Preparation of Poly(ethylene terephthalate)-graft-polystyrene Copolymer†

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The graft copolymerization of proper polymer onto poly(ethylene terephthalate) (PET) and nylon 6 (PA6) was conducted in order to control the ester-amide exchange reaction between these two polymers. This paper focuses on the graft polymerization of poly(ethylene terephthalate) and polystyrene (PS). The PET-g-PS copolymer was prepared at the presence of the dicumylperoxide (DCP) by melt grafted copolymerization. The effects of the reactant ratios, initiator concentrations, reaction time and reaction temperature on the grafting efficiency were discussed. The results indicated that the grafting efficiency of polystyrene was higher at the following conditions: the dicumylperoxide concentration was 0.2 wt %, the ratio of PET/PS was 10:1, the reaction temperature was 270 ºC and the reaction time was 5 min. FTIR, ^{1}H NMR were used to prove that polystyrene had been grafted on poly(ethylene terephthalate) chain.

Keywords: Poly(ethylene terephthalate), Polystyrene, Dicumylperoxide, Grafting efficiency.

INTRODUCTION

Poly(ethylene terephthalate) (PET) has attracted interest in synthetic fiber and packaging materials. Some disadvantages have limited the application of PET as plastic, such as slow crystallization rate, rough surface, long molding cycle, poor impact strength and processing performance. Blending of PET with PA6 is an attractive method for producing new material with desirable properties. However, when PET blends with PA6, the ester-amide exchange reaction would occur. The result of the reaction would lead to rearrangement of molecular, thus affect the morphology and properties of the blends. Although ester-amide exchange reaction can improve the compatibility of polymer blends, it can also worsen the performance of the blend because of an excess of ester interchange reaction[1]. Therefore, the ester-amide exchange reaction of PET/PA6 blend should be inhibited to obtain suitable properties of the blend. The graft copolymerization of proper polymer onto PET and PA6 is an effective method to control the ester-amide exchange reaction. In this article, PET-g-PS was prepared by grafted method at melt blending state.

The free radical initiated on the skeleton of the polymer matrix is important for the reaction of graft copolymerization. Many studies about radiation-induced grafting on PET have

been reported previously[2]. Radiation-grafting method is a relatively simple way of modifying polymers. It could react at homogeneous or heterogeneous state and the presence or absence of functional groups in the polymer matrix has no effect on the reaction[3]. However, radiation-induced graft copolymerization is well known to induce structural changes in the host polymer matrix[4]. Such changes have caused impacts not only on structural, but also on thermal and mechanical properties of the grafted polymer[5]. Chemical initiators, such as H_2O_2, AIBN, BPO are usually used in grafting reaction. Several vinyl monomers, such as styrene[6], methacrylic acid[7,8], acrylic acid[9-11], ethyl acrylate[12], acrylonitrile[13,14], N-isopropyl-acrylamide[15], were grafted onto PET matrix. Dicumyl peroxide (DCP) was used as initiator in this study. Free radicals produced on the skeleton of the polymer chain by chain transfer reaction. Then radical polymerization occurred at the presence of reactive vinyl terminal end groups. The reaction mechanism is as follows:
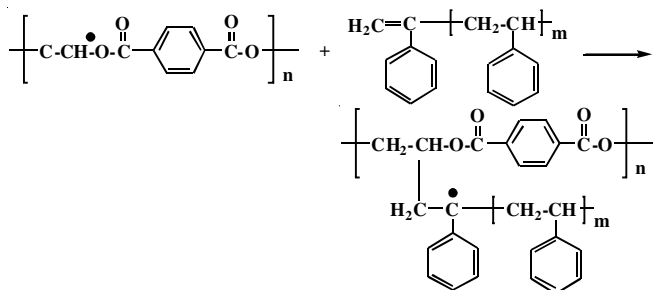
The production of primary radical and the generation of reactive centers on the polymer matrix:
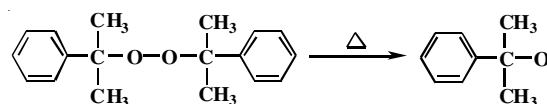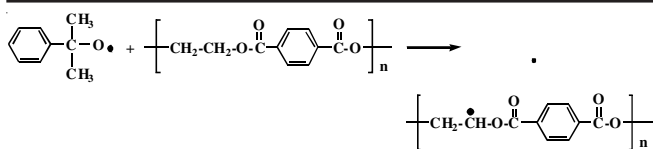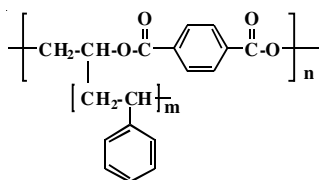
The polymer matrix reacts with active end group of polystyrene to form a new free radical:

Radical termination occurs by chain transfer or collision and grafted copolymer generates:

EXPERIMENTAL

Poly(ethylene terephthalate) (PET, relative viscosity = 0.672, carboxy value = 37.2 mol/L) used in this study was supplied by Xiangtan Chemical Fiber Co., Ltd. (China). Polystyrene was supplied by Jiangyin Jianghua Chemical Products Co., Ltd. (China). Dicumyl peroxide was purchased from Shanghai Chemical Reagent Factory.

Preparation of grafted PET: PET-g-PS was prepared by grafting of polystyrene onto PET using free radical polymerization technique. PS (0.5, 1, 2, 3, 5 g) blended with PET matrix (10 g) was added to a 50 mL three-necked flask. The reactor was purged with nitrogen to eliminate oxygen and heated to a set temperature (270, 275, 280, 290 and 300 ºC) at constant pressure. Then the initiator dicumylperoxide (DCP) was added to the melted mixture. The reaction was continued several minutes (3, 5, 10, 15 and 20 min). The grafted products were extracted, washed thoroughly with toluene and dried under vacuum to a constant weight. The grafting efficiency was gravimetrically determined as a percentage of weight gain in the PS raw material using eqn. 1:

$$\text{Grafting efficiency (GE)} = \frac{W_{g-PS}}{W_{0-PS}}$$

where, W_{g-PS} and W_{0-PS} are the weights of grafted and original PS, respectively.

FTIR measurements: FTIR measurements were performed with a Perkin Elmer spectrometer (Spectrum 2000 Explorer) at ambient conditions in transmittance mode at wave number in the range of 4000-500 cm^{-1}.

^{1}H NMR measurements: The chain structures of PET-g-PS were characterized by a 400 MHz 1H nuclear magnetic resonance (NMR) spectroscopy (AVANCE 500, Bruker, Inc., Germany). CF$_3$COOD/CDCl$_3$ (2:1) was used as a solvent for the NMR characterization.

RESULTS AND DISCUSSION

Effect of reaction conditions on the grafting efficiency: Effect of DCP concentration on the grafting efficiency shows the trend of the grafting efficiency changes with DCP concentration (Fig. 1). As shown in Fig. 1, the grafting efficiency increased first and then decreased with increasing DCP concentration. The reason may be that when the concentration of DCP is relatively low, the radical concentration increases with increasing DCP concentraton. The increased active sites enhanced the grafting efficiency. When the initiator dicumylperoxide (DCP) concentration was 0.2 wt %, the maximum grafting efficiency attained. The grafting efficiency decreased slightly with DCP concentration continued to increase, however, the grafting efficiency was always greater than 50 %. Although the number of initiators continued to increase, the free radical concentration would increase, however, the number of active sites on the PET chain could not be increased so that the termination rate accelerated, thus the grafting efficiency reduced.
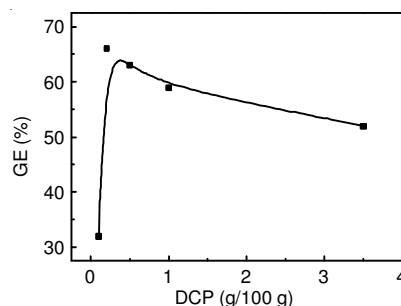

Fig. 1. Curve of grafting efficiency varies with the DCP concentration T = 270 ºC, $W_{PET}:W_{PS}$ = 10:1, t = 5 min

Effect of concentration of polystyrene on the grafting efficiency: The curve of grafting efficiency changing with polystyrene concentration is shown in Fig. 2. The figure shows that the grafting efficiency increases at first, after reaching the maximum it begins to decline with the increasing concentration of polystyrene. The reason may be that the increasing concentrations of PS could enhance the grafting efficiency to a certain extent. However, the number of grafting sites in the PET molecular chain is constant, when the degree of saturation grafting is reached, grafting efficiency will decrease as the concentration of PS increases.
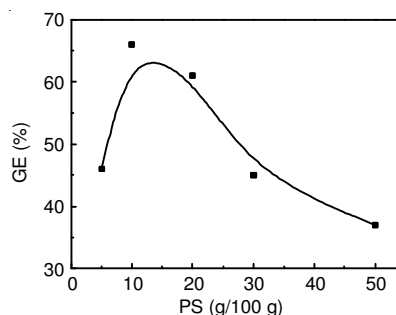

Fig. 2. Curve of grafting efficiency varies with the PS concentration. T = 270 ºC, $W_{PET}:W_{DCP}$ = 10:0.02, t = 5 min

Effect of reaction time on the grafting efficiency: Fig. 3 shows the curve of grafting efficiency varies with reaction time. As shown in Fig. 3, the grafting efficiency gradually increased with the reaction time increasing at the first five minutes. After five minutes, the grafting efficiency was unchanged when the reaction time continued to increase. This is because the number of free radical increases continually at the first five minutes, which leads to the increase of the grafting efficiency. After five minute, a large number of initiators had decomposed completely, so the curve of the grafting efficiency flattened.
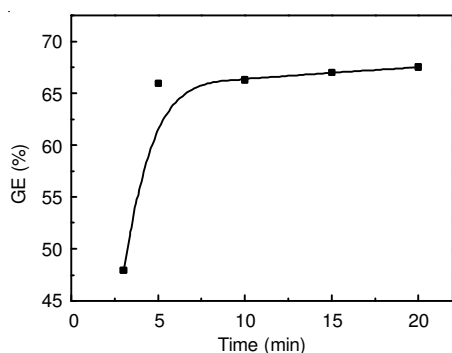

Fig. 3.　Curve of grafting efficiency varies with reaction time. T = 270 ºC, W_{PET}:W_{PS}:W_{DCP} = 10:1:0.02

Effect of reaction temperature on the grafting efficiency: Fig. 4 shows the trend of the grafting efficiency changes with the reaction temperature. As shown in Fig. 4, the grafting efficiency decreased with the reaction temperature increasing. When the reaction temperature is too high, the half-life of the initiator is shortened. The shorter half-life of initiator leads to the high concentration of free radicals in the system at that moment, which causes collision between the free radicals and completely annihilating each other. The content of the initiator radicals reduced, which led to the reduction of the grafting efficiency[16]. Furthermore, DCP would be decomposed at high temperatures into isopropyl radicals, which have lower chain transfer activity and are not conducive for graft copolymerization.
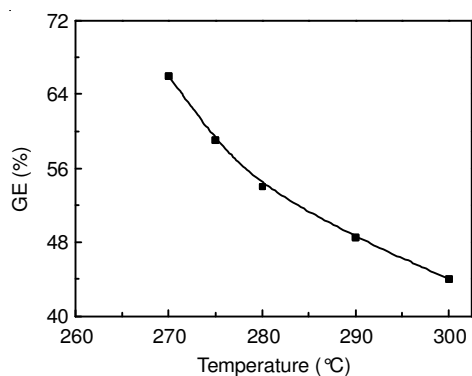

Fig. 4.　Curve of grafting efficiency varies with reaction temperature. W_{PET}:W_{PS}:W_{DCP} = 10:1:0.02, t = 5 min

Characterization of PET-g-PS graft copolymer

FTIR spectroscopy: Fig. 5 shows typical FTIR spectra of the PET matrix and grafted PET-g-PS. As seen from Fig. 5, the characteristic infrared absorption peaks of PET were
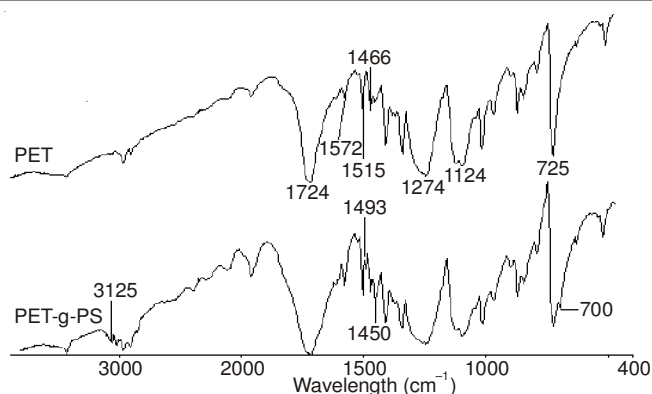

Fig. 5. FTIR spectra of PET and PET-g-PS

detected. The peak of 1724 cm^{-1} is attributed to the stretching vibration of C=O. The skeletal stretching vibrations of C=C in-plane appear at 1572 and 1515 cm^{-1}. Absorption band at 1466 cm^{-1} is due to CH$_2$ bending vibration. The absorbance peaks at 1274 and 1124 cm^{-1} are due to C-O stretching vibrations. A peak at 725 cm^{-1} is originated from bending vibration of the benzene ring. FTIR spectra of PET-g-PS contain not only the characteristic infrared absorption peaks of PET, but also the characteristic infrared absorption peaks of PS. as Absorption bond at 3125 cm^{-1} is due to the CH stretching vibrations of benzene ring in PS. The absorbance peaks at 1493 and 1450 cm^{-1} are due to the stretching vibrations of benzene ring in PS. A peak at 700 cm^{-1} is originated from C-H out-of-plane deformations of the mono-substituted benzene ring . So it could be confirmed that PS were grafted on the PET.

^{1}H NMR spectroscopy: Fig. 6 shows the ^{1}H NMR spectrum of PET, PS andPET-g-PS. As for pure PET, only exist two kinds of protons, the resonance signal which appeared in 8.2 ppm is assignable to the protons of the benzene ring and the resonance signal which appeared in 4.8 ppm is assignable to the protons of methylene. Besides the characteristic infrared absorption peaks of PET, there also existed the characteristic ^{1}H NMR signal of PS (Fig. 6). The resonance signal which appeared in 7.0 ppm is assignable to the protons of the benzene ring in PS. The resonance signals in the range of 1-2 ppm are assignable to the protons of ethyl in PS. So it could be speculated that PS were grafted on the PET.
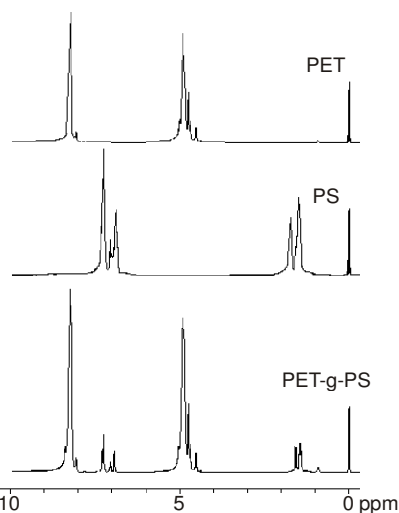

Fig. 6. ^{1}H NMR spectrum of PET, PS and PET-g-PS

Conclusion

In this study, grafted polymers, PET-g-PS, were prepared by radical copolymerization. The FTIR and ^{1}H NMR results confirmed that the polystyrene has been grafted on the skeleton of the poly(ethylene terephthalate) successfully. The effects of reaction conditions (initiator concentrations, reactant ratios, reaction time and reaction temperature) on the grafting efficiency of polystyrene were studied. The results showed that when the dicumylperoxide concentration was 0.2 wt %, the grafting efficiency was up to the highest value. The proper ratio of PET/PS was 10:1. The higher the temperature is, the shorter the half-life of dicumylperoxide. Too short half-life was unfavorable for grafting reaction, so the reaction temperature was controlled at the melt temperature (270 ℃) of poly(ethylene terephthalate). The optimum reaction time was 5 min.

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