

Synthesis and Characterization of Poly(ether-block-amide) and Application as Permanent Antistatic Agent

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ABSTRACT: Poly(ether-block-amide) (PEBA) were prepared by means of a condensation reaction with polyamide-6 as hard segment and polyether as soft segment. The optimal reaction conditions were determined as the followings: 3% of water and 0.35% of catalyst, reaction temperature $260^{\circ}\text{C} \pm 5^{\circ}\text{C}$ and the reaction time 4 h under the N_2 atmosphere, and 1 h under the vacuum, the vacuum <80 Pa. Characterization results of FTIR and $^1\text{H-NMR}$ showed that the block copolymer of polyether and polyamide was synthesized successfully. The obtained PEBA was applied as an antistatic agent for the ABS resin. The research results showed that the blend with the best properties was PEBA2-

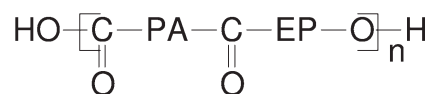
2/ABS and the dosage of PEBA was 12%. PEBA2-2 could obviously decrease the surface resistivity of ABS from 10^{14} to $10^{10}\Omega$ and also exhibit good persistent antistatic ability. The surface resistivity of the blends decreased with the increase of content of PEBA. The increase of ratio of polyether in PEBA was favorable for the decrease of surface resistivity of the blends. The observation of SEM indicated that the PEBA and ABS had good compatibility. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2448–2453, 2010

Key words: polyether; polyamide; block copolymer; antistatic agent

INTRODUCTION

High insulation is one of the major features of polymers. But the characteristic also brought the harm of static. So the antistatic effect of polymeric materials caused more and more attention nowadays. Some low-molecular mass antistatic agents composed mainly of surfactant were often applied to decrease the resistivity of polymer. However, the antistatic effect of surfactants was caused mainly by the equilibrium moisture adsorbed on the surfactant. Also, the surfactant was easily removed by rubbing back and forth or washing and resulted in the disappearance of antistatic effect. Hence, in recent year the amphiphilic block copolymers were applied as antistatic agents to overcome the disadvantages of classical antistatic agents.^{1,2} The macromolecular antistatic agents were less humidity dependent, and difficult to transfer. So they had persistent antistatic ability. The amphiphilic block copolymers consisted of hydrophilic and hydrophobic blocks. The hydrophilic blocks provided the conductivity of the system and the hydrophobic blocks served as mechanical support and provided the compatibility with the other polymers.³

Several amphiphilic block copolymers recently were reported to be used to prepare persistent antistatic resins based on blending with other polymers. Poly(ether-block-amide) (PEBA) was a new member of the persistent antistatic agents whose general structure is



Wherein PA represents the hard polyamide segment with molecular mass between 600 and 4000 and EP is the soft polyether segment with molecular mass between 400 and 2000. The soft and hard segments both are relatively short blocks.^{4–7} There were several reports about application of PEBA on biomedical,^{8,9} drug release,¹⁰ and gas separation,^{11–13} but rarely reports on antistatic property. In this work, a series of PEBA were prepared by condensation with dicarboxylic PA-6 and polytetrahydrofuran glycol and were used farther as an antistatic agent in ABS. The influence of electrical property and morphological structure of PEBA on ABS was investigated.

EXPERIMENTAL

Materials

ϵ -caprolactam (CL), tetrabutyl titanate [$\text{Ti}(\text{OC}_4\text{H}_9)_4$] and adipic acid (AA) were purchased from Shanghai Reagent Company, Chinese Medicine,

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China. Polytetrahydrofuran glycol (PTMG) ($\overline{M}_n = 1000, 2000$) was purchased from Sigma-Aldrich Company.

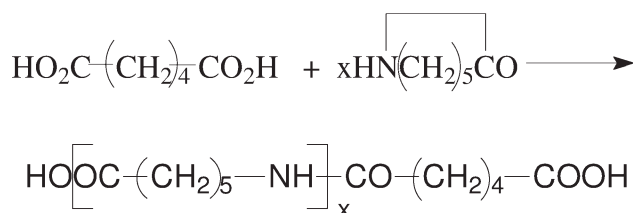
Preparation of the block copolymer and blends

Preparation of dicarboxylic polyamide-6 (PA-6)

CL, AA and 0.35% water were added into a 250 mL 3-neck round bottom flask with reflux condenser, thermometer and nitrogen inlet. The polymerization was carried out under the temperature 250–260°C for 5 h. The dicarboxylic PA-6 was obtained. The addition of AA was calculated by the following equation:

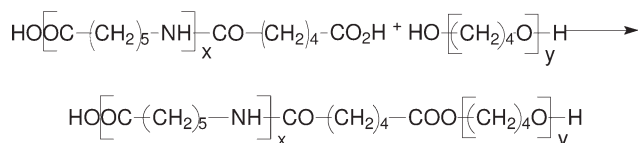
$$M_n = M_b + \frac{a}{b} \times 113$$

where a and b were the mole number of CL and AA, respectively. M_b was the \overline{M}_w of AA. M_n was the average molecular mass of dicarboxylic PA-6.



Preparation of PEBA

PTMG, with the same molar ratio to PA-6, and $\text{Ti}(\text{OC}_4\text{H}_9)_4$ were added into a 250 mL 3-neck round bottom flask with reflux condenser, thermometer and nitrogen inlet. To determine the optimal reaction conditions for the preparation of PEBA. The following reaction conditions were selected that reaction temperature from 240 to 280°C, the reaction time from 5 h under the nitrogen atmosphere to 4 h under the nitrogen and 2 h under vacuum of 80 Pa and the content of the catalytic from 0 to 1%. Then PEBA was obtained.



Preparation of ABS/PEBA blends and their boards

PEBA and ABS were mixed by hand in a small beaker and then was fed into a Thermo Haake mixer (Fisows Rheocord 90, Germany). The temperature was set at 190°C and the rotating speed was set at 65 rpm.

The ABS/PEBA blends were dried in a vacuum oven under 80°C for 24 h. Then the sample board was prepared by preheating to 190°C in 10 min, pressure keeping for 15 min, and then cold pressure keeping for 10 min.

Measurement and characterization

The viscosity of PEBA in 96% concentrated sulfuric acid at 25°C was measured using a U-viscometer.

The solvent extraction ratio of PEBA was carried out by the extraction in Soxhlet extractor with ethanol for 8 h and then the remainder was dried, weighted and calculated the weight loss rate.

For the titration of the end carboxyl group, 0.2 g PEBA was dissolved in 15 mL benzyl alcohol, and diluted by 4 mL methanol/water (1 : 1), then titrated by 0.1 mol/L ethanol as solvent for alkaline.

FTIR analysis was carried out with EQUINOXSS fourier transform infrared instrument (BRUKER Company, Germany) at room temperature in the scanning range of 570–4000 cm^{-1} .

$^1\text{H-NMR}$ spectra was recorded on DMX500 nuclear magnetic resonance apparatus (BRUKER Company, Germany) with trifluoroacetic as solvent.

Surface resistivity was measured at room temperature using ZC-43 high insulation measurement instrument (Shanghai Precision Instrument, China). Before testing, the samples were dried under vacuum under 60°C for 24 h. The durability testing of resistivity was carried out by to scrub the sample surface repeatedly with wet cloth and then dried in natural air.

The morphological structure of ABS/PEBA blends were observed by Quanta 200 FEG environment field emission scanning electron microscope (EFEG-SEM, FEI Company, Netherlands).

RESULTS AND DISCUSSION

Influence of AA on the molecular mass of PA-6

In the synthesis of PEBA the preparation of dicarboxylic PA-6 was the first step. To control the \overline{M}_n of PA-6 and ensure the two-end carboxyl groups, the molecular mass regulator (AA) was used. The experimental results were showed in Table I.

To compare the molecular weight (\overline{M}_n) data obtained from viscosity method with the theoretical value. It could be seen that \overline{M}_n of PA-6 was true well of the formula $M_{PA} = M_b + (a/b) \times 113$. Based on \overline{M}_n from viscosity method, $V_{\text{theoretical volume}}$ could be obtained. According to the ratio of actual concentration of end carboxyl group to theoretical concentration of end carboxyl group is equal to the ratio of actual number of end carboxyl group to theoretical

TABLE I
The Effect of AA on the \overline{M}_n of PA-6 and Contents of End Carboxyl Group^d

Number	CL/AA		η (dL/g)	Contents of end carboxyl group ($\times 10^{-4}$ mol)	\overline{M}_n of PA-6		
	Molar ratio	Mass ratio			Theoretical value ^a	Viscosity method ^b	Titrimetric method ^c
1	7.543	5.831	0.115	3.95	1000	947.2	1012.7
2	19.394	15	0.209	1.70	2337	2258.4	2352.9

^a It was calculated according to the formula $M_{PA} = M_b + (a/b) \times 113$. Thereinto M_{PA} was the \overline{M}_n of PA-6, M_b was the \overline{M}_n of the molecular mass regulator, a was the molecular number of CL, b was the molecular number of the molecular mass regulator.

^b It was calculated according to $[\eta] = KM^\alpha$. Thereinto $K = 6.3 \times 10^{-2}$ mL/g, $\alpha = 0.76$.

^c It was calculated according to $M = 2W/NV$. Thereinto W was the quality of sample, N was substance concentration of titrant, V was the volume of titration.

^d The reaction condition was 260°C for 5 h.

number of end carboxyl group, or the half of actual number of end carboxyl group, the actual concentration of end carboxyl group and theoretical concentration of end carboxyl group were represented by $V_{\text{titrimetric volume}}$ and $V_{\text{theoretical volume}}$ respectively and it could be calculated that there were 1.88 and 1.92 carboxyl respectively at the end of every single molecular chain. This result indicated that the two carboxyl-end groups of PA-6 could be assured basically and the molecular mass could be controlled.

Synthesis of PEBA

Selection of condensation reaction temperature

PEBA was prepared by means of condensation reaction of dicarboxylic PA-6 and PTMG. The temperature of condensation reaction for the reaction extent had marked effect. In this work dicarboxylic PA-6 ($\overline{M}_n = 2000$) and PTMG ($\overline{M}_n = 1000$) were chosen to research the influence of condensation temperature on the intrinsic viscosity of PEBA, which was correlative with the degree of polymerization of PEBA. The reaction time was 4 h under the N_2 atmosphere, and then kept for 1 h under the vacuum. The results were shown as Table II.

The data of Table II showed that PEBA had the maximum intrinsic viscosity number and the minimum solvent extraction ratio when the reaction temperature was 260°C. Because PTMG could dissolve in the ethanol but PEBA was not, so when the temperature was 240°C, solvent extraction ratio was 24.4% (weight loss rate in ethanol), which meant PTMG and PA-6 only blended but did not form the block copolymer. On the other hand when the temperature reached 280°C, the stirring effect decreased with the viscosity of the system increase. It resulted in the local overheat of the system and the oxidation of produces, caused the break of molecular chain. So the solvent extraction ratio rose again.

Selection of condensation reaction time

The influence of condensation reaction time on the relative viscosity of PEBA was researched. Hereon the condensation reaction temperature was set for 260°C. The experimental results were showed in Table III.

The data of Table III showed when reaction was carried out for 5 h under N_2 but without vacuum, the reaction was will be not complete. It resulted in the low intrinsic viscosity and high solvent extraction ratio of product. When the reaction time was adopted for 4 h under the N_2 atmosphere, and then kept for 1 h under the vacuum, the product had the highest intrinsic viscosity number. But in case of the vacuum time prolonged from 1 to 2 h, the color of the product turned dark and the intrinsic viscosity number dropped due to the break of the main chain.

Selection of catalyst dosage

The small amount of acid catalyst is generally required for the condensation reaction. In this work, $Ti(OC_4H_9)_4$ was used as the catalyst of condensation reaction. The effect of catalyst dosage on the degree

TABLE II
The Effect of Reaction Temperature on the Intrinsic Viscosity Number of PEBA

Sample No.	Reaction temperature (°C)	Intrinsic viscosity number (dL/g)	\overline{M}_n^a of PEBA	Solvent extraction ratio (%)
1	240	0.2912	3109.1	24.4
2	250	0.6919	8690.8	16.8
3	260	0.8498	11094.3	3.7
4	270	0.7706	9877.2	13.3
5	280	0.7053	8891.1	16.1

^a It was calculated according to $[\eta] = KM^\alpha$. Thereinto $K = 3.34 \times 10^{-4}$ dL/g, $\alpha = 0.8419$.

TABLE III
The Effect of Reaction Time on the Intrinsic Viscosity Number of PEBA

Sample No.	Reaction time (h)	Intrinsic viscosity number (dL/g)	\bar{M}_n of PEBA	Solvent extraction ratio (%)
6	5 h under N ₂	0.5749	6974.4	18.3
3	4 h under N ₂ and 1 h under vacuum of 80 Pa	0.8498	11094.3	3.7
7	4 h under N ₂ and 2 h under vacuum of 80 Pa	0.7382	9385.9	14.6

of polymerization was shown in Table IV. The condensation reaction carried out at 260°C under N₂ and kept for 4 h. The system was then vacuumized and kept under 260°C and 80 Pa for 1 h.

The data of Table IV showed that the intrinsic viscosity number of the produces reached a biggish value when the 0.35% of catalyst was used. The sequential accretion of catalyst couldn't improve the intrinsic viscosity number of the produces obviously. Therefore the optimum dosage of catalyst was 0.35%.

Polymer structure analysis

According to the aforementioned synthetic method, a series of PEBA were prepared as shown in Table V.

FTIR spectroscopic analysis was performed to detect the condensation reaction between the hydroxyl end groups of PTMG and the acid end groups of PA6.¹⁴ Curves a and c in Figure 1 showed the FTIR spectra of the PA6 and PTMG, respectively. The absorption peak at 3298.5 cm⁻¹ was corresponded to N—H stretching vibration. The peak at 1640.1 cm⁻¹ was corresponded to C=O stretching vibration of amide group. The absorptions at 1540.9 cm⁻¹ and 1263.3 cm⁻¹ were attributed to coupling of C—N stretching vibration and N—H bending vibration. The absorption at 689.3 cm⁻¹ was caused from N—H rocking vibration. All of above were the characteristic absorption peaks of PA6. And peaks at 1108.6 cm⁻¹ and 3465.1 cm⁻¹ indicated the characteristic absorption peaks of the ether bond C—O—C and hydroxyl-terminated of PTMG, respectively. Compared with curve a and c, curve b revealed a strong absorption at 1736.4 cm⁻¹ which attributed to

TABLE IV
The Effect of Catalyst Dosage on the Intrinsic Viscosity Number of PEBA

Sample no.	Catalyst dosage (%)	Intrinsic viscosity number (dL/g)	\bar{M}_n of PEBA	Solvent extraction ratio (%)
8	—	0.6171	7586.5	17.2
3	0.35	0.8498	11094.3	3.7
9	0.75	0.8463	11040.1	3.4
10	1	0.8586	11230.9	3.1

the ester group. The analysis of FTIR indicated that the PEBA was obtained.

NMR is an ideal method for describing the structure of polymer.¹⁵ The structure and connection mode of PA-6 and PTMG were analyzed by ¹H-NMR. ¹H-NMR spectrum of PEBA (Fig. 2) showed a peak at 4.355 ppm for O=C—O—CH₂ indicating the successful preparation of PEBA.

Influence of PEBA on the surface resistivity of ABS resins

To research the influence of dosage of PEBA on the surface resistivity of ABS, the different kind of PEBA with the same EP segment were added into ABS. As shown in Figure 3, the ABS/PEBA2-2 blends had the lowest surface resistivity. PEBA2-2 could obviously decrease the surface resistivity of ABS from 5.6 × 10¹⁴Ω to 2.1 × 10¹⁰Ω. From the cure of ABS/PEBA, it could be found the surface resistivity of ABS decreased with the increase dosage of PEBA from 0 to 12%. But the resistivity kept invariant almost when the dosage of PEBA changed from 12 to 15%. In other words, only when the content of antistatic agent reached a certain value, could polymers exhibit significant antistatic effect. When the addition amount was more than this value, the

TABLE V
Compositions of a Series of PEBA

Sample name	\bar{M}_n of prepolymers		Molar ratio ^b PA : PTMG	PTMG (wt %) ^c
	PA ^a	PTMG		
PEBA1-1	1000	1000	1 : 1	50
PEBA2-1	2000	1000	1 : 1	33.3
PEBA3-1	3000	1000	1 : 1	25
PEBA4-1	4000	1000	1 : 1	20
PEBA1-2	1000	2000	1 : 1	66.7
PEBA2-2	2000	2000	1 : 1	50
PEBA3-2	3000	2000	1 : 1	40
PEBA4-2	4000	2000	1 : 1	33.3

^a \bar{M}_n of PA was the designed \bar{M}_n .

^b Molar ratio was the adding amount ratio of PA/PTMG when synthesizing.

^c PTMG/wt % was the mass percentage of PTMG in each PEBA.

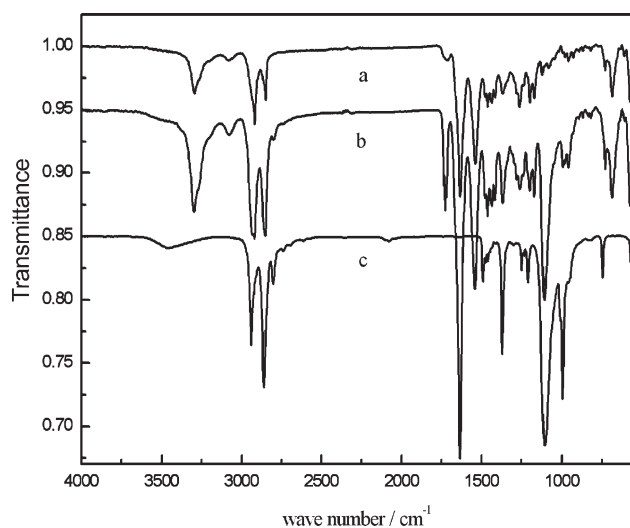


Figure 1 FTIR spectra of PA, PA-block-PTMG and PTMG: (a) PA6 ($M_n = 2000$), (b) PA-PTMG, (c) PTMG ($M_n = 2000$).

antistatic properties would not be improved. In addition, when the molecular mass of polyether kept invariant, the surface resistivity of ABS would decrease with the decrease molecular mass of polyamide (or the increasing ratio of EP/PA). On the other hand when the molecular mass of polyamide reached a certain value, the surface resistivity of ABS would reduce with the increase of molecular mass of polyether and the content of polyether (Fig. 3 inset). This phenomenon indicated that the more polyether chain segments, the more hydrophilic groups in the blend, and the conductive network and pathway were more favorable to be formed.²

The change of surface resistivity of the samples with time was researched with different loading level of PEBA. The results were shown in Figure 4. It can be seen that the surface resistivity of samples

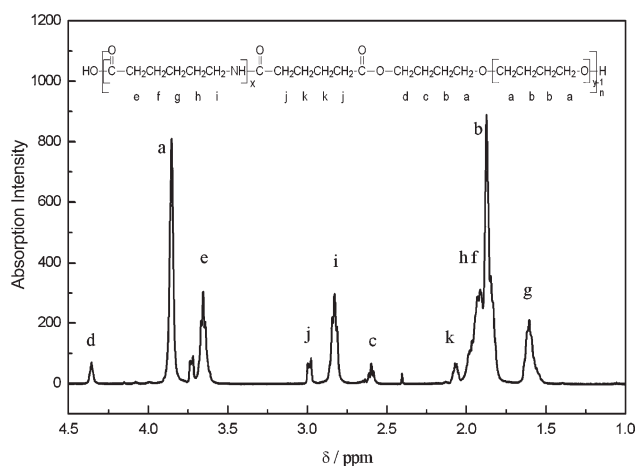


Figure 2 $^1\text{H-NMR}$ graph of PEBA.

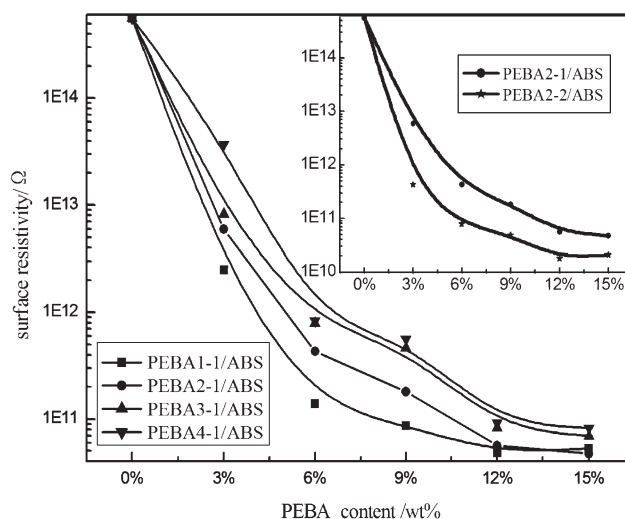


Figure 3 Relation graph of adding amount and resistivity (the same EP segment) Inset: Relation graph of adding amount and resistivity (the same PA segment).

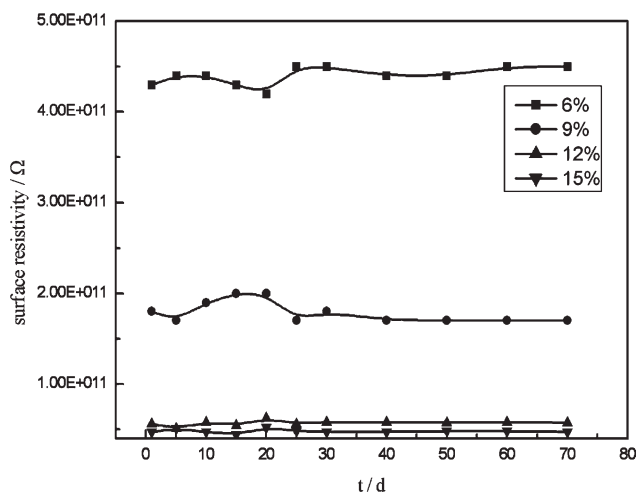


Figure 4 Relation graph of time and resistivity.

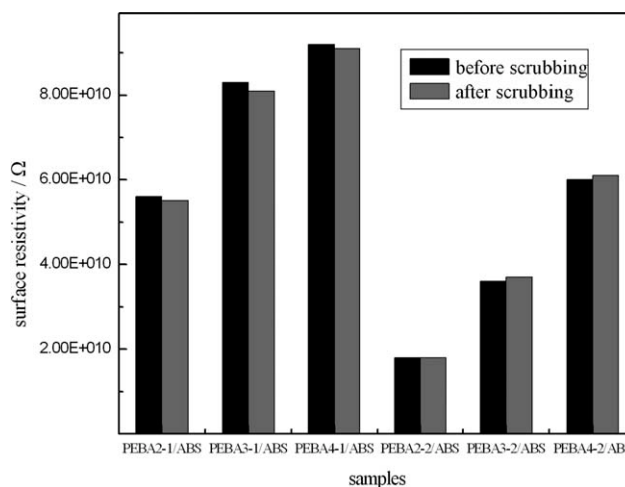


Figure 5 Contrasting pattern of surface resistivity of samples before s and after scrubbing.

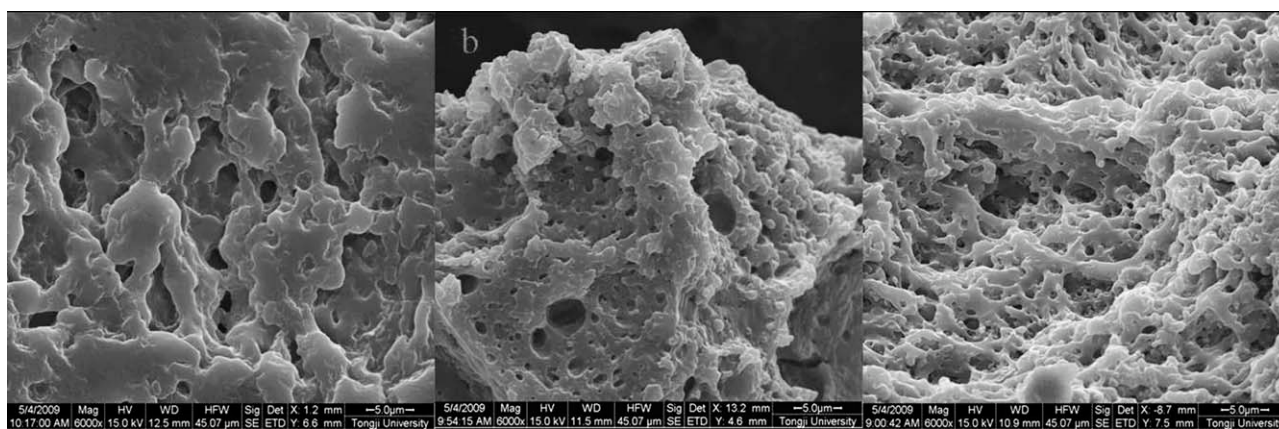


Figure 6 EFEG-SEM micrographs of PEBA/ABS blends: (a) PEBA2-1 (6 wt %)/ABS, (b) PEBA3-2 (6 wt %)/ABS, (c) PEBA3-2 (15 wt %)/ABS.

remained invariable, when the samples were laid at room temperature for 70 days. It exhibited the good durability of the ABS/PEBA blends. Because of friction and washing, the antistatic agent in the plastic products would remove in the using process. Therefore, the scrubbing resistance of antistatic agent was an important performance. Figure 5 showed the surface resistivity before and after scrubbing. It could be seen from the figure that the surface resistivity of samples kept almost unchangeable. It meant that PEBA had an excellent scrubbing resistance of surface resistivity.

Figure 6 showed the EFEG-SEM micrographs of formic acid etched surfaces (having removed the PEBA phase) of ABS/PEBA blends.¹⁶ Comparing Figure 6(a,b) it could be found that the particle cavities were both big and inhomogeneous, which showed poor compatibility. But Figure 6(b) demonstrated a little better compatibility than Figure 6(a) due to the higher content of polyether in PEBA3-2 than in PEBA2-1 (Table V). As shown in Figure 6(c), PEBA3-2 (15 wt %) particle cavities were dispersed in the ABS matrix uniformly. Compared with Figure 6(b), the more content of PEBA were, the better compatibility would be. It indicated that the more contents of PEBA result in the lower surface resistivity of ABS.

CONCLUSIONS

In summary, a series of PEBA containing various amounts of polyether were prepared by condensation of polyether and polyamide with low-molecular mass. The characterization results of FTIR and NMR identified the formation of ester bond and the suc-

cess of condensation reaction. The permanent antistatic PEBA could promote the conductivity of ABS effectively. The research results showed that the surface resistivity of the blends decreased with the increase of content of PEBA and the ratio of polyether. The surface resistivity of ABS could be reduced to below $10^{10}\Omega$ and remained invariable under the laid of time and scrubbing. The nicer dispersivity of PEBA in ABS was helpful to improve the antistatic property.

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