. All samples were fractured in liquid nitrogen, and the cross-sectional areas were coated with a thin layer of gold before observation.

The crystallization and melting behaviors of all samples were measured by differential scanning calorimetry (DSC, TA-Q200) under a nitrogen atmosphere. Samples were heated from room temperature to 220 °C and kept for 5 min to eliminate the thermal history, followed by cooling to 30 °C, and heated to 220 °C again with a heating/cooling rate of 10 °C min⁻¹.

The thermal stability of all samples was assessed by thermogravimetric analysis (TGA, TA-Q600) under a nitrogen atmosphere. All samples were heated from 30 to 650 °C with a heating rate of 10 °C min⁻¹.

The loss tangent (tan δ) and storage modulus (G') were measured by dynamic mechanical analysis (DMA, TA-Q800) with a multifrequency strain mode. All samples were heated from −70 to 190 °C with a heating rate of 3 °C min⁻¹.

Rheological studies of the sample were performed with a physical rheometer (MCR301). The samples were set between two parallel-plate geometries with a plate diameter of 20 mm. The dynamic frequency sweep experiments were carried out at two parallel-plate geometries with a plate diameter of 20 mm. The crysralization and melting behaviors of all samples were measured by dynamic mechanical analysis (DMA, TA-Q800) under a nitrogen atmosphere. Samples were heated from room temperature to 220 °C and kept for 5 min to eliminate the thermal history, followed by cooling to 30 °C, and heated to 220 °C again with a heating/cooling rate of 10 °C min⁻¹.

The author information is included as a separate section.

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