Optimizing hydrogen-bonding miscible binary polymer blends made by concentrated emulsion polymerization

Zhongjie Du · Chen Zhang

Abstract Polystyrene/poly (n-butyl methacrylate) blends were prepared by concentrated emulsion polymerization using (2-hydroxy ethyl) methacrylate and n-butyl methacrylate as hydrogen-bond donor and acceptor respectively. Two concentrated emulsions of styrene/(2-hydroxy ethyl) methacrylate and n-butyl methacrylate monomers were prepared separately, and mixed mechanically after partial polymerization. The products thus obtained consisted of compact particles. The specific formation of hydrogen bond between poly [styrene-co- (2-hydroxy ethyl) methacrylate] with poly (n-butyl methacrylate) were studied by transmission electron microscope and dynamic mechanical thermal analysis. The results showed that the miscibility is induced via hydrogen bonding between the hydroxyl group and the carbonyl groups and that hydrogen bonding plays an important role in the compatibilization of the PS/PBMA blends. The TEM micrographs also showed that the PS/PBMA blends are partially inhomogeneous on a scale of 50 nm, and only a single glass transition temperature was found by DMTA for the PS/PBMA blends containing more than 3.0 ml of (2-hydroxy) methacrylate /100 ml styrene.

Introduction

The use of functional groups including hydroxyl and carboxyl as hydrogen–bond donors to enhance the miscibility in polymer blends has been investigated by many researchers [1–6]. For polymer blends, two polymers are prepared separately and usually solution cased to evaluate the miscibility of the hydrogen–bond donors with hydrogen-bond acceptors [7–11]. All results indicate that hydrogen bonding is a useful measure to improve the miscibility in polymer blends, including poly (methyl acrylate) / poly (vinyl acetate) [12], hydroxy-modified polystyrene/poly (methyl methacrylate) [13], poly (styrene–co–4- vinylbezenephosphonic acid) / poly (n-butyl methacrylate) [14]. In order to simplify the procedure of preparing polymer blends, a novel method of concentrated emulsion polymerization was employed to prepare blends with better miscibility by formation of hydrogen bonds. A concentrated emulsion has the appearance of a paste and differs from conventional ones in that the volume fraction of the dispersed phase (Φ) is greater than 0.74. The compact structure of the concentrated emulsion system has a large interfacial area, which is highly suitable for interfacial reactions [15–17].

Concentrated emulsion polymerization has been used to prepare polymer blends by self-diffusion and functional group reactions. The hydrogen bond donor, for example hydroxyl is introduced into one of the concentrated emulsion systems, and the other concentrated emulsion contains a monomer with hydrogen-bond acceptors, for example acrylate monomers. In the present study, two concentrated emulsions were prepared from different monomers and subjected to partial polymerization until suitable conversions were

Z. Du (✉) · C. Zhang
The Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, P.R. China
e-mail: m94037@mail.buct.edu.cn

reached. The partially polymerized concentrated emulsions were subsequently mixed mechanically, and the mixture was subjected to complete polymerization. During this second polymerization, the formation of hydrogen bonds occurs at the interfaces of the two kinds of cells, which compatibilizes the polymer blends. In the present case, two monomers of styrene containing (2-hydroxy ethyl) methacrylate as hydrogen bond donor and butyl methacrylate as hydrogen bond acceptor were employed to prepare the concentrated emulsions. The compatibilization of the polymer blends thus obtained was characterized by the morphological change. In order to gain a more explicit understanding of the compatibilization, we have used dynamic mechanical thermal analysis to investigate the glass transition temperature of the blends.

Experimental

Materials

Styrene (St, AR, Shanghai Reagent Manufacturer, China), n-butyl methacrylate (BMA, AR, Beijing YILI Fine Chemicals Limited Co., China) and (2-hydroxy ethyl) methacrylate (AR, Beijing YILI Fine Chemicals Limited Co., China) were filtered through an inhibitor removal column before use. Azobisisobutyronitrile (AIBN, AR, Beijing Reagent Manufacturer No.3, China) was recrystallized from methanol. Sodium dodecyl sulfate (SDS, 70%, Beijing QIUXIAN Chemical manufacturer, China), methanol (AR, Beijing YILI Fine Chemicals Limited Co., China) and toluene (AR, Beijing Beihua Fine Chemicals Limited Co., China) were used as received.

Preparation of the concentrated emulsion

An aqueous solution containing SDS was first placed in a flask provided with a magnetic stirrer. The flask was sealed with a rubber septum, and the air was replaced with nitrogen. The dispersed phase (St or BMA monomer) was added dropwise with vigorous stirring into the flask using a syringe, until the volume fraction of the dispersed phase became 0.8. The whole addition process lasted about 15 min at room temperature.

Preparation of the PS/PBMA self-compatibilized alloy

Two concentrated emulsions in water were prepared separately, with styrene and BMA monomers [each

containing an initiator (AIBN, 0.006 g/ml monomer)] as dispersed phases, using the procedure described above. The two concentrated emulsions were partially polymerized at 50 °C until their viscosity increased at a suitable level. Subsequently, the two concentrated emulsions were mixed, and further heated at 50 °C for 12 h to complete the polymerization. The products were washed with methanol and dried in a vacuum oven.

Dynamic mechanical thermal analysis

The thermal behavior of the products was determined by dynamic mechanical thermal analysis with a DuPont instrument (DMTA-V). The sample was heated from 0 to 150 °C at a heating rate of 10 °C min^{-1}.

Scanning electron microscopy (SEM)

The fractured surface of the specimen was coated with a thin film of gold. The surface morphology was examined by scanning electron microscope (Cambridge S-250MKIII, UK).

Transmission electron microscopy (TEM)

The powders of the PS/PBMA blends were mixed using a Haake mixer (R610, Germany) at 200 °C for 5 min, and then cooled to room temperature. The samples thus obtained were subjected to microtoming and dyed with osmic anhydride. The microstructure was examined by transmission electron microscope (Hitachi, H-800-1, Japan).

Results and discussion

Schematic representation

The preparation procedure of polymer blends by concentrated emulsion polymerization is schematically described in Fig. 1. Two concentrated emulsion systems were prepared separately. One contained the monomer with the hydrogen bond donor; the other one the monomer with the hydrogen bond acceptor. After partial polymerization, the two concentrated emulsion systems were mixed mechanically. The products thus obtained have a compact structure. Because of the large interfacial area between the particles of the concentrated emulsion systems, the formation of hydrogen bonds occurs at the interface of different polymer particles. Compared with the mixing of
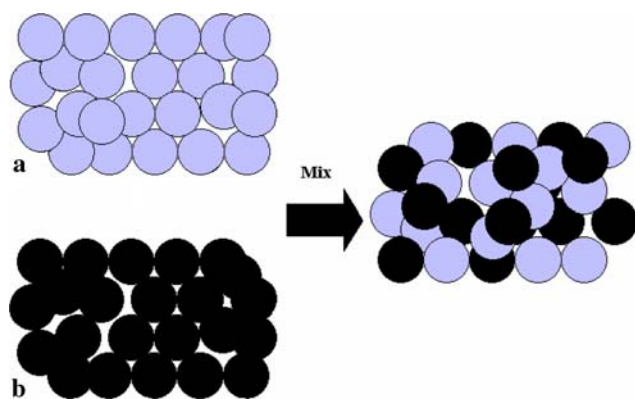
Fig. 1 The schematic diagram of preparation process of binary polymer blends via concentrated emulsion polymerization

polystyrene homopolymer containing the hydroxyl hydrogen-bond donor with poly (butyl methacrylate) homopolymer, the products obtained via concentrated emulsion polymerization have the obvious advantage of the high interfacial association by hydrogen bond.

Determination of the conversion versus time

In order to examine the self-association of polymer blends via concentrated emulsion polymerization, styrene and n-butyl methacrylate monomers were employed. For the concentrated emulsion systems, a droplet containing monomers is an independent reaction cell. The diffusion of monomers among droplets occurs during the early reaction stage. For this reason, partial polymerization of each concentrated emulsion system is necessary to improve the viscosity of the droplets and prevent diffusion of the monomers among droplets. The curves of conversion versus time of styrene and n-butyl methacrylate monomers are shown in figure 2. We have previously demonstrated [15] that the critical conversion of styrene and acrylate mono-
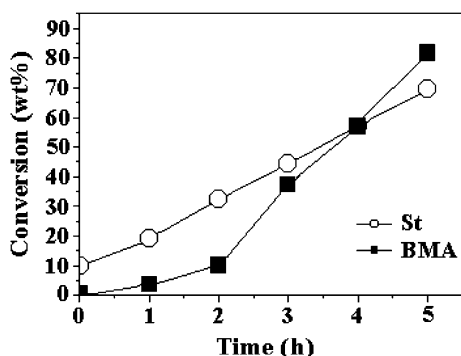
Fig. 2 The curves of conversion versus time of styrene and n-butyl methacrylate monomers

mers in concentrated emulsion systems is 20 wt%, when monomer diffusion among droplets is inhibited. At the same time, it is difficult to mix the partially polymerized concentrated emulsions uniformly above this critical value. Hence, the partial polymerization times of styrene and n-butyl methacrylate of 60 min and 140 min were used respectively.

SEM characterization of PS/PBMA blends

The morphology of the products prepared by concentrated emulsion polymerization was characterized by scanning electron microscope, as shown in Fig. 3. The products have a particulate compact structure where particle size (about 2–10 μm) is controlled by the volume fraction of the dispersed phase. When the (2-hydroxy ethyl) methacrylate monomer was introduced into the dispersed phase of the styrene system, the morphology of particles was slightly changed which resulted from the instability of the concentrated emulsion systems due to the increased hydrophilic capacity of (2-hydroxy ethyl) methacrylate. This change, however, did not destroy the morphology of the particles. An obvious interface among particles can be noticed, which ensured the production of polystyrene containing the hydroxyl group and poly (n-butyl methacrylate) homopolymer of the concentrated emulsions separately.

Phase behavior of polymer blends

The PS/PBMA blends thus obtained was mixed in a Haake mixer for 5 min at 200 °C. The TEM photographs obtained after microtoming and dying with osmic anhydride are shown in Fig. 4. The PS phase is dyed black, and the white represents the PBMA phase. The blends form a phase-separated structure, and the PBMA (white) as the dispersed phase was dispersed in the continuous phase of PS. When no (2-hydroxy ethyl) methacrylate is introduced into the PS phase, the particle size in the dispersed phase is about 100–400 nm. At higher content of (2-hydroxy ethyl) methacrylate, the particle size in the dispersed phase decreases down to about 50 nm as illustrated in Fig. 4d. These observations suggest that the introduction of the (2-hydroxy ethyl) methacrylate results in the formation of hydrogen bonds between the hydroxyl groups and the PBMA hydrogen-bond acceptor. The higher the (2-hydroxy ethyl) methacrylate, the smaller the particle size in the dispersed phase of PBMA, which indicates the improvement of the miscibility between PS with PBMA blends.

Fig. 3 The SEM micrographs of PS/PBMA blends via concentrated emulsion polymerization. The amount of (2-hydroxy ethyl) methacrylate (ml/100 ml styrene): (**a**) 0; (**b**) 3.0; (**c**) 6.0; (**d**) 9.0
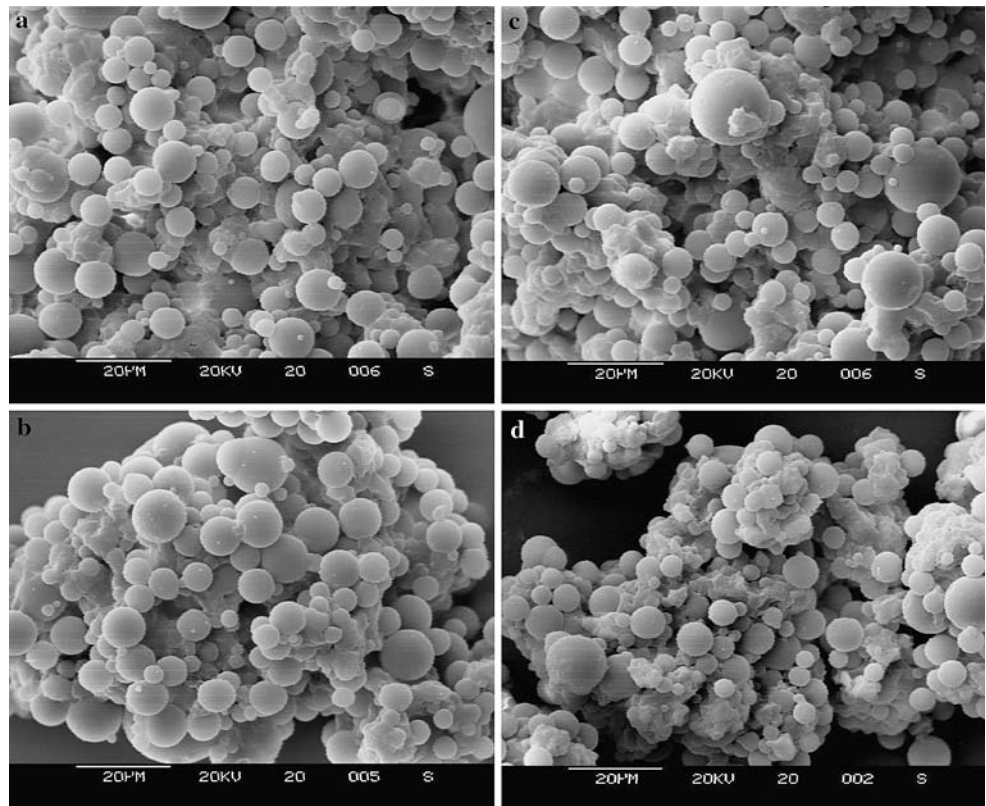
Fig. 4 The TEM micrographs of PS/PBMA blends. The amount of (2-hydroxy ethyl) methacrylate (ml/100 ml styrene): (**a**) 0; (**b**) 3.0; (**c**) 6.0; (**d**) 9.0
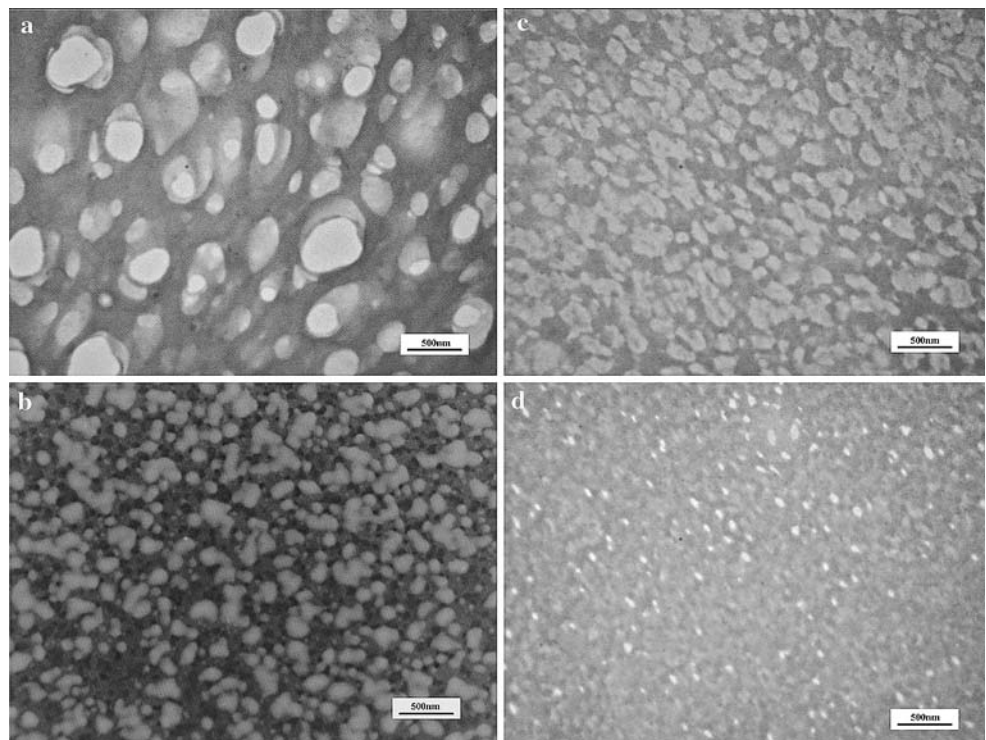

Dynamic mechanical thermal analysis

Figure 5 shows the results of the dynamic mechanical thermal analysis (DMTA) of PS/PBMA blends. E′, E″ representing the storage and loss moduli, and the tgδ = E′/E″. It is worth noting that the number of peaks in tgδ against temperature curves, which provides the glass transition temperature (T_g) of the PS/

Fig. 5 The DMTA results of PS/PBMA blends. The amount of (2-hydroxy ethyl) methacrylate (ml/100 ml styrene): (**a**) 0; (**b**) 3.0; (**c**) 6.0; (**d**) 9.0
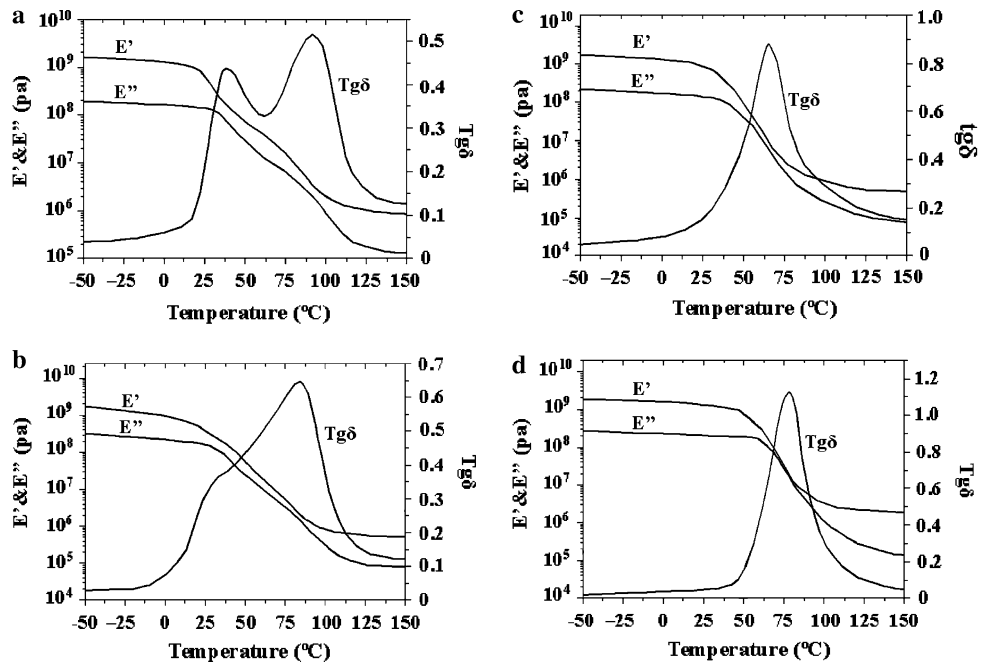
PBMA blends, changes with increasing (2-hydroxy ethyl) methacrylate content. When the (2-hydroxy ethyl) methacrylate content is below 3.0 ml/100 ml styrene, two peaks are present. In contrast, when the (2-hydroxy ethyl) methacrylate content was above 3.0 ml/100 ml styrene, there was only one peak on each of the tgδ curves. The number of peaks can be related to the compatibilization caused by hydrogen bonding between hydroxyl groups and PBMA. For this reason, there are two peaks in curve (a), which is corresponds to a system devoid of (2-hydroxy ethyl) methacrylate. After addition of (2-hydroxy ethyl) methacrylate at a concentration about 3.0 ml/100 ml styrene, the system is compatibilized and the T_g's generated by different species are merged into a single T_g, as illustrated in Curves (c) and (d).

Conclusion

The concentrated emulsion polymerization was employed to prepare compatibilized PS/PBMA blends via hydrogen bonding between hydroxyl groups and acrylate groups. The products thus obtained have a compact structure of PS or PBMA particles. DMTA show that only a single T_g is found for the products when the content of the (2-hydroxy ethyl) methacrylate in PS particles is above critical concentration of 3.0 ml/100 ml styrene. The TEM micrographs illustrated that a higher content of (2-hydroxy ethyl)

methacrylate resulted in smaller particle size in the dispersed phase of PBMA, resulting in better compatibilization of the PS/PBMA blends.

References

1. Kakla JF, Kubo S (2003) Macromolecules 36:7803
2. Huang CF, Chang FC (2003) Polymer 44:2965
3. Li JC, He Y, Ishida K, Yamane T, Inoue Y (2001) Polym J 33:773
4. Zhao Y, Yuan GX, Roche P (1999) Polymer 40:3025
5. Ishida H, Lee YH (2001) J Polym Sci Part B-Polym Phys 39:736
6. Guo Q, Harrats C, Groeninckx G, Koch MHJ (2001) Polymer 42:4127
7. Iriarte M, Alberdi M, Shenoy SL, Iruin JJ (1999) Macromolecules 32:2661
8. Lange RFM, Van Gurp M, Meijer EW (1999) J Polym Sci Part A-Polym Chem 37:3657
9. Hong JL, Lin HJ (1999) Macromol Chem Phys 200:845
10. Zhou CL, Hobbie EK, Bauer BJ, Han CC (1998) J Polym Sci Part B-Polym Phys 36:2745
11. Wu CP, Wu YL, Zhang RY (1998) Euro Polym J 34:1261
12. Asano A, Eguchi M, Shimizu M, Kurotsu T (2002) Macromolecules 35:8819
13. Qiu XP, Jiang M (1995) Polymer 36:3601
14. Zhuang HF, Pearce EM, Kwei TK (1995) Polymer 36:2237
15. Du Z, Zhang C (2003) Polymer J 35:64
16. Li H, Du Z, Huang H (2002) J Appl Polym Sci 83:2915
17. Zhang C, Du Z, Li H (2002) Polymer 43:2945