Reinforcing and Toughening Modification of PPC/PBS blends with Epoxy Terminated Hyperbranched Polymers as Compatibilizer

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Research Article

Keywords: polypropylene carbonate, polybutylene succinate, hyperbranched polymer, toughening

DOI: https://doi.org/10.21203/rs.3.rs-505334/v1

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Abstract

Polypropylene carbonate (PPC)/polybutylene succinate (PBS) blends were prepared by melt-blending with terminal epoxy-based hyperbranched polymers (EHBP) as modifier. The thermal properties, mechanical properties, rheological properties and fracture morphology were characterized by dynamic thermomechanical analyzer (DMA), thermogravimetric analyzer (TGA), electronic universal testing machine, rotating rheometer and scanning electron microscope (SEM), etc. Upon addition of EHBP, the difference between the glass transition temperature of PPC and PBS became smaller, indicating the compatibility of PPC and PBS were improved by EHBP. Furthermore, by adding 0.5phr of EHBP, the impact strength increased from 9.55 kJ/m$^{-2}$ to 17.31 kJ/m$^{-2}$, the elongation at break increased from 136.29–204.39%, and the tensile strength increased from 10.00 MPa to 16.84 MPa. The fracture surface of the PPC/PBS blends became rough with the increase of EHBP, even with large filamentous structures and tiny holes, which further demonstrated that EHBP acted as an excellent toughening effect on PPC/PBS. Gel content analysis confirmed that both physical and chemical micro-crosslinking were formed after incorporation of EHBP.

Introduction

The plastics industry is proliferating continuously and the global plastics production in 2018 has reached around 360 million tones. This has further aggravated the problem of waste plastics, which if not appropriately disposed cause serious environmental problems like land pollution, marine pollution and water source pollution. As an alternative, there has been a paradigm shift from substituting synthetic plastics i.e. fossil-based to bioplastics[1]. In recent years, research and applications of biobased and biodegradable polymer materials[2, 3] have received more and more attention[4]. Polypropylene carbonate (PPC), which is a fully biodegradable plastic, is synthesized from carbon dioxide (CO$_2$) and propylene oxide[5] and is beneficial to slow down the "greenhouse effect" and oil energy consumption. Nevertheless, the presence of a large number of ether bonds has caused the material with low glass transition point, low thermal decomposition temperature and low tensile strength, which limits the application range of PPC[6].

Polybutylene succinate (PBS) is an aliphatic polyester obtained by dehydration of succinic acid and butanediol. It is a typical fully biodegradable material with high crystallinity, excellent processing properties and strong mechanical strength which is equivalent to polypropylene and polyethylene[7, 8]. Generally speaking, the blending of PPC and PBS is an effective method to improve the tensile strength of PPC, but the effect of direct blending is not obvious for the poor compatibility between the two polymers[9, 10].

Hyperbranched polymers (HBPs), which are polymerized with polyfunctional monomers, represent a new polymer form developed in the past 30 years[11]. Compared with linear polymers, HBPs have many unique advantages such as the three-dimensional (3-D) globoid-like structure, a high density of active terminal functional groups at the periphery, abundant internal cavities inside, many branch points, and a
low probability of molecular chain entanglement. Therefore, HBPs are applied in multiple fields such as medicine, biology, engineering and materials[12–14]. Compared with a conventional small molecular modifier, macromolecular HBPs cannot easily be separated out and migrate. In recent years, more and more attention has been paid to improve the resin properties of polymers by using HBPs as a modifier[15–18]. The reported literatures[19, 20] have indicated that if the terminal functional groups of a HBP were used as a proton donor or receptor to act on the resin, hydrogen bonding would be generated among the molecules of the blended polymers. Hydrogen bonding influences several properties of polymeric blends, such as the blending efficiency, glass transition temperature (T_g), melting point, crystallization, and surface energy, etc.

In this study, the synthesis of terminal epoxy-hyperbranched polymer (EHBP) was carried out, and then melt-blended with PPC/PBS. EHBP has the three-dimensional network structure and a large number of highly active terminal epoxy groups[21–23], which was used to improve the combability as well as the mechanical properties of PPC/PBS blends. The results showed that the addition of EHBP could form hydrogen bonding and micro-crosslinking with PPC and PBS, which was beneficial to the improvement of mechanical strength of PPC/PBS system and expand its application range.

Experimental

Materials

Poly(propylene carbonate) (PPC101, Technical Pure, M_w = 7.5 × 104 g·mol⁻¹, DI = 2.17) was purchased from Nanyang Zhongjutianguan Crown Low-carbon Technology Co., Ltd. PBS(HX-Z101) was purchased from the Anqing Hexing Chemical Co. Ltd. (Anhui, China). P-toluenesulfonic acid, boron trifluoride diethyl ether, sodium hydroxide and diaminodiphenylmethane were purchased from Sinopharm Chemical Reagent Co., Ltd. 2,2-Bis(hydroxymethyl)-propionic acid was purchased from Tianjin Weiyi chemical technology Co., Ltd. Trimethylolpropane was purchased from Tianjin Bodi Chemical Co., Ltd. Trichloromethane was purchased from Beijing Chemical Works. Epichlorohydrin was purchased from Chengdu Huaxia Chemical Reagent Co., Ltd.

Synthesis of epoxy-terminated EHBP

HBPE was prepared according to the established protocols[24]. Boron trifluoride diethyl ether was added into the system of EHBP at 75°C. Epichlorohydrin was then added dropwise. After the reaction was carried out for 2 h, the excess of moisture, epichlorohydrin and small molecular by-products were pumped off under reduced pressure. Saturated sodium hydroxide solution was thereafter added and the reaction was continued at 75°C for 2 h. After adding 300 mL of chloroform at room temperature, the product was dissolved in 30 min. The mixture was filtered and the filtrate was purified first using a rotary evaporator and then under vacuum to obtain the desired product as an orange viscous liquid[25]. Figure 1 shows the process and detailed chemical structure schematic diagram of the prepared EHBP.

Preparation of the blends
PPC was dried at 35°C for 12 hours in a vacuum drying oven. PBS was placed at 60°C for 4 hours in an oven. After that, PPC and PBS resin particles were weighed at a ratio of 7/3, and mixed with different of EHBP.

An Internal Mixer (SHR-10A, Zhangjiagang Hongji Machinery Co., Ltd.) was used to evenly blend the PPC, PBS and EHBP. The mixing was carried out at 140°C for 10 min at a speed of 60 rpm. For the purposes of comparison, pure PPC/PBS resins were also melt-blended under the same processing conditions. The blends were then cooled down to room temperature before crushing and granulating through a Crushing Machine (HP-150, Beijing Huanyatianyuan Mechanical and Technical Co., Ltd.).

Standard splines were made through an injection molding machine (TY-400, Hangzhou Dayu Machinery Co., Ltd.). The temperature was set to 145°C, and the injection pressure was 50 bar, and the injection volume was 20%.

**Characterization**

Dynamic mechanical analysis (DMA) was conducted on a machine (DMA7100, Hitachi High-Technologies (Shanghai) Co., Ltd) with a frequency of 1 Hz and a heating rate of 3°C/min from −80°C to 60°C.

Thermo gravimetric analysis (TGA) and derivative thermo gravimetric analysis (DTG) were conducted on a Thermogravimetric analyzer (Q50, TA Instruments, USA) under a N₂ atmosphere. The scanning temperature ranged from room temperature to 550°C at a heating rate of 20°C/min. The temperature at maximum weight loss was determined based on the derivation of the TGA results.

Electronic universal testing machine (CMT6104, MTS Industry System Co., Ltd., Shenzhen, Guangdong Province, PR China) was used to test the tensile strength and the elongation at break of the PPC/PBS/EHBP blends. The tensile rate was set to be 50 mm/min. The size of the spline was determined according to the ISO 527-2:2012 standard: dumbbell shaped spline, L = 150 mm, d = 4 mm.

The unnotched impact tests were carried out using an electronic Izod impact testing machine (XJUD5.5, Chengde Jinjian Testing Instrument Co., Ltd., Chengde, Hebei Province, PR China) according to ISO 180:2019 standard. The size of the unnotched spline was 80 mm × 10 mm × 4 mm. The impact energy of the pendulum was 2 J.

In the circulation system, the sample was dissolved in chloroform at 55°C for 8 hours and dried at 80°C for 4 hours. The gel content was calculated by Eq. 1.

\[
\text{Gel content} = \frac{m_1}{m_2} \times 100\% \tag{1}
\]

Where \(m_1\) and \(m_2\) are the mass of the PPC/PBS/EHBP blends after and before dissolution, respectively.
Rheological tests were carried out by Rotary Rheometer (MARS, Thermo Scientific Co., Ltd.) at 145°C. The angular velocity was set in the range of 0.01–100 rad/s.

Impacted fracture surface of blends were observed with a scanning electron microscope (QUATA250, FEI, USA) operating at 10 kV accelerating voltage after the surfaces were coated with a thin layer of gold.

**Results And Discussion**

**FTIR analysis**

It is well known that FTIR could be used to detect the molecular interactions between two components of a blend. The FTIR spectra of PPC/PBS and PPC/PBS/EHBP blends are shown in Fig. 2. The wide absorption band near 3447 cm\(^{-1}\) corresponded to the stretching vibration of the -OH group. The bands near 2961 cm\(^{-1}\) and 1747 cm\(^{-1}\) corresponded to C-H and C=O stretching vibrations. In addition, the peaks at 1458 cm\(^{-1}\) and 1230 cm\(^{-1}\) were attributed to -C-H bending and -CO vibration. The C-C of methyl had a peak at 980 cm\(^{-1}\), while the methylene deformation had a peak at 788 cm\(^{-1}\). The sharp bands at 1070 cm\(^{-1}\) were attributed to C-O-C vibrations. There was a peak at 651 cm\(^{-1}\), which was attributed to the -COO bending zone. After adding EHBP, one can obviously observe that the vibration absorption peak of methyl in PPC/PBS becomes more sharps. The C=O band of ester carbonyl was at 1747 cm\(^{-1}\), while the absorption peak of C=O in PPC/PBS/EHBP composites was shifted to 1744 cm\(^{-1}\) after the addition of EHBP. The vibration absorption peak of C-O-C was shifted from 1070 cm\(^{-1}\) to 1070 cm\(^{-1}\). The offset of the three different groups proved that the original hydrogen bonding in the blend system was increased. The results showed that the hydrogen bond strength and interaction of the composites were strengthened after adding EHBP.

**Gel content of the PPC/PBS/EHBP blends**

The gel content of the PPC/PB/EHBP blends was measured to demonstrate the presence of the chemical micro-crosslinking effect. During the dissolving process, molecular chains with physical micro-crosslinking are completely dissolved due to the rupture of hydrogen bonds. However, those molecular chains with chemical micro-crosslinking can only be swelled. The pure PPC, PBS, and EHBP can be completely dissolved in chloroform. However, after adding EHBP, the modified products cannot be completely dissolved. The specific gel content measurement results were shown in Fig.3, the addition of different amounts of EHBP will cause different degrees of chemical micro-crosslinking between the blends. The gel content of the pure blends was 1.23%, and when the content of EHBP was 2.0phr, the degree of chemical micro-crosslinking was about 6.63%. The gel content analysis confirmed that there was not only physical micro-crosslinking but also chemical micro-crosslinking between PPC/PBS/EHBP blends upon addition of EHBP.

**Rheological analysis**
It can be seen from Fig.4 that with the incorporation of the EHBP, the storage modulus (\(G'\)), the loss modulus (\(G''\)) and the viscosity of the blends showed a gradual decrease trend. On the one hand, EHBP was of spherical structure and low viscous nature. Consequently, it can lubricate the PPC/PBS molecular chains. With the increase of EHBP content, such a lubrication effect was also increased. On the other hand, there were hydrogen bonding and chemical reactions with the terminal hydroxyl groups and carboxyl groups of PPC/PBS and the epoxy-terminated groups of EHBP, resulting in a small amount of micro-crosslinkings, which gradually made the structure change from a linear state to a micro cross-linked state. However, the lubricating effect of the system was dominant, so \(G'\), \(G''\) and the viscosity gradually decreased.

**Thermal properties**

To investigate the miscibility between PPC and PBS, DMA and DSC of the blends were performed. The DMA and DSC curves and the relative parameters of PPC/PBS blends containing different content of EHBP were shown in Fig.5 and Tab.1. The glass transition temperatures (\(T_{\alpha}\)) values of PBS and PPC were denoted as \(T_{\alpha1}\) and \(T_{\alpha2}\), respectively, and the difference between \(T_{\alpha1}\) and \(T_{\alpha2}\) was denoted as \(\Delta T_{\alpha}\). It can be seen that two glass transitions appeared in the PPC/PBS blends, indicating that the two moieties were partially compatible systems. After adding EHBP, the \(\Delta T_{\alpha}\) reduced from 76.76ºC to 71.13ºC, suggesting the improved miscibility between the two moieties.

As shown in Fig.5 (d), the glass transition temperature (\(T_g\)) values of PBS and PPC were denoted as \(T_{g1}\) and \(T_{g2}\), respectively, the difference between \(T_{g1}\) and \(T_{g2}\) was denoted as \(\Delta T_g\). Similar with \(\Delta T_{\alpha}\), \(\Delta T_g\) was reduced from 76.76ºC to 71.13ºC. The reason for this phenomenon was that after adding EHBP, the active oxygen atom on the epoxy group at the end of EHBP easily formed intermolecular hydrogen bonding with carboxyl groups and ester groups in the PPC molecular chains and PBS molecular chains, and even chemical reactions occurred. Physical and chemical micro-crosslinking points enhanced the entanglement between the PPC and PBS molecular chains, therefore the compatibility between the two-phase interfaces in the PPC/PBS blends was improved. The storage modulus(\(G'\)) of PPC/PBS/EHBP blends with respect to the temperature was shown in Fig.5 (c). It can be seen that with EHBP incorporated, the storage modulus of the blends reduced. The reason would be similar with those the storage modulus in Rheological analysis.

**Tab. 1** Thermal parameters of the PPC/PBS/EHBP blends
| EHBP content/phr | T_α1/°C | T_α2/°C | ΔT_α/°C | T_g1/°C | T_g2/°C | ΔT_g/°C |
|------------------|---------|---------|---------|---------|---------|---------|
| 0                | -41.95  | 34.81   | 76.76   | -42.53  | 26.98   | 69.51   |
| 0.1              | -38.02  | 34.51   | 72.53   | -41.99  | 27.72   | 69.71   |
| 0.5              | -37.50  | 33.78   | 71.28   | -40.65  | 27.56   | 68.21   |
| 1.0              | -39.97  | 33.26   | 73.23   | -41.19  | 27.70   | 68.89   |
| 1.5              | -39.70  | 32.66   | 72.66   | -39.56  | 27.84   | 67.40   |
| 2.0              | -39.20  | 31.93   | 71.13   | -38.73  | 27.27   | 66.00   |

**Thermal stability**

The thermal stability of the PPC/PBS/EHBP blends was studied using TGA and shown in Fig. 3. The thermal degradation temperatures for T_5% (5% weight loss), T_50% (50% weight loss), T_{max} (maximum degradation temperature) and the residual carbon content under 500°C (R_d%) are summarized in Tab.2. Compared with pure PPC/PBS, the stability of PPC/PBS/EHBP blends showed a gradually decreasing trend with the increase of EHBP.

Two major weight loss steps were observed for all samples. The difference in thermal decomposition behavior of the samples can be seen more clearly from the DTG curves. As can be seen, the DTG curves showed double peaks for all samples, which indicated thermal degradation consisted of two major weight loss steps. The peak temperatures, which were the mid-points of the degradation at each major step, were a measure of thermal stability. The incorporation of EHBP shifted the DTG peak to a lower temperature compared to the pure PPC/PBS blends.

The reason for this phenomenon was that the synthesized EHBP was liquid and had lower thermal stability compared with the matrix. After the blending with the PPC/PBS blends, the thermal stability of the blends was decreased. However, the initial decomposition temperature was still much higher than the processing temperature, so it had little effect on the process as well as the applications.

**Tab.2 TGA data for the PPC/PBS/EHBP blends**

| EHBP content/phr | T_{5%}/°C | T_{50%}/°C | T_{max1}/°C | T_{max2}/°C | R_d/% |
|------------------|-----------|------------|-------------|-------------|-------|
| 0                | 277.00    | 310.23     | 302.27      | 399.11      | 3.34  |
| 0.1              | 276.89    | 311.78     | 298.74      | 395.58      | 3.52  |
| 0.5              | 272.40    | 307.35     | 292.69      | 385.49      | 4.14  |
| 1.0              | 271.61    | 303.36     | 287.14      | 374.90      | 4.05  |
| 1.5              | 270.96    | 302.76     | 286.63      | 370.86      | 4.10  |
| 2.0              | 270.84    | 302.76     | 285.12      | 370.36      | 3.40  |
Mechanical properties

Fig. 7 showed the impact strength, the elongation at break and the tensile strength of the PPC/PBS blends with different content of EHBP. It can be seen from Fig. 7(a) that the impact strength of the PPC/PBS/EHBP blends increased firstly and then decreased upon addition of EHBP. The impact strength of the PPC/EHBP blends with 0.5 phr content of EHBP was increased by 81.20%, from 9.55 kJ/m$^2$ of the pure PPC/PBS blends to 17.3 kJ/m$^2$.

As shown in Fig. 7(b), the tensile strength of the PPC/PBS/EHBP blends increased gradually with the increase of EHBP, and then decreased with the maximum value appeared at 0.5phr EHBP. In this case, the tensile strength of the blends reached a maximum value of 16.85 MPa, a 68.7% increase over the tensile strength of pure PPC/PBS (9.99 MPa). Meanwhile, the elongation at break of the PPC/PBS/EHBP blends were increased by 74.90%, from 136.29% to 238.38%, when the content of EHBP was 1.0 phr. The above results showed that the mechanical strength as well as the toughness of the blends could be dramatically improved by certain amount of EHBP.

SEM

Fig. 8 showed the SEM images of the impact fracture morphology of the pure PPC/PBS and PPC/PBS/EHBP blends. It can be seen that the surface of the blends became rougher after adding EHBP, indicating that the toughness of the blends increased. However, with further increase of EHBP (higher than 1.0%), the surface of the blend presented a fuzzy and mushy appearance, indicating excessive EHBP was wrapped on the surface of the blends and certain agglomeration appeared, which would damage the mechanical performances.

The modification mechanism

The strengthening and toughening effect of EHBP on PPC/PBS blends can be divided into the following three aspects: (1) in the blending process, the carboxyl groups and hydroxyl groups in the PPC molecular chain and PBS molecular chain can easily interact with many active oxygen atoms on the epoxy group at the end of EHBP. At the same time, a large number of active epoxy groups at the end of EHBP can react with the hydroxyl groups in the PPC and PBS molecular chain. Therefore, the addition of EHBP improves the compatibility between PPC and PBS. (2) EHBP itself is a highly branched three-dimensional spherical structure, and there are a large number of cavities in the molecule. With the addition of EHBP, these cavities can quickly absorb part of the energy under external force, thus improving the toughness of the blends. (3) due to the chemical interaction and intermolecular hydrogen bond interaction between matrix molecular chain and EHBP, chemical and physical micro-crosslinking points were formed, which increased the molecular entanglement. The blends would change from the initial linear to the later reticular micro-crosslinking structure, and when the external force acted on the surface of the sample, it can be transmitted to the interior of the polymer. When the stress concentration point is encountered, a crack will occur, and when the crack continues to conduct and encounter the "rivet" structure, the crack will bend or turn to a certain extent, and the "rivet" structure will remain stable in the same place. When
the crack turns or bends, a new second-order crack occurs, which absorbs the impact energy. Therefore, the increased entanglement limits the movement of molecular chains to a certain extent, resulting in the increased strength and toughness of the system. With low content of EHBP (below 0.5phr-1.0phr), the tensile strength, elongation at break, and impact strength of the blends increase significantly; but when the content of EHBP is more than 1.0phr, excessive "rivets" as well as the agglomeration resulted in the decreased mechanical properties.

Conclusions

EHBP was successfully synthesized and used as a modifier for the reinforcing and toughening of PPC/PBS blends. Due to the formation of micro-crosslinking structure and hydrogen-bond interaction, the tensile strength, elongation at break and the impact strength all increased. The active oxygen atoms on the epoxy groups in EHBP can form strong hydrogen bonds with the active hydrogen atoms in the hydroxyl groups and carboxyl groups of the PPC/PBS, thereby increase the interfacial compatibility, and $\Delta T_g$ can reduced from 76.95°C to 70.70°C. The impact fracture surface of the PPC/PBS blends became rough with the addition of EHBP, and even obvious filamentous structure and tiny holes could be seen.

Declarations

Acknowledgements

The authors are grateful to the support of Beijing Young Top-notch Personnel Foundation (CIT&TCD201804030) and Beijing Key Project of Natural Science (KZ201810011017). SM acknowledges Beijing Key Laboratory of Quality Evaluation Technology for Hygiene and Safety of Plastics (Beijing Technology and Business University, Beijing 100048, China) for the award of an Open Fund (QETHSP2019004).

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Figures
Figure 1

(a) Synthesis schematic diagram of EHBP-G3. (b) Schematic diagram of the theoretical molecular structure of EHBP
Figure 2

FTIR spectra of the PPC/PBS/EHBP blends.
Figure 3

Gel contents for the PPC/PBS/EHBP blends.
Figure 4

Storage modulus (G') (a), viscous modulus (G'') (b), damping factor (tan δ) (c) and viscosity (d) as a function of frequency for the PPC/PBS/EHBP blends with different content of EHBP.
Figure 5

DMA curves for the PPC/PBS/EHBP blends: PBS part (a) and PPC part (b). Storage modulus ($G'$)-temperature curves (c) and DSC curves (d) for the PPC/PBS blends.
Figure 6

TGA curves (a) and DTG curves (b) for the PPC/PBS/EHBP blends. (c)(d) is an enlarged view of the two peaks of (b).
Figure 7

(a) Impact strength for the PPC/PBS/EHBP blends. (b) Tensile strength and Elongation at break for the PPC/PBS/EHBP blends.
Figure 8

SEM images of the PPC/PBS/EHBP blends with different content of EHBP.
Figure 9

Modification mechanism of EHBP on PPC/PBS blends. (Second Figure 7 in the manuscript.)