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Effect of polymer blending on the electrical conductivity of polypyrrole/copolyester composite films

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Summary

The effect of polymer blending on the electrical conductivity of polypyrrole/copolyester composite film was investigated. Copolyesters containing sodium sulfonate group with various main chain structures were synthesized and blended with PET. The average anionic group contents in the blend samples were controlled to be 3.5 and 6.1 mol%. The polypyrrole composite films were prepared by polymerization of pyrrole through vapor phase absorption onto the copolyester-PET blend films which contained $FeCl_3$. The conductivity of the blend samples containing 3.5 mol% of DMS was greater than that of the copolyester of the same DMS content when the pyrrole vapor exposure time was longer than 30 min. The blends of 6.1 mol% of DMS showed higher conductivity than the copolyesters of the same DMS amount even when the exposure time was short. The high electrical conductivity of the blend samples was thought to be due to the phase separation between PET and copolyesters in amorphous region.

Introduction

Electrically conducting polymer composites, hybrid materials composed of conventional polymer matrices and conductive polymer fillers, have been studied intensively due to the necessity to improve the shortcomings of a conducting polymer such as a poor processability, an environmental instability, and weak mechanical properties[1-3]. Polypyrrole (PPy) has attracted great interest for these applications because it can be easily prepared by electro-chemical or chemical polymerization. Broadly, the chemical oxidative polymerization can occur via three modes: (i) in a homogeneous solution[4-6]; (ii) at an interphase of two immiscible solutions[7,8]; (iii) in the vapor phase[9-11]. In vapor-phase polymerization, a substrate that contains oxidizing agent is exposed to pyrrole vapour so that pyrrole can permeate into the substrate and polymerize.

In the previous study[12] we synthesized anionic group containing copolyesters and examined the effects of the ionic group and the copolyester molecular structures on their electrical conductivity. We found that the conductivity of PPy/copolyester composite films increased with the amount of 5-sodiosulfodimethyl isophthalate (DMS) in the copolyester and reached its maximum when the DMS content reached about 10 mol%. We also knew that the conductivity increased dramatically when DMS content was more than 5 mol%

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that was considered as the critical composition for polypyrrole continuity. However, the copolyester which has large amount of DMS, actually more than 5-7 mol%, is water soluble and has poor mechanical properties. Thus, enhancing electrical conductivity without using such a high DMS content is still necessary. Blending these copolyesters with commercial polymer such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) will be one of the reasonable solutions for these problems.

In this study we examined the effect of polymer blending on the electrical properties of polypyrrole/copolyester composite films when copolyester-PET blend films were used as the substrates for the polypyrrole composites. Since the electrical conductivity of the anion-containing copolyester was strongly dependent of the ionic group content as confirmed in the previous report[12], the phase structure of the blend films could affect the ionic group distribution and consequently affect the electrical conductivity of the conducting polymer composites.

Experimental

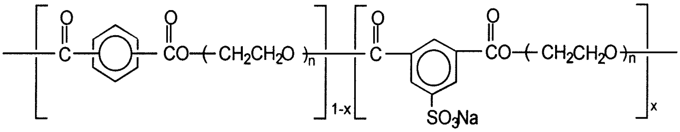
Anion-containing copolyesters

Copolyesters synthesized in the previous study[12] were used. Copolyesters were synthesized by the conventional two-step polymerization in a lab scale polymerization reactor from dimethyl terephthalate (DMT), dimethyl isophthalate (DMI), and 5-sodiosulfodimethyl isophthalate (DMS) as acid derivative parts and ethylene glycol (EG) and diethylene glycol (DEG) as diol parts[13,14]. Details of the reaction were mentioned in the previous report[12].

Since diols can couple each other[15,16], the copolyesters synthesized in this study should be considered as random copolymers synthesized from DMT(T), DMI(I), DMS(S), EG(E), DEG(D), and TEG(Tr), which have the following general structure:

$$\text{-(-T-E-)}_a\text{-(-T-D-)}_b\text{-(-T-Tr-)}_c\text{-(-I-E-)}_d\text{-(-I-D-)}_e\text{-(-I-Tr-)}_f\text{-(-S-E-)}_g\text{-(-S-D-)}_h\text{-(-S-Tr-)}_i\text{-}$$

where subscripts denote mole fractions of the structural units. Since the sulfonate anion will play an important role in conductive polymer formation, we have simplified the above structure as follows:



where n means the average composition of diols and x is the DMS mole fraction in all the diacid derivatives present. Obviously, n and x are equal to (a+d+g)+2(b+e+h)+3(c+f+i) and (g+h+i), respectively. The ring substitution in the first parenthesis is para and meta.

We have synthesized two series of copolyesters: (1) the “A-series” copolyesters synthesized from DMT, EG, and DMS with different DMS contents, which resulted in total eight copolymers based on poly(ethylene terephthalate) having various DMS contents upto about 10 mol%; (2) the “B-series” copolyesters synthesized from different DMT/DMI and EG/DEG ratios although they had similar DMS contents, about 10 mol%. We have blended the B-series copolyesters with PET. In order to compare the conductivities of the blend and the copolyester of the same DMS content, we have set the average DMS contents of the blends be 3.5 and 6.1 mol%, respectively. Because we have found that the electrical conductivity of copolyesters increased dramatically after 5 mol% of DMS in the previous study, we have chosen the two copolyesters below and above 5 mol%. Table 1 shows the characterization of copolyesters used in this study. The details of characterization were mentioned in the previous report[12].

Table 1. Identification of anion-containing copolyesters

Sample	Feed ratio		Composition (mole ratio)		x	N	[η] (dl/g)	T_g (°C)	T_m (°C)
	DMT/ DMI	EG/ DEG	DMT/DMI	EG/DEG/TEG					
A-1	1/0	1/0	1/0	0.922/0.078/0.000	0.035	1.08	0.448	75.1	228.7
A-2	1/0	1/0	1/0	0.963/0.037/0.000	0.061	1.04	0.360	74.7	220.0
B-1	1/0	1/0	1/0	0.457/0.285/0.258	0.103	1.80	0.313	32.2	-
B-2	0.5/0.5	1/0	0.505/0.495	0.473/0.372/0.155	0.103	1.68	0.434	32.6	-
B-3	0/1	1/0	0/1	0.532/0.331/0.135	0.108	1.60	0.317	32.2	-
B-4	1/0	0.5/0.5	1/0	0.331/0.460/0.209	0.116	1.88	0.397	25.9	-
B-5	0.5/0.5	0.5/0.5	0.505/0.495	0.203/0.569/0.228	0.100	2.03	0.414	24.4	-
B-6	0/1	0.5/0.5	0/1	0.217/0.532/0.251	0.104	2.03	0.450	22.8	-
B-7	1/0	0/1	1/0	0.046/0.914/0.039	0.095	2.03	0.462	28.1	-
B-8	0.5/0.5	0/1	0.504/0.496	0.063/0.856/0.080	0.106	2.02	0.470	23.5	-
B-9	0/1	0/1	0/1	0.092/0.762/0.146	0.105	2.05	0.476	24.4	-

Preparation of polypyrrole/(copolyester-PET) composite films

Each copolyester was blended with PET so that all the blend samples would have the same amount of DMS on average, namely 3.5 and 6.1 mol%, in order to be compared directly with copolyester A-1 and A-2. Copolyester, PET, and oxidizing agent ($FeCl_3$, 30wt% of the polymer) were dissolved in phenol/1,1,2,2-tetrachloroethane. The solution was cast onto glass plate and dried in vacuum at room temperature for 72 hours. The final films were of 50-70 μm thickness.

The prepared films were exposed to pyrrole vapor in a glass reactor controlled in a static vacuum of 60 torr. Under reduced pressure liquid pyrrole molecules vaporized and were absorbed in the film. The absorbed pyrrole was polymerized on the anionic sites of copolyesters with the aid of $FeCl_3$. The pyrrole vapor exposure time was selected as 15, 30, and 60 minutes because there showed no significant changes in electrical conductivity after 60 minutes from the preliminary study.

Measurement of Electrical Conductivity

The electrical conductivity of polypyrrole composite films was measured at room temperature by van der Pauw method[17]. The voltage changes (V) when the films were under constant electrical current (I) were measured. The electrical conductivity was calculated from the equation, $\sigma = V^{-1} I\ (\ln 2/\pi d)$, where d is the film thickness.

Results and discussion

Figures 1 to 3 show the variation of conductivity of polypyrrole composites made from (PET/B-series) blend films whose DMS content is 3.5 mol% on average at the polypyrrole vapor exposure time of 15, 30, and 60 min, respectively. The horizontal line shows the

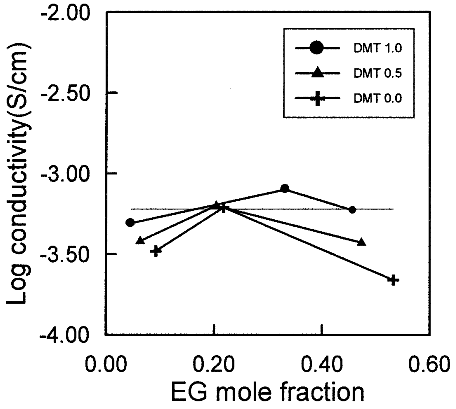


Fig. 1. Variation of conductivity with EG contents for blends (DMS 3.5 mol%) and A-1 copolyester (—) at the pyrrole vapor exposure time of 15min.

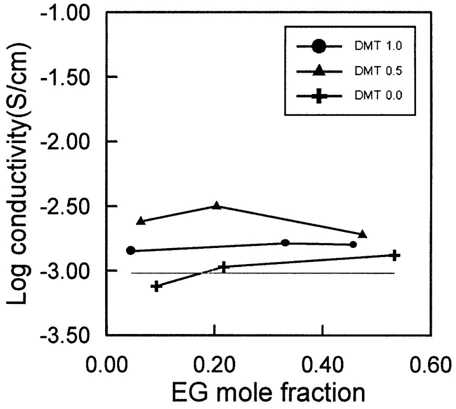


Fig. 2. Variation of conductivity with EG contents for blends (DMS 3.5 mol%) and A-1 copolyester (—) at the pyrrole vapor exposure time of 30min.

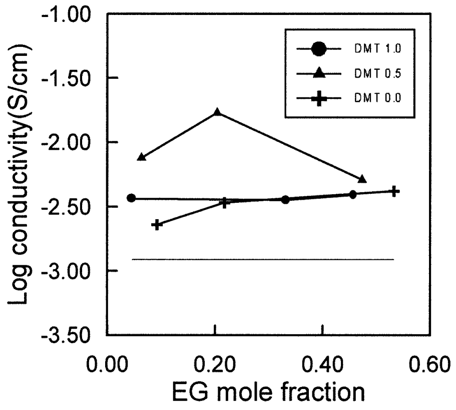


Fig. 3. Variation of conductivity with EG contents for blends (DMS 3.5 mol%) and A-1 copolyester (—) at the pyrrole vapor exposure time of 60min.

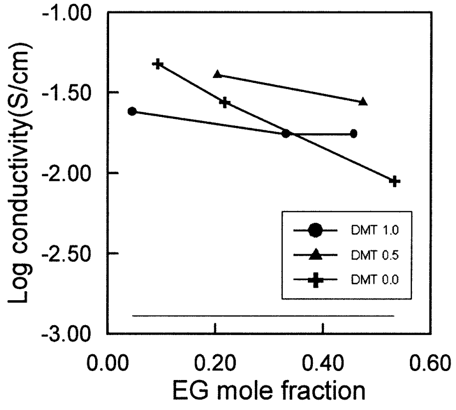


Fig. 4. Variation of conductivity with EG contents for blends (DMS 6.1 mol%) and A-2 copolyester (—) at the pyrrole vapor exposure time of 15min.

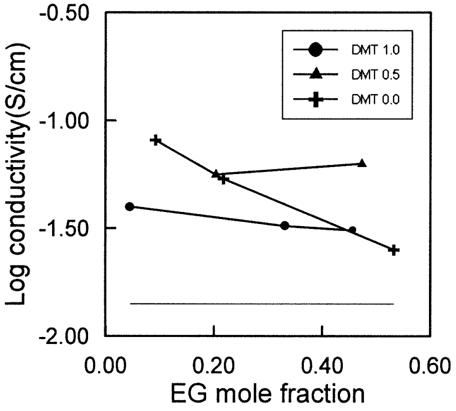


Fig. 5. Variation of conductivity with EG contents for blends (DMS 6.1 mol%) and A-2 copolyester (—) at the pyrrole vapor exposure time of 30min.

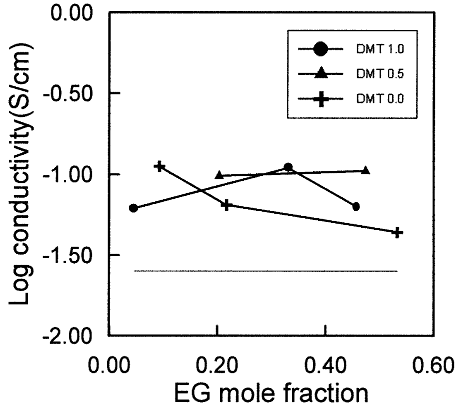


Fig. 6. Variation of conductivity with EG contents for blends (DMS 6.1 mol%) and A-2 copolyester (—) at the pyrrole vapor exposure time of 60min.

conductivity of A-1 copolyester which has the same DMS content, namely, 3.5 mol%. As can be seen in Figures 1 to 3 the blend films had similar conductivity with A-1 when the exposure time was 15 min. However, as the exposure time was extended, the blend showed better conductivity than A-1. When the exposure time was 60 min, they showed pretty high conductivities as compared with the conductivity of A-1 at the same exposure time.

Figures 4 to 6 show the variation of conductivity of (PET/B-series) blend films whose DMS content is 6.1 mol% on average at the pyrrole vapor exposure time of 15, 30, and 60 min, respectively. The horizontal line shows the conductivity of A-2 copolyester which has the same DMS content, namely, 6.1 mol%. As can be seen in Fig. 4 the blend film showed much higher conductivity than A-2 sample even when the exposure time was 15 min. As the exposure time increased, the conductivity of the blend increased steadily though the conductivity gap between the blend and A-2 decreased. At any case the blend samples showed higher conductivity than A-2 copolyester.

As discussed in the previous report, the DMS content is a key parameter in determining the conductivity of a polypyrrole composite film. The DMS unit should be located in the amorphous region of the blends, because the bulky DMS group cannot be included in the crystalline lattice of PET. If PET and the copolyester has a good miscibility in the amorphous region, the blend will have a single amorphous phase. However, if they have a poor miscibility, the amorphous region of the blend will be separated into PET-rich phase and copolyester-rich phase. Consequently, the DMS units will be mainly located in the copolyester-rich phase. This implies that, if the two polymers are immiscible, DMS will be located not evenly throughout the sample but in the the restricted amorphous region, the copolyester-rich phase. In this case, the DMS content in the copolyester-rich phase will be greater than the average DMS content of the blend. If these copolyester-rich amorphous phases form a continuous matrix, the polypyrrole composite prepared from the blend film will show better conductivity than the one from copolyester film which have the same amount of DMS distributed evenly throughout the whole sample.

Fig. 7 shows the DSC thermograms of the PET/B-2 blends which have the average DMS contents 3.5 and 6.1 mol%, respectively. As can be seen in Fig. 7, both the two samples show the two T_g's, which indicates that they have two separated amorphous phase.

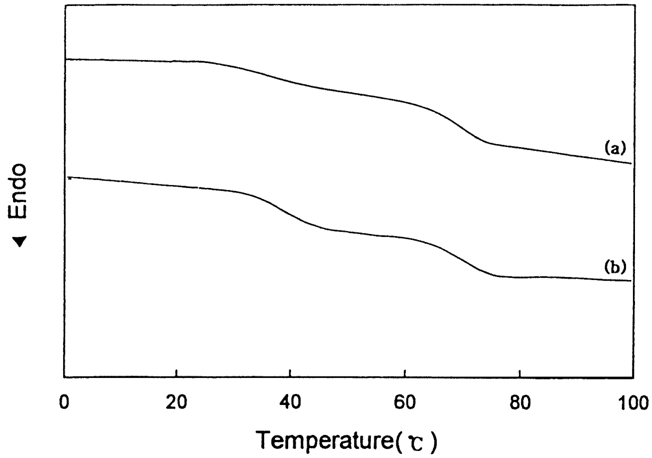


Fig. 7. DSC thermograms of PET/B-2 blend (a) DMS 3.5 mol%, (b) DMS 6.1 mol%.

Since the higher and the lower T_g coincide with the T_g's of PET and B-2, respectively, we can conclude that the blend samples have two amorphous phases: the PET-rich phase and the (B-2)-rich phase, i.e., the copolyester-rich phase. The melting temperature of the PET/B-2 blend film was found to be nearly the same as the melting temperature of PET. It means that the DMS units in B-2 sample can only be located in the (B-2)-rich amorphous phase, neither in the crystalline region nor in the PET-rich amorphous phase. When the copolyester rich phase is continuous, the effective concetration of DMS in the polypyrrole composite will be greater than the average value of the blend, which will be the reason for the higher conductivity of the blend than the copolyesters of the same DMS content. In case of the sample (a) in Fig.7, the weight fraction of B-2 copolyester in the blend is 0.34 and consequently the copolyester rich phase may not be sufficiently continuous. This was thought to be the reason for the low conductivity of the DMS 3.5 mol% blend when the pyrrole vapor exposure time was 15 min. However, as the exposure time increased, the polypyrrole could contact each other and form a conductive path, which could result in the increased conductivity. On the other hand, in case of DMS 6.1 mol% blends, since the weight fraction of copolyester in the blend is 0.59, the copolyester rich phase could form a continuous phase and consequently they could act as an effective conductive path. This was thought to be the reason why they had the higher conductivity than the copolyester of the same DMS content even when the exposure time was short.

In Figures 1 to 6, the blend samples from copolyesters of DMT:DMI=1:1 show higher conductivities than the DMT or DMI only samples, which agrees with the results disscussed in the previous report[12]. However, the effect of EG content of copolyesters is not clear in the blend samples.

Conclusions

The effect of polymer blending on the electrical conductivity of polypyrrole/copolyester composite film was investigated. The polypyrrole composites prepared from the PET-copolyester blend films showed better electrical conductivity than the composites from the copolyesters of the same DMS content. These high electrical conductivity of the blend samples was thought to be due to the phase separation between PET and copolyesters in amorphous region as confirmed by the DSC thermograms.

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