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Improvement in Toughness of Poly(ethylene 2,5-furandicarboxylate) by Melt Blending with Bio-based Polyamide11 in the Presence of a Reactive Compatibilizer

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Electronic Supplementary Information

Abstract The objective of this study was to improve the toughness of bio-based brittle poly(ethylene 2,5-furandicarboxylate) (PEF) by melt blending with bio-based polyamide11 (PA11) in the presence of a reactive multifunctional epoxy compatibilizer (Joncryl ADR®-4368). The morphological, thermal, rheological, and mechanical properties of PEF/PA11 blends were investigated. Compared with neat PEF, the toughness of PEF/PA11 blend was not improved in the absence of the reactive compatibilizer due to the poor compatibility between the two polymers. When Joncryl was incorporated into PEF/PA11 blends, the interfacial tension between PEF and PA11 was obviously reduced, reflecting in the fine average particle size and narrow distribution of PA11 dispersed phase as observed by scanning electron microscopy (SEM). The complex viscosities of PEF/PA11 blends with Joncryl were much higher than that of PEF/PA11 blend, which could be ascribed to the formation of graft copolymers through the epoxy groups of Joncryl reacting with the end groups of PEF and PA11 molecular chains. Thus, the compatibility and interfacial adhesion between PEF and PA11 were greatly improved in the presence of Joncryl. The compatibilized PEF/PA11 blend with 1.5 phr Joncryl exhibited significantly improved elongation at break and unnotch impact strength with values of 90.1% and 30.3 kJ/m², respectively, compared with those of 3.6% and 3.8 kJ/m² for neat PEF, respectively. This work provides an effective approach to improve the toughness of PEF which may expand its widespread application in packaging.

Keywords Poly(ethylene 2,5-furandicarboxylate); Polyamide11; Bio-based polymers; Reactive compatibilization; Toughening

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INTRODUCTION

In the past few decades, the excessive utilization and discarding of petro-based polymers not only exacerbate the over-exploitation of fossil resources but also bring serious environmental problems.^[1,2] Therefore, both academic and industrial communities have been committed to the development of bio-based polymers from renewable resources, which have potential to reduce dependence on traditional petro-based materials.^[3–5]

Poly(ethylene 2,5-furandicarboxylate) (PEF), a bio-based polyester synthesized from bio-derived 2,5-furandicarboxylic acid (FDCA) and ethylene glycol (EG) monomers, has gained growing interests for its improved performance over PET.^[6–8]

Compared with PET, PEF has higher glass transition temperature, higher tensile strength and modulus, lower melt processing temperature as well as superior barrier properties to O₂, CO₂, and H₂O.^[9–12] Unfortunately, PEF is very brittle and its elongation at break is lower than 5%.^[13–17] The poor ductility and impact strength of PEF is attributed to the rigid structure of FDCA, which impedes its widespread application in many fields.^[18] Several strategies have been developed to improve the toughness of PEF, including biaxial orientation, copolymerization, and blending modification.^[6] Recently, van Berkel *et al.*^[19] found that biaxial orientation could endow PEF with high elongation at break (35%–115%), but this method is commonly limited to the preparation of film and sheet products.

Copolymerization is the most common route to PEF materials with desirable flexibility. Many recent literatures have investigated the preparation of PEF-based copolymers using diacids, diols, and polyols as the comonomers.^[20–24] Wang *et al.*^[20] synthesized poly(ethylene sebacate-co-2,5-furandicarboxylate) (PESF) as random copolyesters containing flex-

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ible sebacate units; the elongation at break of the copolyesters was enhanced to 280%, but the tensile modulus decreased from 2080 MPa to 80 MPa. Wang *et al.*^[21] also reported multiblock copolymers poly(ethylene 2,5-furandicarboxylate)-poly(ethylene glycol) (PEFEGs) containing poly(ethylene glycol) (PEG) segments. The elongation at break of the PEFEG6K80 sample was raised up to 61% as the PEG content was 80 wt%, whereas the corresponding strength was only 12 MPa, which was much lower than that of neat PEF (72 MPa). Although copolymerization can improve the toughness by manipulating the chemical structure of polymer chain, the process is very cumbersome and has poor controllability.^[25] Besides, exploring ductile PEF-based copolymers with high tensile strength and modulus at the same time remains a challenge.

Blending modification is another simple and low-cost way to improve the toughness of brittle polymer, and it can balance the superior performance between the components and realize complementary advantages. Researchers attempted to increase the ductility of PEF by blending with some flexible polymers, such as poly(butylene 2,5-furandicarboxylate) (PBF)^[26,27] and poly(butylene succinate) (PBS),^[28] while both PEF/PBF and PEF/PBS exhibited poor miscibility, and the toughening effect was unremarkable. In addition, the strength and modulus of blends may decrease seriously when PEF blends with these flexible polymers.

Polyamide11 (PA11) is an important commercial semicrystalline biopolymer synthesized by renewable castor oil and presents excellent thermal stability, high strength, and high elongation at break.^[1,29–31] By blending PEF with PA11, the high performance of PA11 can compensate the shortage of PEF. Furthermore, interfacial interactions could potentially occur between polyamides and polyesters in the melt blending process, leading to an improvement of compatibility.^[29,32,33] Hence, PA11 is a good candidate for blending with PEF to prepare fully bio-based materials. To the best of our knowledge, few studies have been carried out so far on PEF/PA11 blends.

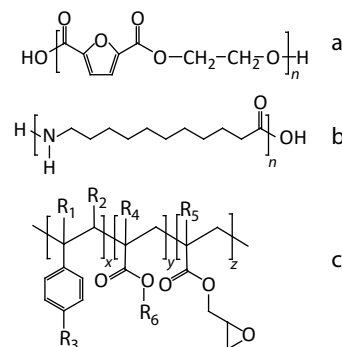
Considering that simple blending PEF with other polymers usually cannot give satisfactory properties because of the poor miscibility between the components, a multifunctional epoxy (Joncryl ADR®-4368) was incorporated into PEF/PA11 blends as a reactive compatibilizer. The multifunctional epoxy contains lots of epoxy functional groups, which might react with both hydroxyl/carboxyl end groups of PEF and carboxyl/amino end groups of PA11. In this study, the phase morphologies, thermal behaviors, dynamic mechanical performances, rheological behaviors, and mechanical properties of PEF/PA11 blends with and without Joncryl are investigated in detail.

EXPERIMENTAL

Materials

Poly(ethylene 2,5-furandicarboxylate) (PEF) was synthesized by our group, and the details of the preparation process were described in our previous work.^[14] Polyamide11 (PA11, Rilsan® BESNO P40 TL) was purchased from Arkema (Colombes, France). Joncryl ADR®-4368 was supplied by BASF (Ludwigshafen, Germany), with average molecular weight of 6800 g/mol and

average functionality on epoxide of 9. Joncryl is allowed by the Food and Drug Administration for food packaging.^[4] The chemical structures of the three materials are shown in Scheme 1.



Scheme 1 Chemical structures of (a) PEF, (b) PA11, and (c) Joncryl ADR®-4368, where R_1 – R_5 are H, CH_3 , a higher alkyl group or combinations of them; R_6 is an alkyl group. x , y , and z are between 1 and 20.

Blends Preparation

PEF and PA11 were dried under vacuum at 70 °C for 24 h before use, and Joncryl ADR®-4368 was also pre-treated under vacuum at 40 °C for 24 h. PEF, PA11, and their blends were melt-blended using a Brabender Mixer (Brabender, Germany) at 230 °C with a rotor speed of 60 r/min for 6 min, and their nomenclature is shown in Table 1. Then all the samples were compression-molded into sheets by a hot press machine at 230 °C and 10 MPa for further characterization.

Table 1 Prepared PEF, PA11, and PEF/PA11 blends with their nomenclature.

Sample	PEF	PA11	Joncryl ADR®-4368
PEF	100	0	0
PEF/J1	100	0	1
PEF/PA11	80	20	0
PEF/PA11/J0.5	80	20	0.5
PEF/PA11/J1	80	20	1
PEF/PA11/J1.5	80	20	1.5
PA11	0	100	0

Characterization

The morphologies of PEF/PA11 blends were characterized by a scanning electron microscope (SEM) (EVO18, Zeiss, Germany). Samples were cryogenically fractured in liquid nitrogen and the fractured surfaces were sputter-coated with platinum before observation. The cross section of tensile-fractured and impact-fractured samples was also treated by the same way.

DSC instrument (TGA/DSC1, Mettler Toledo, Switzerland) was used to investigate the thermal properties of PEF, PA11, and their blends in nitrogen atmosphere. The DSC protocol consisted of four steps: (1) heat from 0 °C to 240 °C at 10 °C/min, (2) hold at 240 °C for 3 min, (3) cool from 240 °C to 0 °C at 100 °C/min, (4) reheat from 0 °C to 240 °C at 10 °C/min.

The thermal dynamic mechanical properties of the samples were measured on a DMA instrument (Q-800, TA Instruments, America) with a fixed frequency of 1 Hz and amplitude of 5 μm . Rectangular samples with the dimension of 20 mm $\times$

5 mm × 0.5 mm were clamped under a tensile mode, and the heating rate was 3 °C/min.

The rheological analyses of PEF, PA11, and their blends were carried out on a Discovery Hybrid Rheometer (DHR-3, TA Instruments, America) using a parallel plate geometry (25 mm diameter) and a 0.9 mm gap at 230 °C. Frequency sweep tests were performed from 0.1 rad/s to 100 rad/s under nitrogen flow.

Tensile properties of the individual components and their blends were tested by using an Instron testing machine (5567, Instron, America) according to the Chinese standard GB/T 1040.1-2006, and the tensile speed was 5 mm/min. The dumbbell-shaped specimens (2 mm × 0.5 mm in neck width and thickness) for tensile testing were prepared, and five specimens were measured to obtain the average values for each sample.

Unnotched Izod impact tests were performed according to the Chinese standard GB/T 1843-2008 on an impact testing machine (GT-7045-HML, Gotech, Taiwan) at 25 °C. The dimensions of all samples were 80 mm × 10 mm × 3 mm. At least five specimens were measured and the results were averaged.

RESULTS AND DISCUSSION

Morphological Analysis

The mechanical properties of the blends were closely related to the compatibility between the components, the concentration of the components, and the change in the phase morphology.^[1] The morphologies of the cryo-fractured PEF/PA11 blends with and without Joncryl were characterized by SEM, and the results are presented in Fig. 1. As can be seen from Fig. 1(a), a typical two-phase morphology was observed although no obvious gaps were found in the interface between PA11 and PEF, which might be explained by the “self-compatibilization” effect of polyamides and polyesters.^[32,33] Coalesced PA11 microspheres were dispersed in the PEF matrix and their size distribution mainly ranged from 1 μm to 3 μm. Some PA11 particles remained in the polymer matrix, while many of them were pulled out during fracture leaving empty cavities, suggesting that the compatibility between PEF and PA11 was still poor.

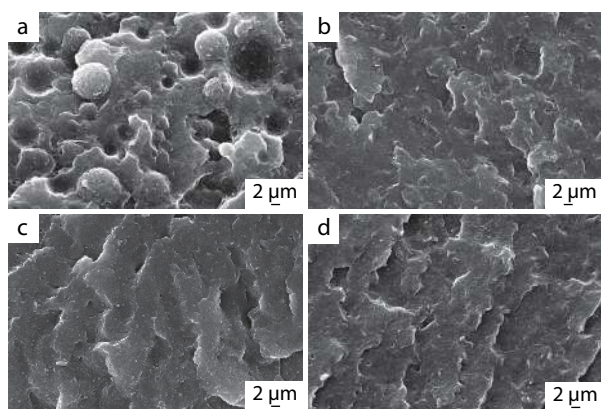


Fig. 1 SEM images of cryo-fractured surfaces of PEF/PA11 blends with and without Joncryl: (a) PEF/PA11, (b) PEF/PA11/J0.5, (c) PEF/PA11/J1, (d) PEF/PA11/J1.5.

When Joncryl was added into PEF/PA11 blends, it could be found that the average size of the PA11 particles was significantly reduced, and the interface between PEF and PA11 became indistinct, as shown in Figs. 1(b)–1(d). Furthermore, overwhelming majority of those PA11 particles remained in the PEF matrix. It might be attributed to the fact that the epoxide groups of Joncryl reacted with the carboxyl (–COOH)/hydroxyl (–OH) end groups of PEF and the carboxyl (–COOH)/amino (–NH₂) end groups of PA11 at the same time, leading to the formation of graft copolymers which could act as interfacial compatibilizers, and thus improve the compatibility between PA11 and PEF and enhance their interfacial adhesion. Besides, the formed graft copolymers were conducive to reduced interfacial tension that stabilized the dispersed PA11 phase in much smaller sizes.

Thermal Properties

The thermal properties of PEF, PA11, and their blends were studied by differential scanning calorimetry (DSC). The DSC thermograms of the second heating scans are shown in Fig. 2, and the corresponding data are summarized in Table 2. Neat PEF exhibited a cold crystallization peak at 151 °C with associated crystallization enthalpy (ΔH_{cc}) of 31.7 J/g, followed by a melting peak at 213 °C. After the melt mixing of PEF and PA11, the cold crystallization temperature (T_{cc}) of PEF decreased from 151 °C to 148 °C, and its crystallization degree (χ_c) increased from 13.7% to 16%, which indicated that PA11 could improve the crystallization ability of PEF in the PEF/PA11 blends.

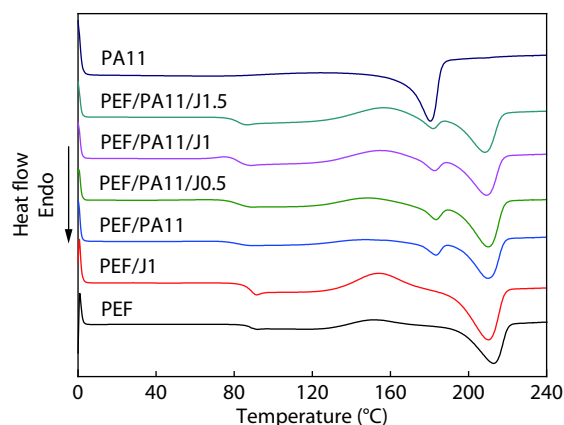


Fig. 2 The DSC thermograms of the second heating scans of PEF, PA11, and their blends.

For the compatibilized PEF/PA11 blends, the presence of Joncryl increased T_{cc} of the blends, and T_{cc} of PEF/PA11 shifted from 148 °C to 156 °C (PEF/PA11/J1.5). Najafi *et al.*^[34] reported that the reduced chain mobility was responsible for the increased cold crystallization temperature. Furthermore, it is worth noting that the crystallinity of PEF decreased from 16.0% to 2.9% with the increase of Joncryl content. The above crystallization behaviors were related to structural modification of PEF chains induced by Joncryl. As mentioned in morphological analysis, Joncryl could react with the –COOH/–OH end groups of PEF and the –COOH/–NH₂ end groups of PA11, and long-chain branched structures were formed. Therefore, the mobility of PEF chains decreased, which dis-

Table 2 DSC parameters obtained from the second heating scans.

Sample	T_g , PEF (°C)	T_{cc} , PEF (°C)	ΔH_{cc} , PEF (J/g)	T_m , PA11 (°C)	ΔH_m , PA11 (J/g)	T_m , PEF (°C)	ΔH_m , PEF (J/g)	χ_c , PA11 (%)	χ_c , PEF (%)
PEF	87.1	151	12.5	—	—	213	31.7	—	13.7
PEF/J1	87.9	154	16.9	—	—	210	32.3	—	11.0
PEF/PA11	80.8	148	9.7	183	3.4	210	27.6	7.5	16.0
PEF/PA11/J0.5	81.2	149	13.5	183	2.5	210	23.1	5.5	8.6
PEF/PA11/J1	82.4	154	17.6	183	2.2	209	23.4	4.9	5.2
PEF/PA11/J1.5	81.3	156	19.0	182	1.8	209	22.3	4.0	2.9
PA11	—	—	—	181	40.6	—	—	17.9	—

Note: The heat of fusion at 100% crystallinity of PA11 and PEF is 226 J/g^[35] and 140 J/g^[36] respectively.

rupted the packing of polymer chains and inhibited the crystallization of PEF in the cooling process.

DMA Measurement

Generally, the temperature corresponding to the loss tangent ($\tan\delta$) peak in dynamic mechanical analysis (DMA) curves is taken as glass transition temperature (T_g). Variations of $\tan\delta$ of PEF, PA11, and their blends were recorded as a function of temperature, and the results are illustrated in Fig. 3(a). Besides, the changes of T_g for PEF component in PEF/PA11 blends with different Joncryl concentrations are exhibited in Fig. 3(b). As shown in Fig. 3(a), neat PEF had a significant T_g at around 97.0 °C, while the PEF/J1 sample showed a higher T_g at 98.3 °C, indicating that the epoxy groups of Joncryl reacted with the —COOH/—OH end groups of PEF and increased the molecular weight of PEF. Similarly, compared with T_g of the PEF/PA11 blend, all the PEF/PA11 blends with Joncryl also exhibited higher T_g s, which suggested that Joncryl had reacted with the end groups of PEF and PA11, and the formed copolymers with high molecular weights hindered the mobility of the PEF chains, thus the T_g of PEF increased. When the content of Joncryl increased from 1 phr to 1.5 phr, the T_g of PEF decreased slightly, and this might be explained as that a part of excessive reactive compatibilizers dispersed in PEF matrix and acted as plasticizers. In Fig. 3(b), the changes of T_g of PEF component in PEF/PA11 blends followed the same trend as obtained by DSC.

In addition, the $\tan\delta$ peak amplitude of all PEF/PA11 blends was only about 1/2 that of neat PEF in spite of the largely predominant PEF content, and it clearly suggests that $\tan\delta$ of the PEF/PA11 blends was more sensitive to the weak damping behavior of PA11 than to the strong one of PEF in the temperature range of main relaxation of the amorphous phase of PEF and PA11 components. Similar results had been reported by Stoclet *et al.*^[37] for PLA/PA11 blends.

Rheological Behavior

Fig. 4 illustrates the storage modulus and the complex viscosity as a function of frequency for PEF, PA11, and their blends with and without Joncryl at 230 °C. In Fig. 4(a), the storage modulus of PEF/PA11 blend was in a range between those of the neat PEF and neat PA11, and it was raised with the increase of Joncryl concentration owing to the formation of some branched chains, which increased the entanglements of polymer chains in the melts. Walha *et al.*^[4] also reported similar results in PLA/PA11/Joncryl blends.

As shown in Fig. 4(b), the complex viscosity of PEF/J1 increased over the whole frequency range with the addition of Joncryl, and it can be explained by chain extension and/or a branching phenomenon of PEF chains, which created more entanglements thus giving rise to higher viscosities. The com-

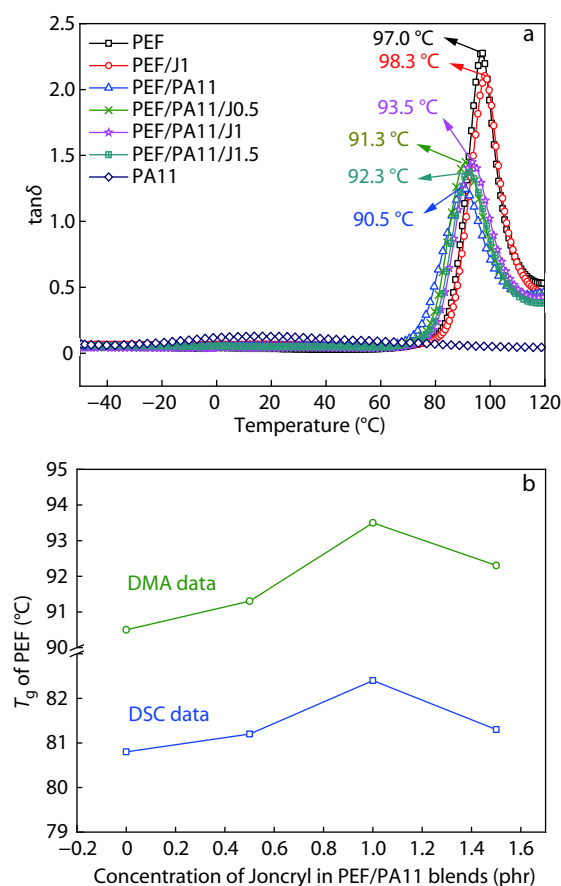


Fig. 3 (a) $\tan\delta$ versus temperature for PEF, PA11, and their blends and (b) T_g of PEF component in PEF/PA11 blends with different Joncryl concentrations obtained by DMA and DSC.

plex viscosity curve of PEF/PA11 was located between the values obtained for the neat polymers. At given shear frequency, the complex viscosities of PEF/PA11/Joncryl blends were much higher than that of PEF/PA11 blend and further increased with the increase of Joncryl concentration. The results revealed once again the occurrence of chemical reactions between the epoxy functions of Joncryl and the —COOH/—OH end groups of PEF as well as —COOH/—NH₂ end groups of PA11 simultaneously, which would form graft copolymers and/or branched polymers with higher molecular weights and increase the entanglements among the polymer chains, and thus increased the complex viscosity of the PEF/PA11/Joncryl blends eventually. Similar results have been reported by Walha *et al.*^[4] in PLA/PA11/Joncryl blends and

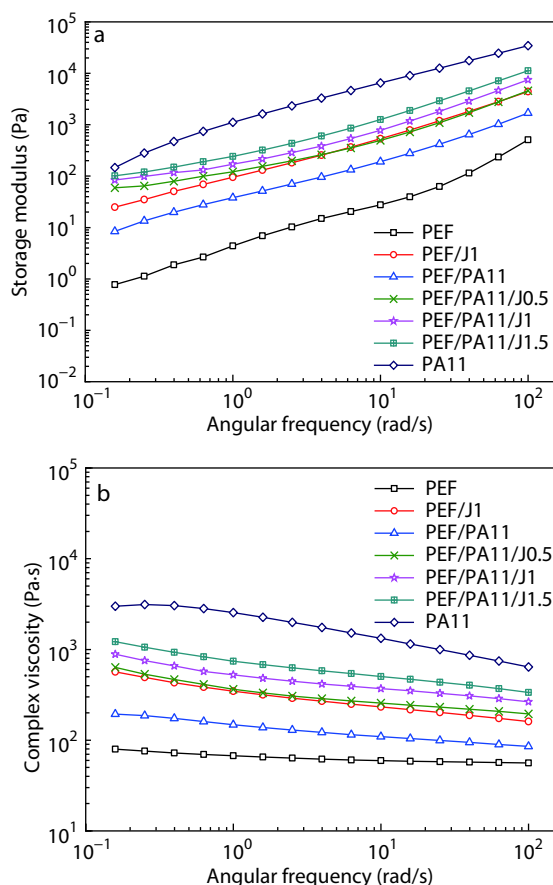


Fig. 4 (a) The storage modulus and (b) the complex viscosity as a function of frequency for PEF, PA11, and their blends.

Al-Itry *et al.*[38] in PLA/PBAT/Joncryl blends. It is worth mentioning that PA11 might be degraded slightly under this condition, resulting in lower viscosity of PA11 and PEF/PA11 blends; however, this did not affect the variation tendency of the viscosity of PEF/PA11 blends with the Joncryl concentration, because all PEF/PA11 blends contained the same amount of PA11.

Based on previous literatures,[4,39] the reactions rates of the epoxide group with $-NH_2$, $-COOH$, and $-OH$ groups are 260, 18, and 1 s^{-1} , respectively. Thus, the proposed reactions between both PEF and PA11 with Joncryl are illustrated in Fig. 5.

Mechanical Properties

The tensile properties of PEF, PA11, and their blends were studied, and the stress-strain curves are shown in Fig. 6; tensile strength, tensile modulus, and elongation at break of those samples are summarized in Table 3. As illustrated in Fig. 6, neat PEF exhibited an obvious brittle fracture behavior without yielding, and its elongation at break was only 3.6% although it possessed high tensile strength with a value of 84.5 MPa. The addition of PA11 did not improve the toughness of PEF, and the tensile strength of PEF/PA11 blend reduced to 67.2 MPa because of the poor compatibility between PEF and PA11 as mentioned above. When Joncryl was incorporated into PEF/PA11 blends, the compatibilized PEF/PA11 blends showed

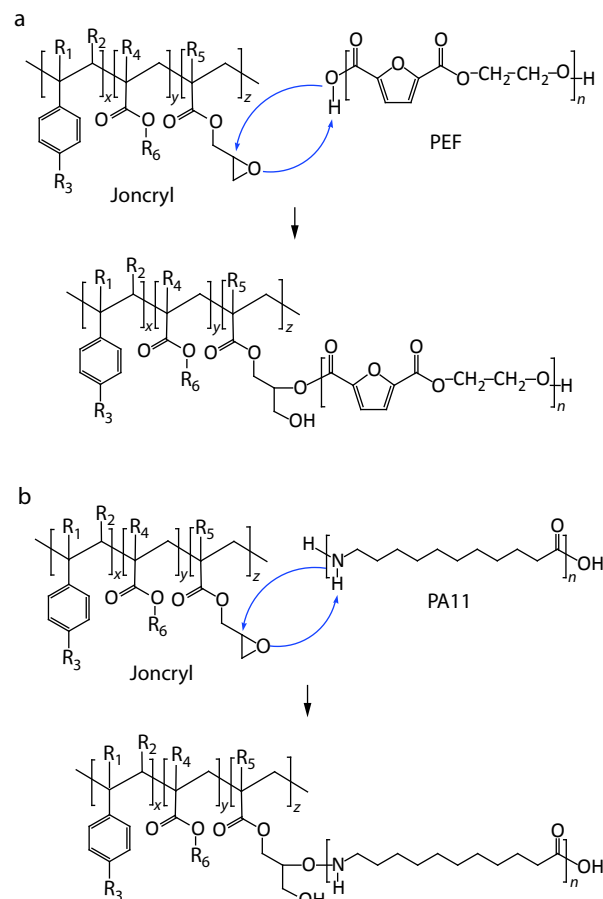


Fig. 5 Proposed reactions (a) between carboxylic end group of PEF and Joncryl and (b) between amine end group of PA11 and Joncryl.

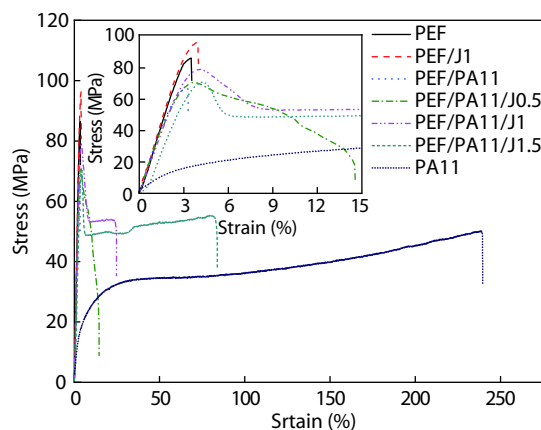


Fig. 6 The stress-strain curves of PEF, PA11, and their blends.

typical yield behaviors, and the elongation at break of PEF/PA11/Joncryl blends was greatly improved, namely, it was increased from 3.5% to 90.1% after adding 1.5 phr of Joncryl. Obviously, the improvement of flexibility of PEF/PA11/Joncryl blends could be attributed to the formation of graft copolymer that reduced the interfacial tension and improved the compatibility between PEF and PA11 as mentioned above in morphological analysis section. The smaller interfacial tension

Table 3 Mechanical properties of PEF, PA11, and their blends.

Sample	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Impact strength (kJ/m ²)
PEF	84.5 ± 2.9	3039 ± 175	3.6 ± 0.8	3.8 ± 0.3
PEF/J1	91.9 ± 4.3	3284 ± 134	4.1 ± 0.3	5.9 ± 0.4
PEF/PA11	67.2 ± 3.5	2964 ± 75	3.5 ± 0.4	3.3 ± 0.9
PEF/PA11/J0.5	70.0 ± 1.7	2955 ± 74	15.8 ± 1.3	9.7 ± 0.9
PEF/PA11/J1	75.6 ± 5.1	2760 ± 11	22.7 ± 5.4	16.7 ± 1.2
PEF/PA11/J1.5	72.2 ± 4.6	2640 ± 89	90.1 ± 13.8	31.3 ± 2.2
PA11	48.6 ± 1.9	532 ± 45	241.1 ± 17.6	N

Note: "N" means no break.

could reduce the size of the PA11 dispersed phase in PEF matrix, which increased the contact area between them, and the improved compatibility increased the interfacial adhesion between PA11 phase and PEF matrix. Moreover, it is worth mentioning that the tensile strength and tensile modulus of PEF/PA11/Joncryl blends did not decrease significantly compared with that of neat PEF.

Fig. 7 shows the appearance of PEF, PA11, and their blends after tensile tests. Brittle fracture behavior was observed for the neat PEF and PEF/PA11 blend with little plastic deformation. In contrast, large stretching deformation was found for the PEF/PA11 blends with Joncryl, indicating the significant improvement in their toughness. Furthermore, as for PEF/PA11/Joncryl specimens, obvious necking phenomenon appeared during stretching in the dumbbell-shaped specimens, corresponding to the yield behaviors of their stress-strain curves.

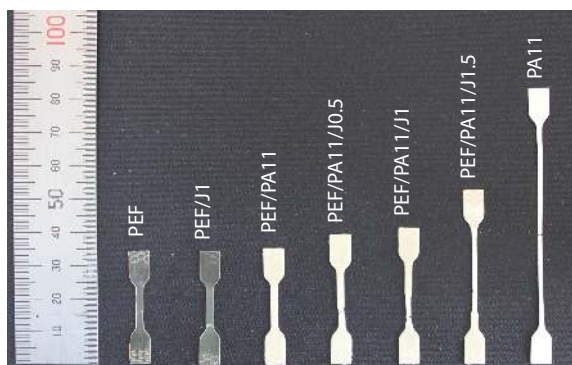


Fig. 7 The appearance of PEF, PA11, and their blends after tensile tests.

In order to understand the mechanism of the distinctly improved flexibility of PEF/PA11 blends caused by the addition of Joncryl, the tensile-fractured surfaces of PEF/PA11 blends are investigated by SEM and the results are shown in Fig. 8. As can be seen in Fig. 8(a), the cross section of PEF/PA11 blend was flat, corresponding to its brittle fracture with low elongation at break. However, the PEF/PA11/Joncryl blends showed different deformation behaviors and their tensile fractured surfaces exhibited fibril-like morphology in Figs. 8(b)–8(d), which was the evidence of large-scale deformation caused by matrix shear yielding.^[40]

Fig. 9 shows the unnotched Izod impact strength of PEF and PEF/PA11 blends with and without Joncryl, and the detailed data are listed in Table 3. Neat PEF presented poor impact strength with a value of 3.8 kJ/m², while neat PA11

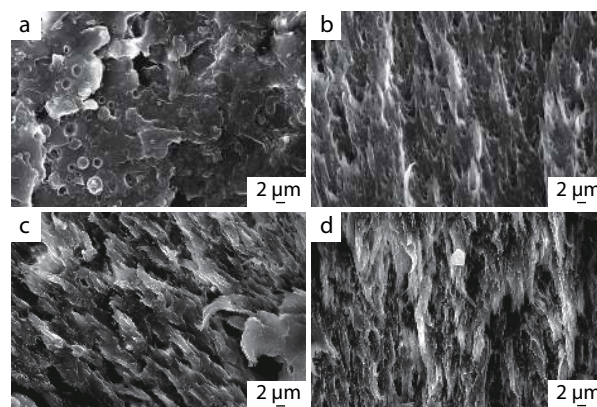


Fig. 8 SEM micrographs of tensile-fractured surfaces of PEF/PA11 blends with and without Joncryl: (a) PEF/PA11, (b) PEF/PA11/J0.5, (c) PEF/PA11/J1, (d) PEF/PA11/J1.5.

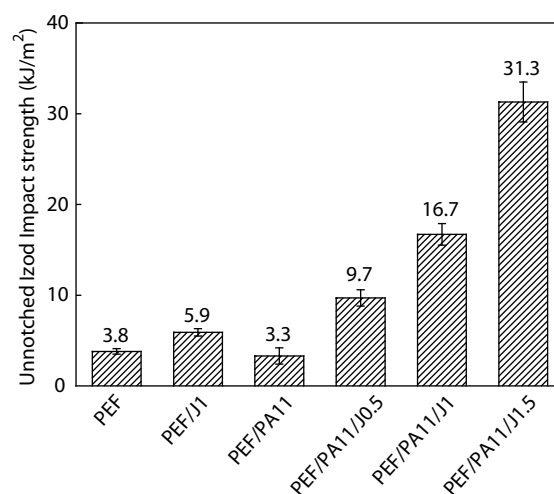


Fig. 9 Unnotched Izod impact strength of PEF and PEF/PA11 blends with and without Joncryl.

showed excellent impact resistance and no break was observed in the impact tests. The PEF/PA11 blend did not exhibit toughness characteristics and its impact strength decreased slightly compared with that of neat PEF, owing to the large interfacial tension between PEF and PA11. The large interfacial tension caused PA11 to coalesce in the PEF matrix, and the coalescence of PA11 under poor adhesion would act as defect in PEF/PA11 blend, leading to lower impact strength. As shown in Fig. 9, the impact strength of PEF/PA11/Joncryl blends increased steadily with the increase of Joncryl content. When the Joncryl content reached 1.5 phr,

the impact strength of PEF/PA11/Joncryl blend increased from 3.3 kJ/m² to 31.3 kJ/m². With the addition of Joncryl, its epoxy-containing groups could react with both PEF and PA11, forming graft copolymers that acted as compatibilizers between PEF and PA11 as discussed above. A much finer dispersion of PA11 phase in the PEF matrix was obtained in all the PEF/PA11/Joncryl blends, which would induce local yielding of PEF around PA11 particles, dissipate the impact energy and improve their impact-resistance performance. In previous work, similar toughening mechanism has been reported by Wang *et al.*^[41–43]

To further investigate the toughening effect, the SEM micrographs of the impact-fractured surfaces of PEF/PA11 blends with and without Joncryl are shown in Fig. 10. In Fig. 10(a), the impact-fractured surface of PEF/PA11 blend without Joncryl was found to be very smooth, and the blend exhibited a kind of immiscible feature, namely, two-phase structure with PA11 dispersing in PEF matrix and the cavitation caused by debonding can also be clearly identified. For PEF/PA11 blends with Joncryl in Figs. 10(b)–10(d), all of them showed clear stress-whitening surfaces. With the increase in concentration of Joncryl in PEF/PA11 blends, the impact-fractured surface of the blends became rough increasingly and more shear yielding was observed, which led to higher impact strength.^[44]

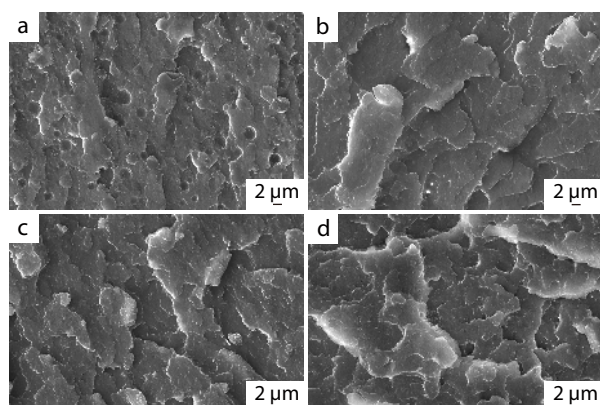


Fig. 10 SEM micrographs of impact-fractured surface of PEF/PA11 blends with and without Joncryl: (a) PEF/PA11, (b) PEF/PA11/J0.5, (c) PEF/PA11/J1, (d) PEF/PA11/J1.5.

CONCLUSIONS

In this work, PEF was melt blended with bio-based PA11 in the presence of a reactive compatibilizer (Joncryl ADR®-4368) with the purpose of overcoming its brittleness. The experimental results showed that the simple blending PEF with PA11 could not achieve the goal of toughening because of the poor compatibility between the two components. When Joncryl with multi-functional epoxy groups was incorporated, the PEF/PA11/Joncryl blends displayed excellent toughness, reflecting in their improved elongations at break and unnotched impact strengths. It could be attributed to the improvement of compatibility and enhancement of interfacial adhesion between PEF and PA11, as confirmed by SEM. The complex viscosities of PEF/PA11 blends increased with the increase of Joncryl concentration, implying that the epoxide

group of Joncryl might react with the —COOH/—OH end groups of PEF and —COOH/—NH₂ end groups of PA11 simultaneously, which would form branched copolymers and increase the entanglement among molecular chains. To sum up, the addition of reactive compatibilizer with multi-functional epoxide groups into PEF/PA11 blends can effectively improve the compatibility between PEF and PA11, thereby raising the toughness of the fully bio-based PEF/PA11 blends.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-020-2449-z>.

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