A Study on Properties of Poly(3-hydroxybutyrate-co-4-hydroxybutyrate) with Various 4HB Contents and Triethyl Citrate Plasticization

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ABSTRACT

Sheets of poly(3-hydroxybutyrate-co-4-hydroxybutyrate)[P(3HB-co-4HB)] with various 4HB contents and triethyl citrate (TEC) plasticization are prepared by melt mixing and compression moulding. The thermal, crystalline and mechanical properties of these sheets are evaluated. Furthermore, fracture surfaces of samples plasticized by TEC are examined by scanning electron microscope (SEM). The results show that the increase of 4HB content can lead to the decrease of thermal parameters of samples such as melting temperature, glass transition temperature, crystalline temperature and crystallinity. However, the elongation-at-break of samples increases with the 4HB content increasing, and the strength-at-break decreases as a whole. The incorporation of 4HB units can improve the thermal stability of copolymer. The effect of TEC on the thermal and mechanical properties of samples is similar with that of 4HB unit. In contrast to 4HB unit, the increase of TEC content can worsen the thermal stability of samples. In addition, the copolymer of P(3HB-co-4HB) is compatible with TEC and its ductility can be improved by incorporation of TEC.

INTRODUCTION

Microbiologically thermoplastic polyester polyhydroxybutyrate (PHB) can be made by various bacteria as intracellular carbon and energy storage material [1-3]. It is of special scientific and practical interest mainly due to possibility of its production from cheap renewable raw materials, biodegradation and biocompatibility. It has been receiving much attention as new environmentally friendly materials, and numerous industrial applications, including new medical applications [4-6].

However, until now there is no large commercial production of PHB products because PHB has

Key Words:
biomaterial;
crystal structures;
mechanical properties;
wide-angle X-ray diffraction;
thermal properties.
higher cost, narrow processability window and brittleness, compared to commercial synthetic polymers. Very low resistance to thermal degradation seems to be the most serious problem related to processing of PHB. Since the melting temperature of PHB is around 170-180°C, the processing temperature should be at least 180-190°C. The thermal degradation of PHB at these temperatures proceeds very quickly. The principle reaction involves chain scission, which results in a rapid decrease in molecular weight [7]. Due to its high crystallinity, PHB is stiff and brittle resulting in very poor mechanical properties with low extension-at-break, which limits its range of application [8].

These drawbacks of PHB can be overcome by internal or external plasticization to improve processability and reduce brittleness of PHB. For the internal plasticization of PHB, various copolymers with 3-hydroxyvalerate [9-11], 4-hydroxybutyrate [2,12,13], 3-hydroxyhexanoic acid [14-16], and 6-hydroxyhexanoic acid [17] have been developed using the bacterial fermentation method. These copolymers can improve the physical and mechanical properties, compared with PHB homopolymer. On the other hand, the external plasticization is more efficient to apply to polymers because it can provide a relatively simple route to improve some mechanical properties of polymer as well as lowering the costs. Plasticizers weaken intermolecular bonds and facilitate conformational changes in polymers. As a result, the glass transition temperature \( T_g \) of the amorphous phase of the polymer decreases, whereas the deformability of the plasticized system at temperatures above \( T_g \) increases; and the flow temperature of the plasticized system also declines. This allows us to reduce the processing temperature which is especially important for PHB.

So far, many blends containing PHB have been studied [18,19], but only a few are totally biodegradable. In case of a packaging formed by different components, some of which are compostable and some are not, the packaging itself, as a whole, is not compostable. From this point of view, citrate-based plasticizers are interesting. Citrate plasticizers are derived from naturally occurring citric acid. They are nontoxic and ecofriendly plasticizers. Moreover, they can reduce significantly the glass transition temperature [20]. It is widely used in the plasticization of copolyester.

In the present work, the blends of P(3HB-co-4HB) with various 4HB contents and triethyl citrate (TEC) are prepared by melt mixing and compression moulding, which is novel and remarkably different with the solvent casting process, as described in a large number of published papers. Compared with solution casting, compression moulding can avoid the remnant of solvent and is close to the real practical process. Based on the sheets prepared by melt mixing and compression moulding, we studied the effects of internal plasticization of 4HB unit and external plasticization of TEC on the properties of P(3HB-co-4HB), in an attempt to enlarge the processing window and reduce brittleness of PHB. Furthermore, the properties of copolymer/plasticizers blends are investigated by DSC, WAXD, tensile experiment and TG. In addition, fracture surfaces of copolymer/TEC blends are examined by scanning electron microscope (SEM) to evaluate the compatibility of TEC with copolymer.

**EXPERIMENTAL**

**Materials**

Poly(3-hydroxybutyrate-co-4-hydroxybutyrate) was supplied by Tianjin Green Bioscience Company. The copolymer compositions were determined by \(^1\)H NMR and the molecular weights were obtained by gel permeation chromatography (GPC). Table 1 shows the compositions and molecular weights of the P(3HB-co-4HB) copolymers. Triethyl citrate, food-grade, was purchased from Guangzhou Gold Sun Chemical Company.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Composition (mol%)a</th>
<th>Molecular weightb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3HB (mol%)</td>
<td>4HB (mol%)</td>
</tr>
<tr>
<td>F-9</td>
<td>90.45</td>
<td>9.55</td>
</tr>
<tr>
<td>F-11</td>
<td>88.09</td>
<td>11.91</td>
</tr>
<tr>
<td>F-17</td>
<td>82.66</td>
<td>17.34</td>
</tr>
<tr>
<td>F-20</td>
<td>79.05</td>
<td>20.95</td>
</tr>
<tr>
<td>F-34</td>
<td>65.26</td>
<td>34.74</td>
</tr>
</tbody>
</table>

\( a \) Calculated by \(^1\)H NMR analysis. \( b \) Obtained from GPC.

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**Table 1. Compositions and molecular weights of P(3HB-co-4HB).**
Preparation of Blend Samples

The powder of P(3HB-co-4HB) was mixed with a quantitative amount of TEC for 3-5 min at 130°C with dual roller mill. The blending was moulded into sheets of ~ 2 mm thickness at 140°C under 15 MPa pressure for 10 min, then it was cooled and stored at room temperature in desiccator over 2 weeks. The tensile specimens were prepared by machine CP-25 with compression moulding sheets.

Characterization

The differential scanning calorimetry (DSC) data of the copolymer were recorded on a Netzsch DSC 204 under a nitrogen flow of 30 mL/min. The samples of 5 mg were encapsulated in aluminium pan. Samples were heated from 25 to 170°C at a rate of 10°C/min (the first heating scan), and held for 2 min at 170°C. After that, samples were cooled from 170 to -60°C at a rate of 10°C/min (the cooling scan), and held for 2 min at -60°C. Then, samples were heated from -60 to 170°C at a rate of 10°C/min (the second heating scan). The melting temperature, $T_{m1}$, was taken as the temperature of the melting endothermal peak in the first heating scan. The glass transition temperature ($T_g$) was taken as the midpoint of the heat capacity change in the cooling heating scan.

The crystalline temperature ($T_{mc}$ and $T_{cc}$) was taken as the peak temperature of the melting endotherm in the cooling scan or in the second heating scan. The melting temperature, $T_{m2}$, was taken as the temperature of the melting endothermal peak in the second heating scan.

Wide-angle X-ray diffraction (WAXD) measurements of P(3HB-co-4HB) samples were made on a D/max 3A system. CuK$_\alpha$ radiation ($\lambda=0.1542$ nm) was used as the source. X-Ray diffraction patterns were recorded at 25°C in the range 2$\theta$ =5-70° at a scan speed of 5°/min.

Tensile properties were measured on Instron1185 tester with 10 mm/min strain rate at room temperature. The sheets were cut into dumb-bell shaped specimens, with the overall length of 50 mm, the width of 4 mm at the narrow parallel portion, and the thickness of 2 mm. All data were calculated on an average of five specimens.

The thermal degradation of the pure and plasticized P(3HB-co-4HB) was carried out thermogravimetrically in the temperature range of 40 to 350°C using a Netzsch 209C system. The nitrogen flow rate was 30 mL/min and the heating rates were 10°C/min.

Fracture surfaces of the sheets were examined by Hitachi S-4700 scanning electron microscope (SEM) with an accelerating voltage of 10-20 kV. The samples were fractured firstly in liquid nitrogen, and then the fracture surfaces were selectively etched in methanol for 1 h at room temperature and dried for 24 h under vacuum at 40°C before observed by SEM.

RESULTS AND DISCUSSION

The Effects of Internal Plasticization of 4HB Unit on Properties of P(3HB-co-4HB)

Thermal Properties

Figure 1 shows the DSC thermograms of P(3HB-co-4HB) with different 4HB contents. Table 2 summarizes $T_{m1}$, $\Delta H_{m1}$, $T_{mc}$, $\Delta H_{mc}$, and $T_g$. It can be observed from Table 2 that for P(3HB-co-4HB), these data decrease with the increase of 4HB content, resulting from the decrease of regularity and increase of flexibility of P(3HB-co-4HB) chains with 4HB content increasing.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>First heating scan</th>
<th>Cooling scan</th>
<th>Second heating scan</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{m1}$ ($°C$)</td>
<td>$\Delta H_{m1}$ (J/g)</td>
<td>$T_{mc}$ ($°C$)</td>
</tr>
<tr>
<td>F-9</td>
<td>126.0</td>
<td>37.2</td>
<td>76.0</td>
</tr>
<tr>
<td>F-11</td>
<td>123.0</td>
<td>34.8</td>
<td>63.5</td>
</tr>
<tr>
<td>F-17</td>
<td>107.1</td>
<td>16.9</td>
<td>-</td>
</tr>
<tr>
<td>F-34</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

- Not found.
With the increase of 4HB content from 9 to 11 mol%, melting crystalline peaks become wider and shorter, and $T_{mc}$ decreases in Figure 1b. Moreover, with 4HB content reaching to 17 mol%, no crystalline peak appears in the cooling scan and a cold crystalline peak appears on the curve of F-17 in the second heating scan in Figure 1c. The cold crystalline peak is caused by reactivation of the frozen chain segment to crystallize due to a rise in temperature. In addition, when 4HB content is 34 mol%, there is not any crystalline peak at all in three scans. Those results suggest that increase of 4HB content can diminish the crystalline ability of P(3HB-co-4HB) resulting from destruction in regularity of the main chain by incorporation of 4HB unit.

It can also be observed from Figure 1 that two melting peaks can be observed in the second heating scan, especially for the curves of F-11. The one at a lower temperature should be the melting peak and the other one at a high temperature is melting peak of recrystallized phase forming during the melting process at lower temperature, because the intensity of the peak at the high temperature decreases with increasing the heating rate in comparison with the peak at lower temperature [21-23]. Moreover, the intensity of melting peak of recrystallized phase for F-11 is stronger than that of F-9, indicating that there are more recrystallized phases for F-11 at the same heating rate of 10ºC/min. These results suggest that incorporation of 4HB can enhance the motion of the chain segments.

**Dynamic Thermogravimetric Degradation**

Figure 2 shows the TGA and DTG curves of the thermal degradation of P(3HB-co-4HB) with various 4HB contents at 10ºC/min. The DTG curve shows only a single rate of mass loss peak, which indicates that the thermal degradation consists of one weight loss step. The thermal degradation temperature ($T_d$) of the copolymer shifts to a higher temperature with the increase of 4HB content, which suggests that the incorporation of 4HB unit can improve the thermal stability of copolymer. At the same time, it can be obtained that $T_{m1}$ shifts to a lower temperature with increasing 4HB content according to DSC analyses. Thus, the difference between $T_d$ and $T_{m1}$ becomes bigger with increasing 4HB content, indicating that the
range of the processing temperature of copolymer is enlarged. Therefore, the processing property of P(3HB-co-4HB) could be improved by incorporating 4HB units.

**Crystalline Properties**

Figure 3 shows WAXD patterns of melt moulding P(3HB-co-4HB) samples containing various contents of 4HB units. With 4HB content increasing from 9 to 34 mol% (Table 3), the degree of crystallinity obtained from the WAXD analysis is decreased from 37.72% to 1.39% because 4HB units cannot crystallize in the sequence of 3HB units and act as defects in the P(3HB) crystal lattice [24]. In spite of that, the crystallinity of copolymer in the present work is lower than that of the solution-cast films, especially for P(3HB-co-4HB) containing 34 mol% 4HB, which is smaller than that of P(3HB-co-42 mol% 4HB) film reported by Kunioka et al. [24]. This is due to the difference of crystallization time and viscosity in polymer melting state or solution. In solution, solvent evaporation rate is slow and crystallization can take place in sufficiently long time. In contrast to solution, the cooling rate of melt is fast and the chain segment has not enough time to arrange to form more perfect
crystal than that in solution. In addition, the viscosity of solution is lower and the chain segment can easily arrange to form a crystal. However, the viscosity in melt state is higher and the chain segment is difficult to move freely to form a crystal. So, the crystallinity of film produced through solution cast is higher than that of sample by melting compression moulding.

The (020), (110), (131) and (040) d-spacings of P(3HB-co-4HB) samples from WAXD patterns are included in Figure 3. The d-spacings of (020), (110) and (131) decrease slightly with variation of the 4HB content, while that of (040) plane changes little, indicating that the crystal lattice parameters of the P(3HB) unit cell are slightly reduced by the increase of 4HB content.

Mechanical Properties

The tensile properties of the copolymers with different 4HB contents are shown in Table 3. The yield strength and modulus of copolymers decrease with the 4HB content increasing, because the crystallinity decreases at the same time. However, the elongation-at-yield and elongation-at-break increase as well.

The strength-at-break also decreases with the increase of the 4HB content except for F-20 which exhibits a highest strength-at-break of about 18.74 MPa. This may be resulted from high mobility of F-20 chain with proper 4HB content which can enhance the motion of the chain segments interpreted in DSC analysis. During the tensile process at the given tensile rate, the crystallites are broken and the main chains orient so that a higher tensile strength can be obtained. However, more 4HB units can lead to destroy the regularity and low crystallinity shown in Table 3, which can reduce the tensile strength so that F-34 has a low tensile strength about 0.8 MPa. In addition, the strength-at-break of the sheets obtained in present work is smaller than that of the solution-cast films, because the tensile strength depends strongly on the crystallization condition discussed above [25].

The Effects of External Plasticizer of TEC on Properties of P(3HB-co-4HB)

From the above discussion, we can learn that F-17 possesses higher strength, higher elongation, and higher thermal stability at the same time, indicating more application potential as tissue engineering materials [4]. Therefore, the properties of F-17/TEC blends are discussed in the following part.

Thermal Properties

The DSC diagrams including three scans of F-17/TEC blends are shown in Figure 4, and all the thermal data are summarized in Table 4. It can be observed from Table 4 and Figure 4 that melting points (T_m1s) decrease with the increase of TEC content and ΔH_m1 shows a maximum value at 10 wt% TEC. These results indicate that TEC can destroy the crystal structure of the polymer leading to the decrease of T_m1. The incorporation of 10 wt% TEC can increase the number of crystallite leading to the increase of ΔH_m1, because a little of TEC can promote the mobility of chain segments.

It can be observed that no melting crystallization peak is found in the cooling scan in all blends except for pure F-17, because the incorporation of TEC decreases the crystalline ability and the chains cannot form high ordered crystal lattice in such short time under the cooling rate of 10°C/min in presence of TEC. However, the cold crystallization peaks (T_{cc}) appear in the second heating scan, as the chains are

### Table 3. Mechanical properties and crystallinity of P(3HB-co-4HB) with different 4HB contents.

<table>
<thead>
<tr>
<th>Sample</th>
<th>σ_Y (MPa)</th>
<th>ε_Y (%)</th>
<th>σ (MPa)</th>
<th>ε (%)</th>
<th>E (MPa)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-9</td>
<td>20.45(1.87)</td>
<td>11.90(0.78)</td>
<td>16.93(1.02)</td>
<td>37.02(9.31)</td>
<td>206.85(55.19)</td>
<td>31.91(5)</td>
</tr>
<tr>
<td>F-11</td>
<td>16.56(1.17)</td>
<td>17.12(0.65)</td>
<td>11.63(0.58)</td>
<td>283.99(11.51)</td>
<td>113.51(16.30)</td>
<td>17.65(5)</td>
</tr>
<tr>
<td>F-17</td>
<td>10.05(1.30)</td>
<td>20.89(0.82)</td>
<td>8.025(1.36)</td>
<td>565.10(23.66)</td>
<td>67.63(6.10)</td>
<td>13.08(5)</td>
</tr>
<tr>
<td>F-20</td>
<td>5.792(0.80)</td>
<td>32.53(0.93)</td>
<td>18.74(2.45)</td>
<td>859.74(33.32)</td>
<td>29.92(0.64)</td>
<td>13.37(5)</td>
</tr>
<tr>
<td>F-34</td>
<td>0.87(0.09)</td>
<td>159.71(1.45)</td>
<td>0.82(0.14)</td>
<td>1173.75(116.56)</td>
<td>0.58(0.03)</td>
<td>1.39(5)</td>
</tr>
</tbody>
</table>

Notes: σ_Y: strength-at-yield; ε_Y: elongation-at-yield; σ: strength-at-break; ε: elongation-at-break; E: modules of material; Crystallinity is determined by WAXD. The number in bracket is standard deviation.
reactivated for the rising temperature and begin to crystallize on the basis of orientation in the cooling scan.

Melting crystallization temperature (T_{mc}) and cold crystallization temperature (T_{cc}) are generally used to evaluate the rate of crystal nucleation and the rate of crystal growth, respectively. With the higher value of T_{mc} the faster the rate of crystal nucleation would be; and with smaller T_{cc} the faster the rate of crystal growth would be. It can be observed from Figure 4b that when TEC content is bigger than 10 wt\%, T_{mc} disappears. This indicates that incorporation of TEC can reduce the rate of crystal nucleation. In addition, it can be also seen from Figure 4c that T_{cc} decreases with the increase of TEC content. This suggests that incorporation of TEC can promote the rate of crystal growth. In conclusion, the incorporation of TEC can suppress the rate of crystal nucleation and promote the rate of crystal growth of F-17/TEC blends.

The glass transition temperatures (T_g) decrease with TEC content increases, as shown in Figure 4 and Table 4. It is reasonable that the incorporation of TEC can enlarge the interchain distance, which makes the polymer chains move more freely, resulting in the decrease of T_g.

T_{m2} decreases with the increase of TEC content given in Table 4. It can be seen that \Delta H_{m2} is far smaller than \Delta H_{m1} as a whole, indicating that the crystallinity of the second crystallization is smaller than those for the initial one. This suggests that recrystallization could still take place after the cooling scan when the samples are stored at room temperature. The difference between \Delta H_{m2} and \Delta H_{m1} decreases with the increase of TEC content, which means that the incorporation of TEC can diminish the degree of recrystallization at room temperature.

**Dynamic Thermogravimetric Degradation**

Figure 5 shows the TGA and DTG curves from the thermal degradation of F-17/TEC blends at 10ºC/min. Thermal degradation of pure P(3HB-co-4HB) occurs through two steps, which is characterized by two peaks on DTG curves. In addition, the onset degradation temperature shifts to a lower temperature with increasing amount of TEC, while its end temperature and inflection temperature of degradation hardly change. At the same time, T_{m} becomes lower with the
increase of TEC content according to DSC analyses. Therefore, the incorporation of TEC can enlarge the range of the processing temperature of copolymer just as that of 4HB unit does. Though the range of the processing temperature of copolymer enlarged, the thermal stability of F-17/TEC blends is deteriorated because the onset of degradation temperature becomes lower with the increase of TEC content.

**Crystalline Properties**

The WAXD patterns of F-17/TEC blends are given in Figure 6, which exhibit four intensive peaks at 13°, 17°, 25°, and 27°. The intensity of the peak at 13°

![Figure 5](image)

(a) TGA, and (b) DTG curves of the thermal degradation of P(3HB-co-4HB) with various TEC contents.

![Figure 6](image)

Figure 6. WAXD Patterns of F-17/TEC blends with various TEC contents.

### Table 4. Thermal data of F-17/TEC blends with various TEC contents.

<table>
<thead>
<tr>
<th>TEC containing (wt%)</th>
<th>First heating scan</th>
<th>Cooling scan</th>
<th>Second heating scan</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T&lt;sub&gt;m1&lt;/sub&gt; (ºC)</td>
<td>ΔH&lt;sub&gt;m1&lt;/sub&gt; (J/g)</td>
<td>T&lt;sub&gt;g&lt;/sub&gt; (ºC)</td>
</tr>
<tr>
<td>0</td>
<td>107.1</td>
<td>16.9</td>
<td>-10.0</td>
</tr>
<tr>
<td>10</td>
<td>105.7</td>
<td>27.1</td>
<td>-16.0</td>
</tr>
<tr>
<td>20</td>
<td>102.9</td>
<td>13.6</td>
<td>-20.7</td>
</tr>
<tr>
<td>40</td>
<td>98.5</td>
<td>10.0</td>
<td>-26.5</td>
</tr>
</tbody>
</table>

![Figure 6](image)

(b) WAXD Patterns of F-17/TEC blends with various TEC contents.
decreases with the increase of TEC content, and the intensity of the peaks at 17º, 25º, 27º shows a maximum value when TEC content is 10 wt%. This suggests that the addition of TEC can destroy the crystal lattice structure at 13º. Moreover, the 10 wt% TEC can enhance the form of the crystal structure for the other peak because the peak intensity at 17º, 25º, and 27º is maximum in all blends, which is consistent with the variety of ΔH_m1 from DSC analysis. However, the TEC can also destroy the crystal structure at excessive contents.

It can be observed from Figure 6 that d-spacings of four planes change in small range with the incorporation of TEC, indicating that TEC can slightly change the crystal lattice parameters of the blends. In addition, the crystallinity of the blends in Table 5 decreases rapidly with the increase of TEC content, and achieves 4.38% when the TEC content is 40 wt%. This is resulted from the embedding of TEC, which can destroy the crystalline phase and inhibit its formation.

Mechanical Properties
The mechanical properties of F-17/TEC blends are shown in Table 5. It can be seen that the strength-at-yield, the strength-at-break, and the modulus of blends decrease with the increasing of the TEC contents. When the TEC content increases from 0 wt% to 10 wt%, the modulus significantly decreases from 67.63 MPa to 3.8 MPa. However, the modulus changes slightly when the TEC content increases from 10 wt% to 40 wt%. The elongation-at-yield increases with the increase of TEC content. These phenomena can be attributed to the addition of TEC, which could improve the mobility of the chains and cause the change of crystallinity. In addition, the elongation-at-break increases exhibit a maximum value with the increase of TEC content. This indicates that the incorporation of the proper TEC content can make the chains move freely, leading to the improvement of the elongation-at-break. However, the excessive content of TEC will damage the physical crosslink and the network structure of F-17/TEC blends, resulting in a decrease in elongation-at-break.

Scanning Electron Microscope Analysis
Figure 7 shows SEM micrographs of the etched Figure 6. Scanning electron micrographs of F-17/TEC blends with various TEC contents.
fracture surfaces of F-17/TEC blends. As observed in the figures, even when TEC content is 40 wt%, there is no big hole formed due to the erosion of the conglomerate of TEC by methanol just as that reported by Choi et al. [20]. This result suggests that TEC is compatible with F-17. Moreover, the etched fracture surfaces become rougher with the increase of TEC content, which indicates that TEC can improve the ductility of the blends. Therefore, TEC can improve the ductility of copolymer without any phase separation in the blends.

CONCLUSION

The unit of 4HB and the plasticizer of TEC present significant effect on the thermal, crystalline and mechanical properties of P(3HB-co-4HB). The increase of the 4HB content can decrease the majority of thermal data such as $T_{m1}$, $\Delta H_{m1}$, $T_{mc}$, $\Delta H_{mc}$ and $T_g$, and diminish the crystallization ability. In addition, with the increase of 4HB content, elongation strength of copolymer can increase as a whole and at the same time the crystal lattice parameters of P(3HB) unit cell are slightly reduced. The effect of TEC content on the properties of F-17/TEC blends is similar to that of 4HB content. However, the thermal stability of F-17/TEC blends is deteriorated which is contrary to the effect of 4HB unit. Moreover, TEC can greatly improve the ductility of copolymer without any phase separation in the blends.

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