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Refractive Index Engineering as a Novel Strategy toward Highly Transparent and Tough Sustainable Polymer Blends

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Electronic Supplementary Information

Abstract High transparency and toughness are prerequisites for sustainable polymers if they are to find wide application as alternatives to petroleum-based polymers. However, the utility of sustainable polymers such as commercially available polylactide (PLA) is limited by their inherent brittleness and high cost. Unfortunately, toughening PLA-based materials *via* cost-effective blending strategies without sacrificing transparency remains a challenge. Herein, we report a novel strategy involving active refractive index matching for creation of highly transparent and tough PLA blends. Specifically, we engineered the refractive index of a promising renewable poly(epichlorohydrin-co-ethylene oxide) elastomer by introducing polar ionic moieties *via* a simple chemical method, and we blended the resulting ionomers with PLA. The best blend showed an impact strength of > 80 kJ/m², an elongation at break of 400%, and high transparency (90%). These characteristics are of great importance for potential applications such as packaging. Our strategy offers a versatile new way to prepare high-performance sustainable polymer materials with excellent transparency.

Keywords Polylactide; Blending strategies; Refractive index matching; Poly(epichlorohydrin-co-ethylene oxide); Ionomers

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INTRODUCTION

The development of biobased sustainable polymers as alternatives to petroleum-based polymers has recently attracted intense interest because of increasing concerns about global warming, environmental pollution, and the depletion of nonrenewable resources associated with the production and consumption of conventional petroleum-based plastics.^[1–7] If sustainable polymers are to replace petroleum-based polymers, the former must possess properties that are complementary to or better than those of the latter, including high transparency, excellent mechanical performance, and low cost and weight. However, most of the commercially available bioplastics, such as polylactides (PLAs) and polyhydroxyalkanoates (PHAs), are inherently brittle and are expensive compared with their petroleum-based counterparts. Blending is a simple, cost-effective, and practical way to improve the properties of these bioplastics,^[8–10] but blends usually show lower essential

transparency, which is a prerequisite for a wide range of applications, especially in packaging. Given that packaging applications account for 26% of the total volume of plastics used, there is a high demand for bioplastics that exhibit both excellent mechanical performance and high transparency. Bioplastics can be used as ecofriendly replacements for petroleum-based polymers such as poly(ethylene terephthalate) and polyethylene in packaging applications.^[11] To date, most of the efforts to improve the transparency of bioplastic blends have concentrated on the compatibilization method, with a particular focus on decreasing the feature size of additive islands *via* reactive blending or adding a copolymer. However, this method is unsuitable for toughening polymer blends because a phase-separated structure with relatively good interfacial adhesion is key for achieving optimum toughness; that is, an elastomer that is fully miscible with the polymer matrix cannot act as a toughening agent. Consequently, despite extensive research,^[12–16] obtaining tough and optically transparent biobased polymer blends as well as composites *via* the compatibilization method remains difficult.^[17]

According to the Rayleigh theory,^[1,18,19] loss of transparency in a multiphase system such as a polymer blend or composite can be attributed to the scattering of light by the dis-

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persed phase or by particles with different refractive indices (RIs).^[20] For discrete spherical particles embedded in a matrix, the reduction of light intensity due to scattering is given by Eq. (1):

$$T = \exp \left\{ - \left[\frac{3\phi r^3}{4\lambda^4} \left(\frac{n_p}{n_m} - 1 \right) \right] s \right\} \quad (1)$$

where T is transmittance, ϕ is volume fraction of particles, r is particle radius, λ is wavelength of light, s is optical path length (film thickness), n_p is RI of the particles, and n_m is RI of the matrix. The difference between n_p and n_m is defined as the RI mismatch (Δn); decreasing Δn decreases scattering loss and increases transmittance. Therefore, controlling RI of the polymer matrix can be expected to improve transmittance.^[19] Recently, Macosko *et al.*^[5] reported that they obtained a transparent, tough PLA blend by carefully selecting a series of Pluronic surfactants with RI values that closely matched RI of the PLA matrix as modifiers. This work suggests that RI matching is an effective method for fabricating transparent, tough polymer blends. However, because there are only a few types of polymer pairs that have closely matched RIs, finding a known modifying agent that is suitable for a given sustainable polymer matrix is difficult. That is, properly choosing a modifier among the existing polymers greatly limits the effectiveness of RI matching strategy. We hypothesized that if we could use a chemical strategy to tune that of a commercial elastomer to match that of the matrix, we could achieve a transparent blend. To the best of our knowledge, active RI tuning has never been explored as a strategy for obtaining optically transparent, tough sustainable blends.

To test our hypothesis, we selected PLA as a biobased polymer matrix because of its high transparency, good mechanical strength, and ecofriendliness;^[19,21–24] and we selected poly(epichlorohydrin-co-ethylene oxide) (ECO), a promising renewable elastomer, as the dispersed elastomer. Our choice of ECO was based on two important considerations. First, renewable epichlorohydrin monomers derived from palm oil and other vegetable oils have been successfully brought to market as a result of extensive work carried out in academia and industry, and ECO has been shown to be a promising renewable toughening agent for PLA.^[9] Second, the chloromethyl groups of ECO provide highly reactive sites at which functional groups designed to actively tune the RI over a wide range can be introduced by simple, efficient synthetic methods.^[25,26] In present contribution, we actively tune the RI of the ECO elastomer to make it match with that of the PLA matrix by a facile chemical method. Here, we prepared the ECO-based ionomers by the quaternization reaction of designable imidazole and the ECO copolymer. Diversity and designability of cation and anion of these ionomers was reported to offer us widely tunable RI values of the ionomers.^[27] The miscibility, physical performance, and transparency of the PLA and ECO-ionomer blend are thoroughly investigated and the native mechanisms for toughening and high transparency are discussed.

EXPERIMENTAL

Materials

Poly(lactic acid) (PLA, 3001D) was purchased from NatureWorks

Inc, U. S. A. Poly(epichlorohydrin-co-ethylene oxide) (ECO, Epichlomer C 49 mol% epichlorohydrin unit) was purchased from Osaka Soda Co., Ltd., Japan. PLA and ECO were dried in vacuo prior to melt processing. 1-Butylimidazole (98%), lithium hexafluorophosphate (LiPF₆, 98%), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 98%), and lithium tetrafluoroborate (LiBF₄, 98%) were used as received from J&K Scientific LTD., China.

Synthesis of Chloroether Rubber-Butylimidazole Chloride (ECO-Cl)

ECO-Cl was synthesized by quaternization of ECO with 1-butylimidazole. A 1000 mL three-neck round bottom flask was charged with ECO (30.0 g, 18.45 wt% Cl, 0.05 mol chloromethyl functionality), and 1-butylimidazole (118.5 g, molar ratio of Cl/imidazole monomer is 1/6) was slowly added under nitrogen. 1-Butylimidazole was used both as reactant and solvent. The viscous mixture was homogenized under mechanical stirring. After refluxing at 115 °C in an oil bath for 20 h, the mixture was cooled to room temperature, precipitated from ethyl ether, and washed multiple times with ethyl ether. The crude product was then re-dissolved in ethanol and precipitated from ethyl ether. The pure product was dried in a vacuum oven at 40 °C for 48 h to remove the solvent, yielding yellowish-brown viscous product (45.77 g, 92%). ¹H-NMR (400 MHz, DMSO-d₆, δ , ppm): 9.93 (d, J = 140.8 Hz, 1H), 8.00 (s, 2H), 4.62–4.22 (m, 4H), 1.79 (s, 2H), 1.24 (s, 2H), 0.88 (s, 3H). ¹³C-NMR (101 MHz, DMSO-d₆, δ , ppm): 137.70, 137.46, 123.85, 122.59, 76.53, 70.58, 70.20, 69.13, 50.16, 48.88, 31.96, 19.23, 13.78.

Synthesis of Chloroether Rubber-Butylimidazole Hexafluorophosphate (ECO-PF₆)

ECO-PF₆ was obtained by the ion exchange reaction. ECO-Cl (10 g, 18.5 mmol) was dissolved in deionized water, and the ECO-Cl aqueous solution was added dropwise into an aqueous solution of LiPF₆ (4.30 g, 27.75 mmol). The reaction mixture immediately turned milky, and then yellowish precipitate was formed. After stirring for 30 min, the yellowish polymer was obtained by filtering from the aqueous LiCl solution, and the polymer (ECO-PF₆) was dried in a vacuum oven at 40 °C for 48 h. Yield: 12.6 g, 98%. ¹H-NMR (400 MHz, DMSO-d₆, δ , ppm): 9.05 (s, 1H), 7.79 (s, 1H), 7.68 (s, 1H), 4.50–4.15 (m, 4H), 1.78 (q, J = 7.5 Hz, 2H), 1.25 (q, J = 7.5 Hz, 2H), 1.01–0.82 (m, 3H). ¹³C-NMR (101 MHz, DMSO-d₆, δ , ppm): 137.02, 123.85, 122.58, 76.50, 70.59, 70.17, 69.09, 50.28, 49.16, 31.84, 19.58, 19.23, 13.65.

Synthesis of Chloroether Rubber-Butylimidazole Bis(trifluoromethanesulfonyl)imide (ECO-TFSI)

Following a procedure similar to that for ECO-PF₆, ECO-TFSI was also obtained in yield of 98%. ¹H-NMR (400 MHz, DMSO-d₆, δ , ppm): 9.08 (s, 1H), 7.81 (s, 1H), 7.65 (s, 1H), 4.47–4.12 (m, 4H), 1.78 (p, J = 7.4 Hz, 2H), 1.25 (p, J = 7.4 Hz, 2H), 0.90 (d, J = 7.9 Hz, 3H).

Synthesis of Chloroether Rubber-Butylimidazole Tetrafluoroborate (ECO-BF₄)

Following a procedure similar to that for ECO-PF₆ and using methyl alcohol solution instead of aqueous solution, ECO-BF₄ was obtained in yield of 95%. ¹H-NMR (400 MHz, DMSO-d₆, δ , ppm): 9.04 (s, 1H), 7.80 (s, 1H), 7.63 (s, 1H), 4.29 (d, J = 78.1 Hz, 4H), 1.91–1.64 (m, 2H), 1.34–1.19 (m, 2H), 1.04–0.76 (m, 3H).

Preparation of Blends

PLA, ECO, and ECO-X ($X = \text{PF}_6$, TFSI, BF_4) were dried in vacuo at 70 °C for 24 h prior to melt blending. Melt blends were prepared by using a Haake batch intensive mixer (Haake Rheomix 600, Germany) with a batch volume of 60 mL at a screw speed of 80 r/min for 6 min at 175 °C. In the mixing process, the torque was continuously monitored. PLA was mechanically mixed with ECO, ECO- PF_6 , ECO-TFSI, and ECO- BF_4 at the same ratio of 90:10, respectively. To explore the impact of different ratios of the same ion on the blends, PLA was mechanically mixed with ECO- PF_6 , which exhibited the best performance for PLA blending overall in three ions, from 5 wt% to 40 wt%, respectively. Similarly, as a control group, neat PLA was subjected to the mixing treatment to have the same thermal history.

Testing and Characterization Methods

Nuclear magnetic resonance spectroscopy (NMR)

All the ^1H -NMR spectra were recorded with a 400 MHz Bruker AVANCE III spectrometer by relating the signal to the solvent residual signal (^1H -NMR DMSO- d_6 2.5 ppm) obtained at room temperature, which confirmed the chemical structures of the synthesized functionalized elastomeric ionomers.

Dynamic mechanical analysis (DMA)

The dynamic mechanical properties of the blends were determined using a DMA Q800 system (TA Instruments) operated in single-cantilever mode with an oscillating frequency of 1 Hz. The test temperature range was selected from -60 °C to 120 °C with a heating rate of 3 °C/min.

Mechanical test

Tensile tests were performed on a universal testing machine (Instron 3360) equipped with a 1 kN electronic load cell and mechanical grips. The elastomeric specimens were prepared in the form of dumbbell shaped with 5 mm in width, ~1 mm in thickness, and ~10 mm in length. The tests were conducted at room temperature using a crosshead speed of 100 mm/min for elastomeric specimens and 10 mm/min for blends according to ASTM D638 (Type I). Cantilever impact strength tests were conducted by using a GOTECH pendulum impact tester at room temperature using a cantilever of 2.75 J according to the ASTM D256. For accuracy, at least six replicated specimens were tested for each sample to get an average value.

Differential scanning calorimetry (DSC)

Thermal analysis was performed on a TA Q2000 under a N_2 atmosphere. The samples were heated from 25 °C to 180 °C at a rate of 10 °C/min and held at 180 °C for 3 min. Then, after being rapidly quenched to -80 °C at a rate of 30 °C/min, the samples were heated again to 180 °C at 10 °C/min after stopping at -80 °C for 5 min.

Thermogravimetric analyses (TGA)

TGA (Q500 IR TA instrument) instrument was used to evaluate the composition and thermal behavior of ionomers and PLA blends. TGA were conducted with 5–10 mg of samples, in the temperature range from 25 °C to 600 °C with a heating rate of 2 °C/min under a N_2 atmosphere.

Scanning electron microscopy (SEM)

Cryofracture surfaces morphology of the samples was observed by a scanning electron microscope (SEM, HITACHI S-4800 instru-

ment). After dried in a vacuum oven at 60 °C for 12 h, the specimens were mounted on an aluminum stub using a conductive paint and finally sputtered with gold prior to examination. The morphologies of fracture surface of tensile and impact samples were obtained after tensile and impact test, respectively.

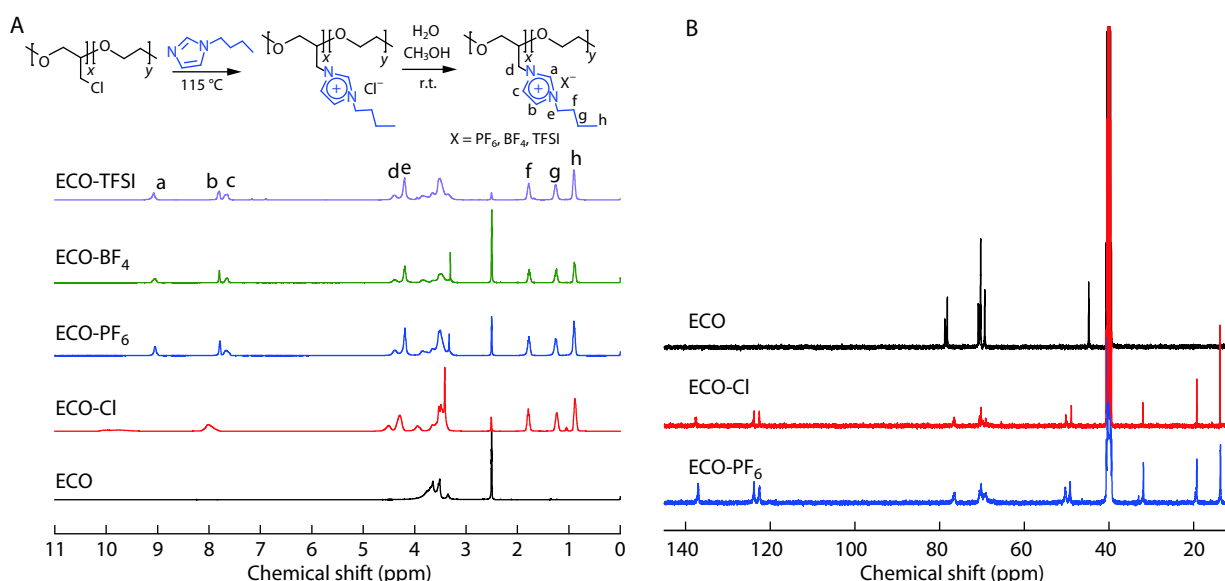
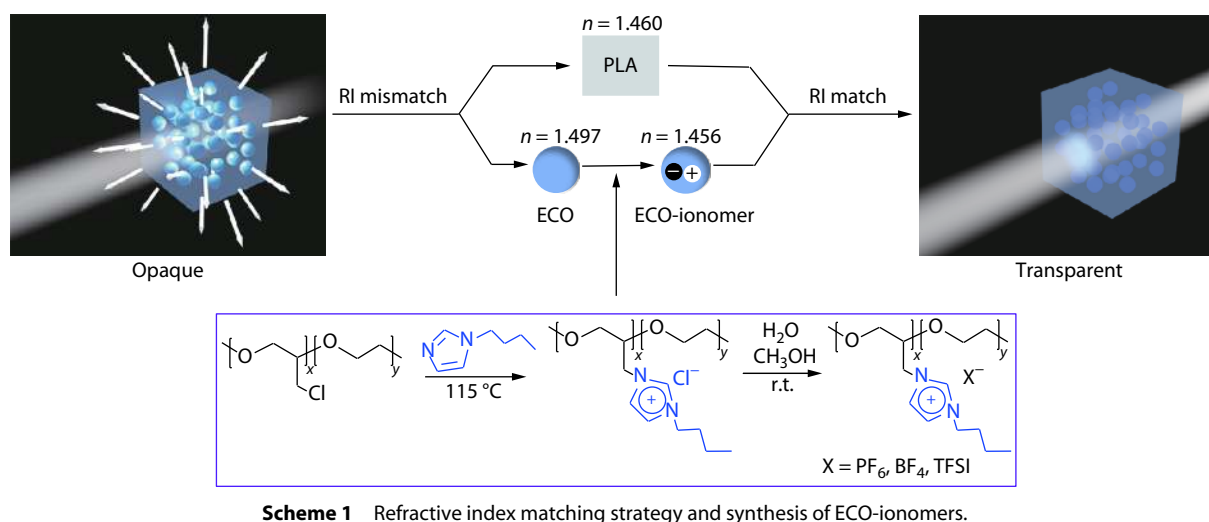
RESULTS AND DISCUSSION

Synthesis and Characterization of the ECO-elastomeric Ionomers

RI is well known to be strongly correlated with the nature of the introduced functional polar group including molecular polarizability and dispersive force.^[27,28] For example, RI of the imidazolium-based ionic liquids was recently reported to be tunable in a wide range from 0.986 to 1.629 by changing the chemical structure of the cations and anions.^[27] In the present study, to achieve a better match of RI between PLA matrix and ECO elastomer, we tuned the latter by introducing imidazolium-based ionic liquid moieties *via* a quaternization reaction with imidazole to afford cationic polyether, which was then subjected to ion exchange with various anions (Scheme 1). Specifically, we carried out one-pot quaternization reactions between the commercial ECO elastomer and 1-butylimidazole after optimizing the previously reported reaction conditions;^[29,30] subsequent ion exchange reactions with hexafluorophosphate (PF_6), tetrafluoroborate (BF_4), and bis(trifluoromethane)sulfonimide (TFSI) afforded the desired ECO ionomers.

This simple, efficient method for post-chemical modification of the ECO elastomer provided us with sufficient quantities of ECO ionomers for subsequent melt processing and characterization by ^1H -NMR and ^{13}C -NMR spectroscopy. All the ionomers were well-defined characterized by ^1H -NMR and ^{13}C -NMR spectra, respectively (Fig. 1). As shown in Fig. 1, compared to the ^1H -NMR spectrum of commercial ECO elastomer, the resonances for the imidazolium ring (signals a, b, and c, 9.1–7.5 ppm in Fig. 1), *n*-butyl group (signals f, g, and h, 1.7, 1.2, and 0.9 ppm, respectively), and methylene groups attached to N atom of the imidazole group (signal d, 4.3 ppm; e, 4.2 ppm) are clearly demonstrated in the ^1H -NMR spectra of ECO ionomers. This result confirms the successful quaternization reaction between ECO with imidazoles. In addition, it is also found that the resonances of proton a in the imidazole group of the ion-exchanged ionomers (a, 9.1 ppm; b, 7.8 ppm; c, 7.6 ppm) shift to lower field relative to that of ECO-Cl ionomer (about 9.8 and 8 ppm) in ^1H -NMR spectra. This phenomenon is reasonable because PF_6^- , BF_4^- , and TFSI^- are more electronic-withdrawing than Cl^- .

We were pleased to find that introduction of imidazolium and various counterions afforded ECO ionomers with novel and attractive performance characteristics, which is consistent with our earlier reports.^[31,32] The RIs (measured in the visible range by Abbe refractometer and ellipsometer), Δn values, thermal behavior, mechanical performance, and rheological properties of PLA, ECO elastomer, and ECO ionomers are shown in Table 1 and Fig. 2(a). By measuring at 632 nm, neat PLA has RI of 1.4613 and 1.4585, whereas neat ECO elastomer has a RI of 1.4978 and 1.4931; these values give a Δn of 0.0365 and 0.0346, which is consistent with the poor transmittance of PLA/ECO blends. In comparison, RIs of the ECO ionomers were closely matched to that of PLA, and interestingly the



counter anion affected the Δn value. The change of Δn was presumably attributed to the introduction of imidazolium cation and varied anions into the ECO ionomers.^[27] The ECO- PF_6 ionomer had the smallest Δn (-0.0024), suggesting that ECO- PF_6 would be an ideal modifier for obtaining highly transparent PLA-based materials.

The physical properties of the ionomers (thermal stability, thermal behavior, and mechanical properties) are also important determinants for the performance for PLA/ionomer blends during thermal processing. In the ECO ionomers, ionic interactions between the imidazolium moieties and the counter anions create physical cross-links between polymer chains, which leads to aggregation.^[33–35] As a result, the thermal behavior and physical properties of the ECO ionomers differed markedly from those of the ECO elastomer. For example, the glass transition temperatures (T_g) of the ionomers are higher than that of the neat ECO elastomer because the ionic clusters formed by the ionic chains limit the mobility of polymer segments in the former (Fig. 2b). In addition,

Table 1 RIs and Δn values for PLA, ECO, and ECO ionomers.

Sample	RI ^a	Δn ^a	RI ^b	Δn ^b
PLA	1.4613	—	1.4585	—
ECO	1.4978	0.0365	1.4931	0.0346
ECO- PF_6	1.4589	-0.0024	1.4545	-0.0040
ECO- BF_4	1.4644	0.0031	1.4655	0.0070
ECO-TFSI	1.4560	-0.0053	1.4447	-0.0138

^a Refractive index (RI) and refractive index mismatch (Δn) were measured by Abbe refractometer. ^b Refractive index (RI) and refractive index mismatch (Δn) were measured by ellipsometer.

tion, the ECO elastomer shows typical tensile behavior of a flexible elastomer (low tensile strength and high elongation at break), whereas all the ECO ionomers show higher tensile strengths with no obvious loss of flexibility (Fig. 2c). Note that the ECO-TFSI ionomer is sticky at room temperature, which prevents us from preparing a sample for the tensile test. The mechanical performance of ECO- PF_6 is notable: the tensile strength is greater than 3 MPa, and the elongation at break is

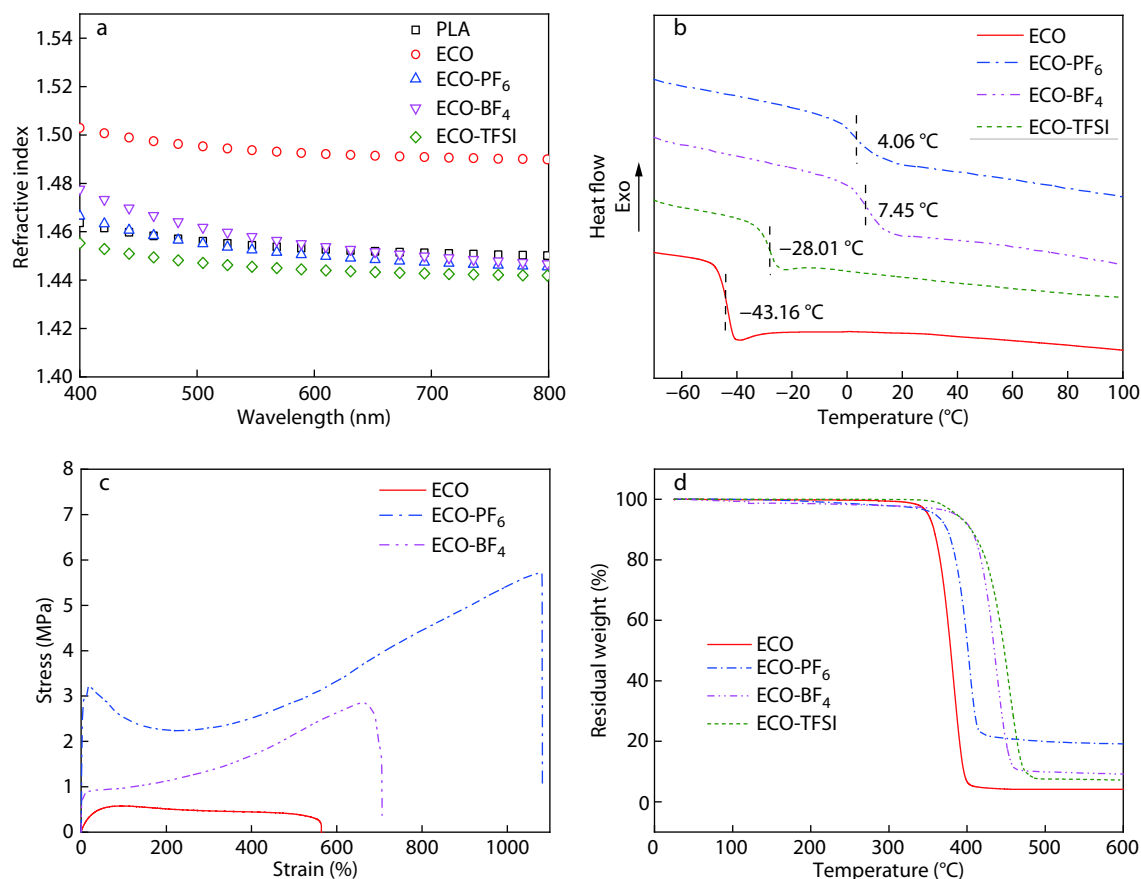


Fig. 2 (a) RIs of PLA, ECO, and ECO ionomers in the visible range; (b) Differential scanning calorimetry curves for ECO and ECO ionomers; (c) Tensile test data for ECO and ECO ionomers; (d) Thermogravimetric analysis data for ECO and ECO ionomers.

close to 1100%. In addition, the strain-stress curve of this ionomer shows a yield behavior characteristic of plastic. At the same time, introduction of the ionic groups imparts greater thermal stability to the ECO ionomers relative to that of the ECO elastomer. The results of thermogravimetric analysis demonstrate that the ionomers have higher thermal degradation temperatures (about 400 °C) than the ECO elastomer (Fig. 1d); the high thermal degradation temperature is conducive to thermal processing of PLA/ECO-ionomers blends (Fig. S2 in ESI). The combination of excellent RI matching, balanced mechanical performance, and good thermal stability indicates that the new ECO ionomers prepared in this study are very promising materials for toughening of PLA.

Transparency of PLA/ECO and PLA/ECO-ionomer Blends

We prepared PLA/ECO-PF₆ films with thicknesses of 0.12, 1.15, and 3.30 mm and compared them with PLA and PLA/ECO films of the same thicknesses. Fig. 3(a) shows photographs of these films, along with the transmission spectra of PLA, PLA/ECO, and the PLA/ECO-ionomer blends. The neat PLA film shows excellent transparency, but the blend composed of PLA and 10 wt% ECO elastomer, which has a quite different RI value, is very opaque. It shows a much lower transmittance than the PLA film (Fig. 3b). Interestingly, however, 90/10 PLA/ECO-ionomers blends show excellent transparency. In particular, the 90/10 PLA/ECO-PF₆ blend shows an impressive transmittance of 85%–92% in the

visible range, which is close to the value for neat PLA (Fig. 3b). To our knowledge, this transmittance is better than that of any of the previously reported PLA-based blends. More importantly, because the RI matching method used to generate the blends in this study differs from the compatibilization method, the transparency of these blends shows almost no dependence on the film thickness or ionomer content. We assessed the transparency of PLA/ECO-PF₆ films with thicknesses of 0.12, 1.15, and 3.30 mm, which correspond to the thicknesses that are commonly used in a wide variety of applications, such as films, sheets, and plastic injection parts, respectively. As can be seen in the images in Fig. 3(a), background patterns are clearly visible through the neat PLA film and the PLA/ECO-PF₆ film, even at a thickness of 3.30 mm, whereas the PLA/ECO blend is opaque. We also investigated how the proportion of ECO-PF₆ and PLA in the blends influenced their transparency (Fig. 3c). All the blends except one containing 40 wt% ECO-PF₆ still show satisfying visible-light transmittances (> 80%). These results clearly suggest that the RI matching strategy is superior to the compatibilization method, which is very concentration dependent. These unique advantages clearly suggest that the RI matching strategy by means of chemical modification is a very useful strategy for realizing good transparency.

Miscibility and Phase Behavior of the Blends

As mentioned above, the transparency of polymer blends is affected by two main factors: (1) the difference in RI between

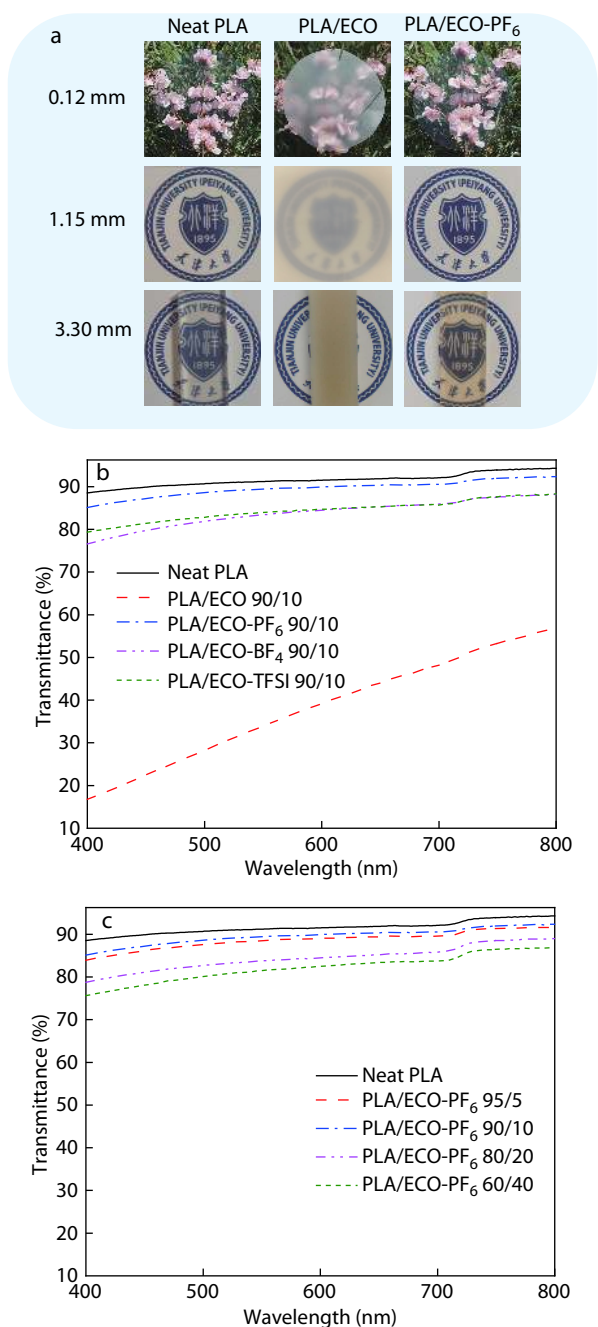


Fig. 3 (a) Photographs of PLA, PLA/ECO, and PLA/ECO-PF₆ films with thicknesses of 0.12, 1.15, and 3.30 mm; (b) Transmission spectra of PLA, PLA/ECO, and PLA/ECO-ionomer blends (thicknesses of films is 0.12 mm); (c) Transmission spectra of PLA and PLA/ECO-PF₆ blends with various amounts of ECO-PF₆.

the two phases^[36] and (2) the feature size of the additive particles in the blend.^[37,38] To determine whether or not miscibility and a decrease in dispersed particle size contribute to the excellent transparency of the PLA/ECO-ionomer blends in this study, we employ dynamic mechanical analysis (DMA) and scanning electron microscopy (SEM) to assess the miscibility and morphology of the blends (Fig. 4). PLA shows a clear damping ($\tan\delta$) peak at 77.3 °C (Fig. 4a), which corresponds to its T_g . In

contrast, the PLA/ionomer blends show two obvious peaks, corresponding to the glass transitions of PLA and the ionomer, respectively. These results demonstrate the limited compatibility between the PLA matrix and the ECO ionomers. Compared with the other ionomers, ECO-PF₆ shows slightly better compatibility with the PLA matrix, which plays a positive role in improving the mechanical properties of the PLA/ECO-PF₆ blend. The plots of $\tan\delta$ versus temperature for PLA/ECO-PF₆ blends with various ECO-PF₆ contents show that the T_g values of the two components are the closest for the 40 wt% ECO-PF₆ blend (Fig. 4b). However, the shift of the peak is very small, indicating very limited compatibility.

SEM images of the cryo-fractured surfaces of PLA/ECO and PLA/ECO-ionomer blends reveal a typical phase-separated morphology for all the blends (Figs. 4c and 4d), indicating the limited miscibility of the components. That is, the ionic groups play a negligible role in compatibilization between the elastomer and the PLA matrix. In fact, the dispersed particles of the ECO ionomers are slightly larger than those of the neat ECO elastomer (Fig. 4c). A slightly semi-continuous phase is observed in the 60/40 PLA/ECO-PF₆ blend (Fig. 4d). The morphology of a dispersed phase in a polymer blend is known to be determined by multiple factors, including composition, viscosity ratio, and component miscibility.^[18] The introduction of ionic groups to the ECO elastomer may have increased the viscosity of the blends, and such increase may in turn have increased the size of the dispersed phases. Taken together, the results of our investigation of the morphological structures of the PLA/ECO-ionomer blends indicate strongly that the transparency of the blends is not due to improvements in compatibility.

Mechanical Properties

Poor ductility and poor toughness are the major bottlenecks preventing the widespread application of PLA-based materials. Therefore, we compared the mechanical properties of the PLA/ECO-ionomer blends with those of PLA/ECO by means of tensile tests and notched Izod impact tests. Representative stress-strain curves for PLA and the PLA/ECO-ionomer blends are presented in Fig. 5, along with their impact strengths (details regarding the mechanical properties are provided in Tables S1 in the electronic supplementary information, ESI). The tensile test results clearly indicate that whereas neat PLA is brittle, the blends exhibit a ductile fracture behavior. During the tensile test, both the 90/10 PLA/ECO blend and the 90/10 PLA/ECO-PF₆ blend show an initial strain softening after yielding and then undergoes considerable cold drawing (Fig. 5a).

For all the blends, we observed an obvious stress platform of plastic deformation after the yield point, accompanied by necking shrinkage and stress whitening, resulting from shear yielding during stretching. Neat PLA is typically brittle and stiff with a poor elongation at break (only 6.8%) and a high tensile strength (~85.5 MPa). In contrast, the PLA/ECO blend shows the much higher ductility than PLA; the elongation at break is 212%, approximately 30 times as high as that of neat PLA. However, the flexibility of PLA/ECO blend is achieved at the cost of transparency. The PLA/ECO-ionomer blends also exhibit higher elongation than that of neat PLA; notably, the 90/10 PLA/ECO-PF₆ blend shows a remarkably high elongation at break (237%) and a tensile strength of about 60 MPa.

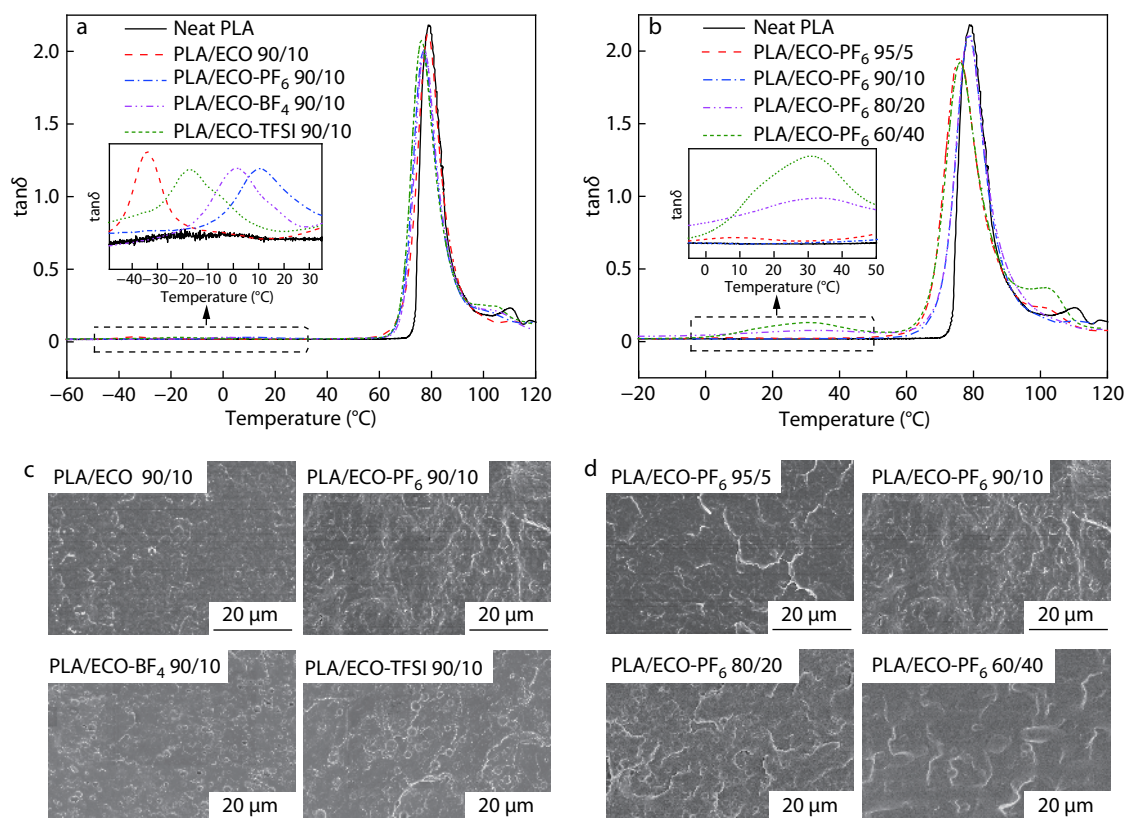


Fig. 4 (a) Plots of damping ($\tan\delta$) versus temperature for neat PLA, 90/10 PLA/ECO, and PLA/ECO-ionomer blends; (b) Plots of $\tan\delta$ versus temperature for neat PLA and for PLA/ECO-PF₆ blends with various amounts of ECO-PF₆; Scanning electron microscopy images showing the cryo-fractured surfaces of (c) 90/10 PLA/ECO and PLA/ECO-ionomer blends and (d) PLA/ECO-PF₆ blends with various amounts of ECO-PF₆.

These values are even better than those of the 90/10 PLA/ECO blend. Moreover, this excellent mechanical performance is gained without compromising transparency. The enhancement in tensile strength is attributed to the presence of ionic groups in the ionomer chains. It has been suggested that intermolecular interactions, such as hydrogen bonds and ion-dipole interactions, that form between imidazolium cations and anionic groups in the PLA matrix probably play a role in improving transfer of stress between the phases.^[39] However, increasing the proportion of ECO-PF₆ in the blend does not result in additional increases in flexibility (Fig. 5b), probably because of the larger size of dispersed ECO-PF₆ phases with a limited compatibility in these formulations and the slight degradation of the PLA matrix (Fig. S1 in ESI). As shown in Fig. 5(c), the ECO-ionomers still play a role of toughening agent in PLA. The impact strength of these PLA/ECO-ionomers blends is improved relative to neat PLA, about 6.4 kJ/m².

Fig. 6 presents the SEM images of the impact-fracture surface of neat PLA and PLA blends. The images indicate that cavitation and microvoid formation *via* interfacial debonding initiating the surround matrix shearing yield is the dominant toughening mechanism in present system.^[40–42] Some voids and shear yielding of the PLA matrix can be clearly observed throughout the entire impact fracture surface. However, a relatively brittle fracture surface with poor

interfacial adhesion between the phases is exhibited for all of the binary blends. Based on these results, to further improve the impact toughness of the blends, we envisage two promising strategies: (1) adding a suitable compatibilizer with a matched RI to improve the compatibility and (2) changing the cation and counter anion of the ionomers to realize a stronger interaction between ECO-ionomer and PLA while retaining the RI matching. These promising routes are now in progress in our lab.

CONCLUSIONS

In this study, we developed a novel active RI engineering approach for designing highly transparent, tough PLA/elastomer blends by means of a simple and efficient quaternization reaction involving the commercially available ECO elastomer and an imidazole monomer. These ECO ionomers with excellent balanced mechanical performance and RI values matching that of the PLA matrix were demonstrated to be very promising modifiers for the fabrication of tough and transparent PLA blends, leading to a remarkably high visible-light transmittance (90%) and high impact toughness (80 kJ/m²). These results clearly suggest that our novel active RI engineering strategy will be practical for developing highly transparent sustainable polymer materials for wide applications like packaging and will thus make an important contribution to achievement of a

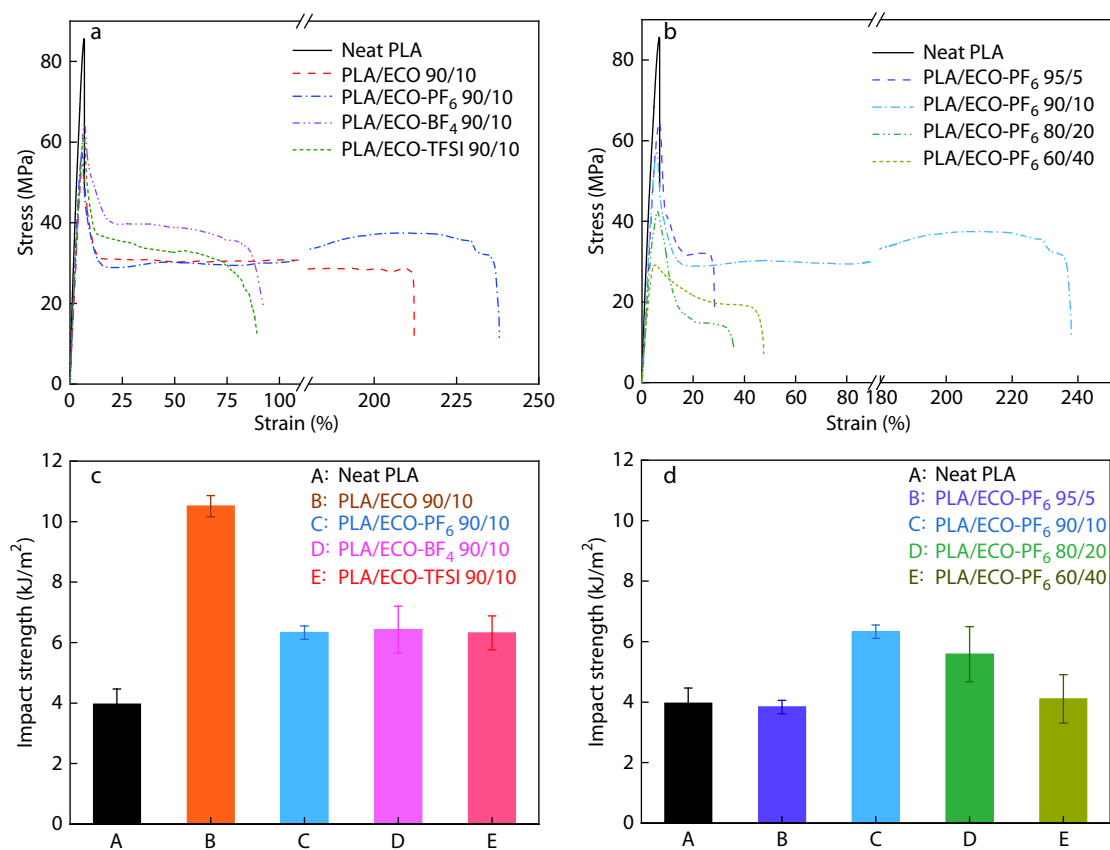


Fig. 5 (a) Tensile curves for neat PLA and 90/10 PLA/ECO and PLA/ECO-ionomer blends; (b) Tensile curves for neat PLA and PLA/ECO-PF₆ blends containing various amounts of ECO-PF₆; (c) Impact strengths of neat PLA and 90/10 PLA/ECO and PLA/ECO-ionomer blends; (d) Impact strengths of neat PLA and PLA/ECO-PF₆ blends with various ECO-PF₆ contents.

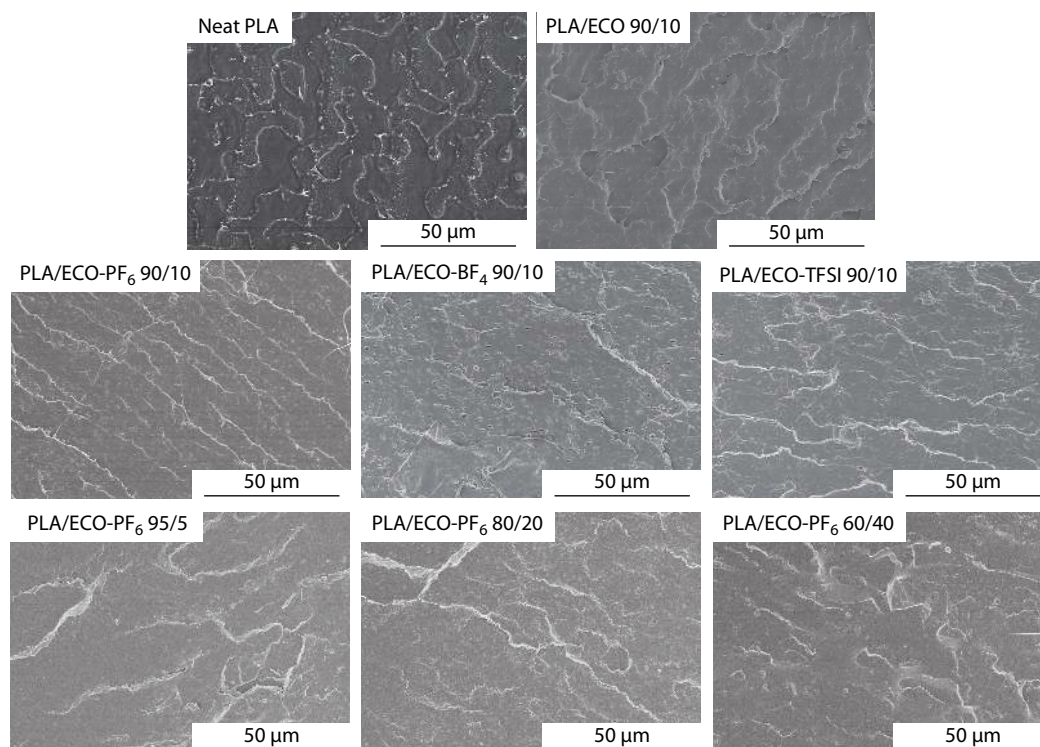


Fig. 6 SEM images of impact-fracture surface of neat PLA and PLA blends.

sustainable society.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-020-2439-1>.

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