Supertough and Transparent Poly(lactic acid) Nanostructure Blends with Minimal Stiffness Loss

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ABSTRACT: This contribution is an attempt to explore the effectiveness of a series of newly obtained thermoplastic elastomers (TPEs) as a toughening agent for modifying poly(lactic acid) (PLA). The TPEs, including ionically modified isotactic polypropylene-graft-PLA (iPP-g-PLA) copolymers with explicit graft length, graft density, and ionic group content, and an iPP-g-PLA copolymer with a very high molecular weight and explicit graft density, were elaborately designed and synthesized. The semicrystal or rubbery copolymer backbone originated from polypropylene-based ionic group was also added during graft onto reaction. All of these graft copolymers were identified with randomly distributed PLA branches, bearing a very high molecular weight (33–398×10^4) and very high PLA content (57.3–89.3 wt %). Unprecedentedly, with a very small amount of newly designed TPE, the modified PLA blends exhibited a significantly increased elongation at break (up to about 190%) and simultaneously retained the very high stiffness and excellent transparency. The nanometer-scale phase-separated particles with good compatibility and refractive index matching to the PLA matrix were demonstrated to play a crucial role in the excellent performance. The findings suggested that the newly designed iPP-g-PLA copolymers are very economic, promising, and effective modifying agents for developing highly transparent and tough PLA-based sustainable materials.

INTRODUCTION

Poly(lactic acid) (PLA), as an important and promising alternative to petroleum-based polymers with wide application, has been successfully commercialized from renewable sources and attracted increasing attention because of the concern of sustainable development.1−4 In particular, owing to its good optical clarity, high modulus, and strength, PLA is of great significance in short-life applications such as daily necessities packaging.2−4 Many modified PLA-based containers, including bottles, films, and thermoformed containers, have found their place in the packaging market and become increasingly popular because of the environmental concern.5 However, besides the high cost of producing PLA, the intrinsic brittleness of PLA (low elongation, ca. 2−7%) greatly hampers its widespread application.4−7 In recent years, tremendous efforts have been devoted to reducing the cost of production and improving the flexibility and toughness of PLA through various strategies such as plasticization,5,8−11 blending with other rubbery materials,5,7,12−17 copolymerization with other monomers18−21 adding nanofiller,22 etc. Among these strategies, blending PLA with other flexible elastomers is still the most economic and efficient approach to fabricate PLA materials with improved performance.5,17 However, the inevitable decrease in stiffness and/or transparency caused by the addition of soft toughening agents and the limited miscibility between the most ordinary toughening agents and PLA have been challenging in achieving a satisfactory improvement in PLA.3,5,17−21 Therefore, developing an effective and economic toughening agent to overcome the above-mentioned disadvantages for obtaining transparent PLA materials that simultaneously exhibit rigidity and toughness is of great importance and remains challenging.

Some block and graft copolymers have been utilized as efficient modifiers for polymer blends to achieve new materials with unique nanostructure and high performances. Bates et al. achieved progress in toughening PLA without compromising its optical clarity by a poly(ethylene oxide)-b-poly(butylene oxide) (PEO-b-PBO) copolymer.32 The addition of only 5 wt % PEO-b-PBO copolymer efficiently
improved the tensile toughness of the neat amorphous PLA (over an order of magnitude higher) without a significant reduction in transparency; however, an about 50% decrease in the yield strength was observed. Among the various previously reported PLA-containing toughening agents, including block and graft copolymers or linear polymers bearing reactive functional groups, PLA graft copolymers performed better in improving the compatibility of PLA and immiscible rubbery materials. Evidently, multiple graft points and a long rubbery main chain of graft copolymers play an important role in efficient chain entanglement and stress transfer. However, the synthesis of these kinds of graft copolymers via a simple, economic, and controlled reaction is still challenging due to the synthetic difficulty. Compared with classical, natural, and synthesized rubbers, thermoplastic elastomers containing both hard and soft segments, for example, poly(styrene-b-butadiene-b-styrene) or polyolefin copolymers, usually exhibit better processing performance and excellent tensile properties. Some non-biodegradable block polymers, therefore, based on the highly cost-effective linear low-density polyethylene (LLDPE), also perform very well in PLA toughening. Polypropylenes (PPs), as a kind of mature recyclable materials, offer both advantageous properties and low cost, in contrast to most thermoplastics. Moreover, many companies such as Braskem and Dow have achieved progress in the development of bio-based PP from renewable resources. Consequently, PP-based materials are very promising modifying agents for PLA to prepare high-performance materials. We have recently reported a series of isotactic polypropylene (iPP) with reactive terminal iodine, which could be easily transformed into various functional groups, thus leading us to fabricate a novel kind of efficient and promising toughening agent for modifying PLA. Moreover, iPP-based thermoplastic elastomers can be easily tuned by varying the amount of comonomer incorporation, from a semicrystalline plastic with a high melting point to an amorphous elastomer, which is another advantage in addition to their low cost. On the other hand, we also found that ionic aggregation plays an important role in achieving good compatibility of the ionicly modified bromobutyl rubber (BIIR) and the PLA matrix. Based on the above-mentioned aspects, an elastomeric ionomer containing an iPP-based main chain and PLA branch associated with organic cations, which is very likely to be a very efficient toughening agent for PLA without adding any compatibilizer, is very intriguing and worth exploring.

In this contribution, we attempt to develop a series of new thermoplastic elastomers based on iPP and PLA. The syntheses, characterization, and performance PLA toughening of a series of iPP-g-PLA ionomers and copolymer will be disclosed. The effects of these graft copolymers on the tensile properties, transparency, and native mechanism of the improvement in toughness and transparency were thoroughly studied based on the identification of chain structure and phase behavior.

### RESULTS AND DISCUSSION

#### Synthesis and Characterization of the TPEs

According to the rubber toughening mechanism, several criteria need to be fulfilled to achieve effective toughening. For instance, the rubber must be distributed as small domains in matrix, which should be thermally stable in the processing temperature, have a moderate molecular weight, show good interfacial adhesion, and immiscible with the polymer matrix. Therefore, we elaborately designed the following TPEs to improve the inherent brittleness and maintain the high transparency of PLA, by not very much reducing its tensile strength and modulus. The semicrystal or rubbery copolymer backbone originated from iPP was designed to improve the toughness and maintain a relatively high strength, while the grafted PLA side chain was to ensure a high level of compatibility with the PLA matrix. To obtain a further increase in the interfacial reinforcement, an imidazolium-based ionic group was also added during grafting onto the reaction. Two routes were adopted to obtain well-designed TPEs. I ionically modified iPP-g-PLA copolymers with explicit graft length, graft density, and ionic group content were synthesized via grafting (route 1), as presented in Scheme 1, by reacting the terminal imidazole group with the iodine group of iPP-11-iodo-1-undecene (IUD) copolymers via quaternization reaction. The PLA with $M_n$ in the range of $(2.3\times 10^3)$ was synthesized via the ring-opening polymerization of $\varepsilon$-lactide using N-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD) as a catalyst and N-(2-hydroxyethyl)-imidazole as an initiator (Table S1). The comblike propylene-11-iodo-1-undecene (IUD) copolymers bearing a pendant iodine group (iPP-IUD$_x$, where $x$ denotes the molar fraction of IUD; copolymers have $x = 6.5, 9.9$, and
12.8), was synthesized in this study (see Table 1) according to our previous report.\(^4\) To investigate the effect of graft copolymer with a higher graft density on PLA toughening, an iP-P-g-PLA copolymer with a very high molecular weight and an explicit graft density was designed and synthesized via grafting (route 2), as shown in Scheme 1. The direct copolymerization of propylene with a hydroxyl group containing a comonomer to give a functional iP-P is very challenging and has never been achieved previously. It was found that the Hf catalyst exhibited good tolerance toward the functionalization of the terminal iodine atom of the high-molecular-weight PP, as well as achieving satisfactory molecular weight and high content of PLA as well as the moderate ionic group content (around 4 mol %) of the synthesized ionomer ionomers 4 (GC-4) and 5 (GC-5) grafted with a longer PLA chain (M\(_w\) = 4500) were synthesized from iP-P-IUD\(_{6.5}\) and iP-P-IUD\(_{12.8}\), in which the conversions of the terminal iodine were determined by 1H NMR spectra and calculated according to the 1H NMR spectra.

As presented in Table 2, iP-P-g-PLA ionomers 1 (GC-1), 2 (GC-2), and 3 (GC-3) were obtained via the reaction of iP-P-IUD\(_{6.5}\) and iP-P-IUD\(_{12.8}\) with low-molecular-weight PLA (M\(_w\) = 2300), via 54.8, 40.2, and 33.0 mol % conversions of the terminal iodine, respectively. In addition, iP-P-g-PLA ionomers 4 (GC-4) and 5 (GC-5) grafted with a longer PLA chain (M\(_w\) = 4500) were synthesized from iP-P-IUD\(_{6.5}\) and iP-P-IUD\(_{12.8}\) in which the conversions of the terminal iodine were 50.6 and 23.8 mol %, respectively. The relatively low conversion of the above reaction was due to the fact that the terminal iodine atom of the high-molecular-weight iP-P copolymer was easily embedded by the long main chain and therefore not easily reacted with the terminal imidazole of PLA.\(^4\) However, GC-3 still has the largest PLA branches (or the ionic group content) among GC-1 to GC-3, after taking into account the IUD incorporation in the iP-P-IUD copolymer, conversion of iodine group, and the molecular weight of the graft ionomer together. The high molecular weight and high content of PLA as well as the moderate ionic group content (around 4 mol %) of the synthesized ionomer are expected to lead to excellent performance in PLA modification, including maintaining the strength, improving the elasticity of PLA, as well as achieving satisfactory compatibility with the PLA matrix.

As shown in Table 1, the iP-P-AUD copolymer with AUD incorporation as high as 15.5 mol % and molecular weight up to 42.8 \times 10^4 could be easily obtained under similar reaction conditions (iP-P-AUD\(_{15.5}\) in Table 1). After the deprotection reaction, the terminal hydroxyl group was used to initiate the ring-opening polymerization of lactide at 55 °C in a mixed solvent of toluene and chloroform, giving the iP-P-g-PLA copolymer with an extremely high molecular weight of up to 398 \times 10^4 (GC-6 in Table 2). As identified by Figure 2, all of the hydroxyl groups have participated in the ring-opening polymerization when MTBD was used as a catalyst. Therefore, the graft density of GC-6 was equal to that of the AUD incorporated in this case. However, the length of the PLA branch in GC-6 was not the same, as evidenced by a broad molecular weight distribution (PDI = 6.37) in the GPC curve. The content of the PLA branch in GC-6 is high, up to 89.2 wt %, calculated according to the increase in molecular weight, while it is 77.44 wt % based on the 1H NMR analysis (Figure 2), and therefore, this graft copolymer will surely exhibit very high compatibility with the PLA matrix during blending due to its high PLA content. As shown by the red rectangles in Figure 2, the disappearance of the methylene proton peak indicates a complete conversion of the hydroxyl group. Moreover, as

### Table 1. Summary of Copolymerization of Propylene and IUD or AlIBu\(_3\)-Protected AUD

| entry | IUD/AUD (mmol) | yield (g) | act. | incorp. (mol %) | M\(_w\) (x10^4) | PDI | T\(_g\) (°C) | T\(_m\) (°C) |
|-------|----------------|-----------|------|----------------|----------------|-----|-------------|-------------|
| iP-P  | 0              | 5.20      | 6.2  |                | 14.1           | 2.17 | 164.5       | 117.9       |
| iP-P-IUD\(_{6.5}\) | 1.79 | 3.01 | 3.6  | 6.5            | 27.7           | 1.98 | 132.3       | 87.9        |
| iP-P-IUD\(_9\)     | 3.57 | 3.48 | 4.2  | 9.9            | 30.3           | 1.69 | 114.6       | 69.3        |
| iP-P-IUD\(_{12.8}\)| 7.14 | 4.55 | 5.5  | 12.8           | 45.3           | 1.95 | 114.6       | 69.3        |
| iP-P-AUD\(_{15.5}\)| 9.96 | 0.48 | 0.6  | 15.5           | 42.8           | 2.34 |             |             |

\(^{a}\)Copolymerization conditions: catalyst = 5 μmol, propylene pressure = 1 atm, AlIBu\(_3\) = 0.55 mmol, [Ph\(_3\)C][B(C\(_6\)F\(_5\))\(_4\)] = 10 μmol, V\(_{in}\) = 40 mL, temperature = 25 °C, reaction time = 10 min, iP-P was prepared under similar conditions without the addition of comonomer as a control sample.

\(^{b}\)Activity: 10\(^8\) g mol\(^{-1}\)Hf\(^{-1}\) h\(^{-1}\).

\(^{c}\)Polydispersity index (PDI) = M\(_w\)/M\(_n\) obtained by gel permeation chromatography (GPC) versus standard polystyrene at 150 °C. Determined by differential scanning calorimetry (DSC) during the second heating and first cooling.

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Figure 1. 1H NMR spectra of the iP-P-IUD\(_{6.5}\) copolymer (black line), PLA with terminal imidazole (red line), and GC-1 (blue line).

Figure 2. 1H NMR spectra of the iP-P-IUD\(_{6.5}\) copolymer (black line), PLA with terminal imidazole (red line), and GC-1 (blue line).
shown in Figure 3, compared to the neat iPP, the copolymers exhibit more balanced physical performance. GC-1 and GC-2 are still semicrystalline and show higher yield strengths, while the other graft copolymers are all amorphous. All graft copolymers exhibit good ductility as common thermoplastic elastomers. They also exhibit good thermal stability with a high pyrolysis temperature ranging from 221 to 379 °C, which is very suitable for application as a toughening agent for the PLA matrix.

Phase Behavior of PLA and iPP-g-PLA Ionomer Blends. It is well known that the phase morphology and interfacial structure have a profound influence on the physical performance of the multiphase blend.4,40 To determine the relationship between the phase structure and physical property, we studied the morphologies of the blends through scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Figure 4 shows the representative SEM images of the graft copolymer-modified PLA blends. For all of the blends, we clearly observe that the added copolymer phases present as small particles (PP core diameter < 500 nm) uniformly distributed throughout the PLA matrix. Increasing the concentration of the graft modifier leads to more particles with a slight increase in the size and polydisperse dimensions.

Compared to the PLA/GC-1 blend, the PLA/GC-2 blend shows smaller dispersed phase size and better interfacial adhesion, indicating the improved compatibility of the GC-2 modifier with the PLA matrix.35,79 As for the PLA and GC-6 (with a high branched content) blend, the excellent compatibility with the PLA matrix is also observed for the dispersed phase. However, the size of the dispersed phase is slightly larger than those of the other blends, which may be due to the remarkably high molecular weight of the GC-6 copolymer. The uniformly distributed GC phases with a suitable interfacial adhesion are believed to make a great contribution to the excellent toughening effect.35,40 Figure 5 presents the TEM images of the representative PLA/GC-2 and PLA/GC-6 with 5 wt % graft copolymer content. The dispersed phase particle size of the PLA/GC-2 blend (Figure 5a–c) is around 180.4 nm due to the high compatibility with

| sample | Ex-polymer | conv. b (%) | Mw of PLA | PLA' (wt %) | Mw.d (×10^4) | Tm (°C) | Tc (°C) |
|--------|------------|-------------|-----------|-------------|--------------|---------|---------|
| GC-1   | iPP-IUD6.5 | 54.8        | 2300      | 58.8        | 67.2         | 144.3   | 82.2    |
| GC-2   | iPP-IUD9.9 | 40.2        | 2300      | 58.4        | 72.9         | 104.1   |         |
| GC-3   | iPP-IUD12.8 | 33.0       | 2300      | 57.3        | 106.0        |         |         |
| GC-4   | iPP-IUD6.5 | 50.6        | 4500      | 72.1        | 99.0         |         |         |
| GC-5   | iPP-IUD12.8 | 23.8       | 4500      | 65.4        | 131.0        |         |         |
| GC-6   | iPP-AUD15.5 | 100        | 3300      | 89.3        | 398.0        |         |         |

4Graft copolymerization conditions: VDMF = 50 mL, Vtoluene = 50 mL, PLA with terminal imidazole group, Mw = 2.3 or 4.5 × 10^3, reacted for 15 h at 55 °C. aConversion and weight fraction of PLA in the copolymer were determined by 1H NMR spectroscopy in 1,1,2,2-tetrachloroethane (TCE-d2) using integrals of the characteristic signals. bPLA content in the graft copolymer. cWeight-average molecular weight determined by GPC at 150 °C in 1,2,4-C6Cl13H3 versus narrow PS standards. dDetermined by DSC during the second heating curve and first cooling. eAverage molecular weight of PLA based on the GPC result.
the PLA matrix and the ionic aggregation effect. Consistent with the SEM results, the particle size of the dispersed GC-6 phase in the blend (Figure 5d–f) is relatively higher (348.8 nm) compared to that of the PLA/GC-2 blend. In the PLA/iPP-g-PLA blend, the poor miscibility of the iPP-based backbone with the PLA matrix leads to microphase separation, while the PLA grafts tend to form a homogeneous phase with the PLA matrix.

A combination of these two opposite driving forces results in a microphase-separated structure with very small dispersed phases. Considering the complex chemical structure of the graft copolymers, the dispersed particles should be a heterogeneous structure on various scales. Taking the GC-1 copolymer for example, the copolymer phase will include the crystals and nanodomains from the iPP-based backbone, the PLA phase formed by the high content of PLA graft densely locating at the interfaces, and the ionic aggregation formed by the ionic groups. Consequently, the dispersed particles of the copolymer are heterogeneous elastomers with the average diameter ranging from 100 to 500 nm. This feature is also clearly reflected in some parts of the TEM images, SEM images, and atomic force microscopy (AFM) results (Figures S5 and S6).

**Mechanical Properties.** With the well-defined iPP-g-PLA ionomers and copolymer in hand, we further explored their performance in modifying the commercially available PLA. First, a certain amount of graft copolymer was dissolved in toluene at 100 °C and then mixed with a chloroform solution of PLA under stirring. The mixture was stirred for 12 h at 55 °C to blend well. Figure 6 presents the representative stress–strain curves of neat PLA and the blend under tensile test. We thoroughly investigated the effect of the graft density, the $M_w$ of the graft PLA, the content of the ionic group, and the composition on physical performance. As demonstrated in Figure 6a, all of the additives can effectively toughen PLA even at a low loading of 5 wt %, and only a slight reduction in elastic modulus is observed. Compared to the blends (GC-1 and GC-3) with low graft density and short PLA segment, the blends with higher graft density and longer graft PLA chain exhibit better mechanical properties. The addition of 5 wt % of GC-5 remarkably improved the elongation at break to 68% without greatly reducing the elastic modulus. Figure 6b shows that increasing the portion of the graft copolymer in the blend further enhances the flexibility of the blend. The blend with 15 wt % GC-3 shows an extensive neck formation and cold drawing with a high elongation at break of up to 156%, increasing by 23 times over that of the neat PLA (6.5%). Moreover, the yield strength only slightly reduced relative to PLA. The minimal stiffness loss may be due to the increasing crystallinity of the PLA in the blend (Figures S7 and S8).

Keeping the graft copolymer at the optimum composition of 15 wt %, as shown in Figure 6c, we can learn that the high graft density is more beneficial for improving the flexibility. These...
results clearly suggest that the chemical structure of the copolymeric ionomers has a profound influence on the physical performance of the blends. Accordingly, to achieve the desirable toughening effect, we further increase the graft density of PLA to 15.5 mol % (GC-6), which leads to a considerable increase in the mechanical performance with a very high elongation of up to 192% (Figure 6d). The blend more clearly displays the necking and cold-drawing stage, suggesting the shear yielding of the PLA matrix.

In recent years, toughening of a brittle polymer like PLA by heterogeneous rubber microparticles or rubber nanoparticles from phase-separating complex copolymer architectures has stimulated intensive research interesting because of the high efficiency and balanced performance. Bates et al. reported that nanoscale particles formed by block and graft copolymers can effectively toughen brittle polymers such as PLA and iPP. According to the theories of Wu, the entanglement density, $\nu_e$, is one of the main factors governing the deformation mechanism of brittle polymers. Super-toughening is generally achieved at an optimum $\nu_e$ of 0.1 mmol/cm$^3$, as massive crazing and yielding of the matrix occurs at this level of $\nu_e$. PLA is predicted to have $\nu_e$ in the range of 0.12–0.14 mmol/cm$^3$. According to Wu’s relationship between optimum rubber particle size, $d_0$, and $\nu_e$

$$\log d_0 = 1.19 - 14.1\nu_e$$ (1)

the $d_0$ value for PLA can be calculated to be in the range of 0.16–0.31 $\mu$m. In the present work, the GC copolymer with the PLA graft was proved to have a tendency to form heterogeneous rubber particles with a nanometer-scale (range of 100–300 nm) phase-separated structure derived from the iPP-based backbone and PLA grafts. To investigate the toughening mechanism besides the excellent toughening effect, the tensile-fractured surfaces of the present blends were studied using SEM, as shown in Figure 7.

As shown in Figure 7b, blurry particles and cavities are clearly found in the highly deformed matrix. In the highly stretched region, more and longer fibrils from the higher deformed matrix appear aligned parallel to the stretch direction. In the present system, the nanoscale GC particles serve as stress-concentrated sites for the high elasticity over PLA, and the following concentrated stress can initiate cavitation in these soft nanoparticles and at the interfaces. The densely pendent PLA grafts entangle with the chains of the PLA matrix, resulting in an effective stress transfer. The multiple-crazing and matrix shear yielding lead to significantly enhanced toughness. A similar mechanism was also suggested by Bates et al. in PLA and block copolymer blends. In summary, owing to the phase structure of the particles and suitable interfacial compatibility with the matrix, the cavitation of the soft nanoparticles (around 100–300 nm) followed by matrix shear yielding is the main toughening mechanism of these blends.

**Optical Transparency.** Toughening PLA by blending without reducing its transparency remains a great challenge for
PLA and flexible elastomer blends because of the macrophase separation between PLA and most flexible elastomers. The heterogeneous structure of the nanometer-scale domains in the GC particles not only make a crucially important contribution to the toughening effect but also play an important role in retaining the excellent transparency of the blends. In the multiphase system, based on the Rayleigh theory, Novak proposed the following equation for describing the reduction of light intensity in multiphase systems

$$ T = e^{-\frac{3\mu r^3}{4f} \left( \frac{n_i^m - 1}{n_m^e - 1} \right)} $$

where $T$ is the transmittance, $\varphi$ is the volume fraction of particles, $r$ is the particle radius, $\lambda$ is the wavelength of light, $s$ is the optical path length (film thickness), $n_m^e$ denotes the refractive indices (RI) of the particles, and $n_m^i$ is the RI of the matrix.\(^{52}\) According to eq 2, two strategies can be adopted to maintain the essential transparency of the PLA material: decreasing the size of the dispersed phases ($r$) and RI matching by tuning the RI of the dispersed phases. As shown in Figure 8.

\[Figure 8.\] Refractive indices of iPP, PLA, and the graft copolymers.

As indicated in Figure 9, the GC-1, GC-2, and GC-3 copolymer exhibits greatly improved RI-matching degree of polyolefin with that of the PLA matrix. For the ultrahigh PLA content, the refractive index of GC-6 is almost coincident with that of the PLA matrix at the wavelength range of 500–800 nm. The improved RI-matching degree of the nanometer particles will greatly decrease the scattering of visible light in the blend. As proved in Figure 9, all of the blends show excellent transparency with an optical transmittance of around 90% in the visible light. The excellent transparency of the blends may be attributed to the following factors: decreasing the size of the uniformly distributed graft copolymer originated from the improved miscibility and RI matching. First, the presence of a large amount PLA-grafted segments will enhance the compatibility between the copolymer and the PLA matrix, which is beneficial for decreasing the dispersed phases. This is also identified by the morphological structure characterization and dynamic viscoelastic (tan $\delta$ versus temperature) curves (Figure S9). Second, as shown in Figure 8, compared to the iPP homopolymer, the GC copolymers show higher RIs because of the presence of PLA segments and polar ionic groups.\(^{36–39}\) The refractive index of GC-6 is almost coincident with the PLA matrix in the wavelength range of 500–800 nm. The effective RI matching helps keeping the transparency of the blend, especially for the PLA/GC-6 blend with ultrahigh PLA content. As demonstrated in Figure 9, the PLA/GC-6 blend shows the highest transmittance among the blends. In contrast, GC-1, which has the lowest graft density and PLA length, not only possesses the largest difference in RI but also retains the highest crystallinity (as shown in Figure S7) in the copolymer, leading to the reduction of light transmittance.

**CONCLUSIONS**

Polypropylene copolymer-based thermoplastic elastomers, iPP-g-PLAs, were efficiently synthesized and blended with PLA without the addition of any compatibilizer. A low-molecular-weight iPP-g-PLA ionomer was uniformly dispersed as nanoscale particles in a commercial high-molecular-weight glassy PLA plastic. These particles toughen the thermoplastic matrix through concurrent cavitation, crazing, and shearing yielding, producing a synergistic effect and resulting in a greater than 20-fold increase in the tensile toughness over the unmodified PLA plastic in the glassy state. An increase in the molecular weight of the PLA branch results in a better toughening effect on the PLA matrix due to the effective chain entanglement. After the addition of the modifier to the PLA,
the original transparency is still well preserved. This investigation advances the field of graft copolymer-modified thermoplastics. In addition, this series of graft copolymers will hopefully play an important role in the compatibilization category of polyester and polyolefin.

**EXPERIMENTAL SECTION**

**General Considerations.** All work involving air- and/or moisture-sensitive compounds was carried out in an MBraun glovebox or under a nitrogen atmosphere using the standard Schlenk technique. Based on our previous investigations, propylene/IUD copolymerization was carried out using the dimethyl (pyridyl-amido) hafnium catalyst (route 1 in Scheme 1) to prepare the reactive iodinated iPPs possessing high molecular weight ($M_w > 27.7 \times 10^4$). Another comonomer, 10-undecen-1-ol (AUD, from Alfa, 99%), was dried by a molecular sieve and distilled before use. When AUD was used as a comonomer (route 2 in Scheme 1), an additional equimolar ratio of AlBu3 was added into the AUD before adding into the catalyst system for hydroxyl group protection. t-LA purchased from TCI Instruments was recrystallized twice and drained under vacuum before use. Poly lactide (PLA, 3001D, NatureWorks, Inc.) was used as supplied.

**Characterization.** High-temperature $^{13}$C NMR($^1$H) data of polymers were collected by a Bruker AM-400 spectrometer at 120 °C with 1,1,2,2-tetrachloroethane-$d_2$ as a solvent. The glass-transition temperature ($T_g$) and melting point ($T_m$) were measured through differential scanning calorimetry (DSC), using a TA Instruments Q2000 calorimeter under a nitrogen atmosphere, at a heating and cooling rate of 10 °C/min under a nitrogen atmosphere. The molecular weights ($M_w$) and the molecular weight distributions ($M_w/M_n$) of the polymer samples were determined by a PL-GPC 220-type high-temperature gel permeation chromatograph at 150 °C. The mechanical tensile property of the samples was tested by Instron 5969 Machine using ISO 527-1 as a standard with a tensile rate of 50 mm/min. To ensure accuracy and repeatability, five duplicate experiments were performed.

The structural characterization of copolymers was done by a 400 MHz Bruker AVANCE III NMR spectroscopy using deuterated chloroform (CDCl$_3$, Innochem, 99.8 atom % D + 0.03% v/v TMS), methyl sulfoxide-$d_6$ (DMSO-$d_6$, Innochem, 99.8 atom % D + 0.03% v/v TMS), or deuterated 1,1,2,2-tetrachloroethane-$d_2$ (TCE-$d_2$, Acros Organics, 99 atom % D) as a solvent. The melting temperature, crystallization temperature, and related enthalpy of the polymer were determined by differential scanning calorimetry (DSC, TA Instruments, model Q2000). Samples (10 mg) were measured in a hermetic aluminum pan at a heating and cooling rate of 10 °C/min. The thermal degradation of the sample was studied using thermogravimetric analysis with a TA Q50 machine. For this test, samples with a typical weight of 10 mg were heated from 20 to 700 °C, with a ramp of 10 °C/min under a nitrogen atmosphere.

The relative molecular mass and molecular mass distribution of the polymers were measured on PL-GPC 220 at 150 °C. The elute solvent 1,2,4-trichlorobenzene (TCB) was stabilized with 0.0125% BHT at a flow rate of 1.0 mL/min, and the standard sample was Easi-Cal PS-1 (PL Ltd.). The infrared spectra of polymer films were measured using a Bio-Rad FTS-135 spectrometer in either reflective or transmissive mode. All samples had been dried under vacuum at 60 °C for 12 h before testing. The thickness of the sample is 100 μm.

The dynamic mechanical properties of the blends were measured with a DMA Q800 (TA Instruments) in a tension-film mode with an oscillating frequency of 1 Hz and test temperature ranging from −50 to 110 °C at a heating rate of 3 °C/min. The cross-sectional morphology of the blend polymer was scanned by a Hitachi s4800 scanning electron microscope equipped with a field emission electron gun. The cross section of the test sample was prepared by a rapid brittle fracture of the blend sheet after it was frozen in liquid nitrogen. A layer of gold was evenly sprayed on the cross-sectional surface before the test.

The UV−vis spectrum was measured by a Shimadzu UV-1600PC spectrometer. The optical path length of the color plate was 1 cm, and the scanning speed was 200 nm/min. The thickness of the film was 30−100 μm.

The film morphology of the polymers was investigated using tapping-mode atomic force microscopy (AFM) on a SPA400HV instrument with an SPI 3800 controller (Seiko Instruments). The phase morphologies of all of the blends were also measured by a TEM (Hitachi H-800) instrument operated at an accelerating voltage of 200 kV. The samples were sliced into 70−90 nm slices with a freezing microtome, and the vapor was stained by ruthenium tetroxide for 4 h. Particle size analysis using ImageJ indicated that the dispersed phase was a polyolefin dispersed in a PLA matrix. The average particle size is calculated using at least 150 particles, and the particle size distribution approximates normal distribution.

Tensile testing data were measured at room temperature using a universal mechanical testing machine (Instron 1211, Canton, MA), referenced to ASTM D638. A certain amount of graft copolymer was dissolved in toluene at 100 °C and then mixed with a chloroform solution of PLA under stirring. The mixture was stirred for 12 h at 55 °C to blend well. The blend was precipitated in sufficient ethanol solvent, and then the solvent was filtered off. The blend was placed in a vacuum oven for 24 h at 80 °C to remove the solvent. The samples for the tensile test were prepared by the melt-pressing method into a 0.5 mm thick plate at 180 °C and physical aging before the test according to the ASTM standard. A punch was used to prepare dog-bone samples with a total length of 26 mm, gauge length of 6 mm, width of 12 mm, and gauge thickness of 0.5 mm. The samples were tested at a speed of 5 mm/min until failure.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01165.

Synthesis data of PLA; NMR $^1$H spectrum and $^{13}$C($^1$H) spectrum of graft copolymers; SEM and AFM images of PLA and PLA blends; and DSC and DMA curves of PLA and PLA blends (PDF)

**AUTHOR INFORMATION**

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