

Preparation and Properties of Poly(ether-ester-amide)/Poly(acrylonitrile-*co*-butadiene-*co*-styrene) Antistatic Blends

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ABSTRACT: A novel antistatic agent poly(ether-ester-amide) (PEEA) based on caprolactam, polyethylene glycol, and 6-aminocaproic acid was successfully synthesized by melting polycondensation. The structure, thermal properties, and antistatic ability of the copolymer were characterized by Fourier transform infrared spectroscopy, differential scanning calorimetry, thermogravimetric analyses, and ZC36 megohmmeter. Test results show that PEEA is a block copolymer with a melting point of 217°C and a thermal decomposition temperature of 409°C, together with a surface resistivity of $10^8 \Omega/\text{sq}$. Antistatic poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS) materials were prepared by blending different content of PEEA to ABS resin. The antistatic performances, morphology, and mechanical properties were investigated. It is indicated that the surface resistivity of PEEA/ABS blends decrease with the increasing PEEA con-

tent, and the excellent antistatic performance is obtained when the antistatic agent is up to 10–15%. The antistatic performance is hardly influenced by water-washing and relative humidity, and a permanent antistatic performance is available. The antistatic mechanism is investigated. The compatibility of the blends was studied by scanning electron microscopy images. The ladder distribution of antistatic agent is formed, and a rich phase of antistatic agent can be found in the surface layer. The elongations at break of the blend are improved with the increasing antistatic agent; the tensile strength and the notched impact strength kept almost the same. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 12–18, 2011

Key words: poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS); poly(ether-ester-amide); antistatic; surface resistivity; blends

INTRODUCTION

Poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS) is widely used in various fields such as automobile industry, electrical and electronic parts, and automotive components because of its good mechanical and thermal properties.¹ ABS resin is inherently an electrical insulator, exhibiting a surface resistivity of $10^{15} \sim 10^{16} \Omega/\text{sq}$. The static charge that easily builds up on such molded parts by contact or rubbing may cause an electrostatic discharge, which becomes a serious problem because there may be electrostatic damage to sensitive semiconductor devices and interference with circuit operation.² To solve these problems, a lot of antistatic agents are often incorporated into the polymer at the molding process or

applied to the surface of the products in a finishing process to control the surface resistivity of the molded part to $10^{11} \sim 10^8 \Omega/\text{sq}$.^{3–6}

Generally, some antistatic agents, such as carbon blacks, metal powders, surfactants, or other hydrophilic substances can be blended with polymer matrix to dissipate the electronic charge. However, carbon blacks as an antistatic agent make the materials black, if some light color materials are needed; thus, carbon black cannot be selected.^{7–9} If some low-molecular-weight antistatic agents like surfactant are used, their antistatic effect is brought about by the equilibrium moisture adsorbed on the surfactant; therefore, sufficient antistatic effect is not achieved under low humidity. Furthermore, the surfactant is removed by rubbing or washing back and forth, and the antistatic effect disappears easily.^{10,11} Many high-molecular-weight antistatic agents are studied as their different antistatic mechanism with low-molecular-weight antistatic agents. A conductive network is formed in the antistatic blends by high-molecular-weight antistatic agents, and distributed in the surface layer of the materials mainly, which remained if the materials are wiped or water-washed; thus, they have permanent antistatic properties. It is a research hotspot of antistatic agent in recent years^{12–15}

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because of its different antistatic mechanism. High-molecular-weight antistatic agent is a new research field in antistatic technology. It will have potential applications, and it is a new revolution in antistatic technology.

In this study, a novel ABS antistatic agent, poly(ether-ester-amide) (PEEA), was synthesized, characterized, and blended with ABS resin as a permanent antistatic agent. PEEA is a multiblock copolymer, which was synthesized by caprolactam and polyethylene glycol (PEG). This high-molecular-weight antistatic agent has a high melting point because of crystallization of polyamide blocks, and the polyether blocks are hydrophilic polymers, and the antistatic property of materials can be obtained by them.^{16–18} PEEA was blended with ABS resin, and excellent antistatic effect on the blend can be observed, a permanent antistatic performance of the blend is confirmed, and the antistatic mechanism is investigated.

EXPERIMENTAL

Materials

Caprolactam, PEG, sebacic acid, and 6-aminocaproic acid used for this study were purchased from Sino-pharm Chemical Reagent Co., Ltd., China. Tetrabutyl titanate, glycol, and sodium dodecylbenzene sulfonate (SDBS) were obtained from Ling Feng Chemical Reagent Co., Ltd., Shanghai, China. All the chemicals used were chemically pure except 6-aminocaproic acid (BR). ABS resin was offered by Taiwan's Chi Mei Industrial Co., Ltd. MAH-g-ABS (grafting yield 1.5 ~ 1.8%) was supplied by Ningbo Nengzhiguang New Materials Technology Co., Ltd.

Synthesis of antistatic agent PEEA

PEEA copolymers were synthesized with caprolactam, 6-aminocaproic acid, sebacic acid, glycol, and PEG by melting polycondensation method. All raw materials were added into a three-necked flask equipped with a stir bar and a thermometer. The reaction mixture was heated and stirred at 230 ~ 260°C under a nitrogen atmosphere, reacted for 5 hr with the catalysis of tetrabutyl titanate, and vacuumed for 1 ~ 2 hr. Finally, the final product was discharged from the outlet and was rapidly cooled by cooling water, purified, and dried. The high-molecular-weight antistatic agent PEEA was synthesized. The typical PEEA copolymer was prepared by mixing the following components: caprolactam 60 g, 6-aminocaproic acid 3 g, sebacic acid 5.54 g, glycol 2 g, and PEG (PEG6000) 40 g, tetrabutyl titanate 0.8 mL. By changing the mole ratio of caprolactam and PEG (PEG2000 ~ 10,000), different properties of the copolymers were obtained.

Preparation of antistatic materials

ABS resin, PEEA, and MAH-g-ABS (amount of 3 ~ 5 wt % in the blend) were kept dried under vacuum at 70 ~ 80°C for 2 ~ 4 hr before use. Blends of ABS and PEEA were melting mixed by using a single-screw extruder with a screw diameter of 12.5 mm and a length-diameter ratio of 25. The barrel was set with temperature of 220°C and a screw speed of 100 rpm. The blends were extruded strand and cut into pellets for injection molding. The extruded pellets were dried for 4 hr at 90°C before molding and molded into the standard specimens using an injection molding machine (Taiwan's Chen Hsong Injection Molding Machine Co., Ltd.). The set temperature for the nozzle, cylinder, and the mold were 220, 230, and 50°C, respectively. Molding cycle was 32 sec. SDBS/ABS antistatic material was also prepared by this method.

Instruments and methods

Fourier transform infrared (FTIR) spectra of the samples were recorded between 4000 and 500 cm^{-1} on a Nicolet 5700 FTIR spectrometer (Thermo Nicolet Corp., USA). The pellets were dispersed in potassium bromide and analyzed in the form of pressed discs. Thermal analysis was carried out on a modulated DSC2910 scanning calorimeter (DSC) (United States TA Instruments). About 8 ~ 10 mg of polymer was heated under nitrogen from 20°C to 250°C at 10°C/min. Thermogravimetric analyses (TGA) were done on the samples by using DSC-SP thermal analyzer (NETZSCH-STA 409, Germany). The PEEA samples were heated from 20°C to 600°C at a heating rate of 10°C/min under a steady flow of nitrogen atmosphere. Surface resistivity of each sample was measured with a ZC36 megohmmeter (Shanghai Precision Instrument Co., Ltd., China) according to GB/T 1410-2006. Each sample was kept at 23°C, 50% relative humidity (RH) for 24 hr. Antistatic persistence of PEEA/ABS blend was immersed into distilled water, and the sample surface was scrubbed with absorbent cotton. After this process and repeating five times, the sample were exposed to air for drying under the conditions of ambient temperature, 50% RH for 24 hr, and then the figures of surface resistivity were measured. Influence of RH was observed in the following way. Each sample was kept at 23°C at a predetermined humidity for 24 hr, and then, the surface resistivity of each was measured with a ZC36 megohmmeter. The morphology of the fractured surface was examined by a JSM-6360LV scanning electron microscope (Japan Electron Optics Laboratory). Before observation, the samples were fractured in liquid nitrogen and gold-coated in a vacuum chamber to make the surfaces

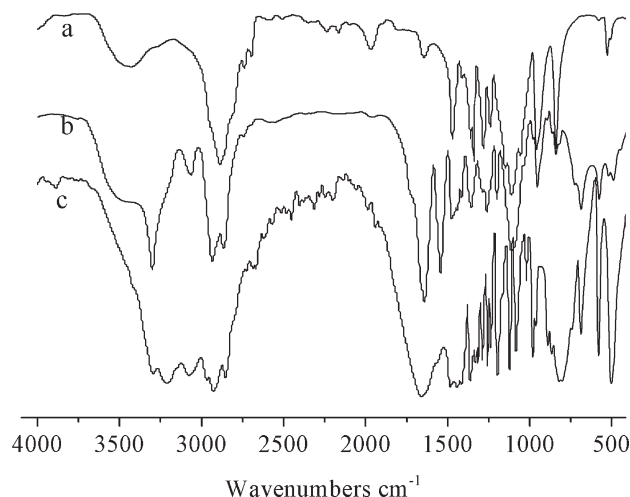


Figure 1 FTIR spectra of PEG (a), poly(ether-ester-amide) (b), and caprolactam (c).

conductive. The mechanical properties of PEEA/ABS antistatic materials were tested by JJ-20 Memory-type Impact Testing Machine and Tensile Testing Machine (Changchun City Intelligent Instrument Equipment Co., Ltd. China) according to GB-T 1040-1992 and GB/T 1043-1993. The notched impact samples were prepared in 45° angle and with impact energy of 4 J. The tensile samples were tested at a velocity of 50 mm/min. All the mechanical properties were tested at a temperature of 23°C.

RESULTS AND DISCUSSION

Structure characterization

The FTIR spectra of PEG, PEEA, and caprolactam are shown in Figure 1. The peaks at 3300.5 and 3063.4 cm^{-1} corresponds to N-H antisymmetric and symmetric stretching vibration in the group of $-\text{CONH}-$, and 1641.4 cm^{-1} is the stretching vibration of the group $\text{C}=\text{O}$, which are the characteristic absorption bands of the $-\text{CONH}-$ group. The absorption band at 1544.1 cm^{-1} is the in-plane bending vibration of the group N-H, which is called amide I band. All these absorption bands are the absorption of amide. The peaks at 1106.7 and 1110.9 cm^{-1} are the $\text{C}-\text{O}-\text{C}$ stretching vibration absorption band in polyether. All these information indicate that the copolymer PEEA was synthesized successfully, which composed of two blocks, polyether and polyamide.

Thermal properties

The thermal behaviors of the copolymers were investigated by differential scanning calorimetry and TGA. Typical differential scanning calorimetry traces of PEEA containing 30 wt % and 40 wt % PEG are

shown in Figure 2. It can be found that PEEA have two melting points. The melting peaks in the two traces are about 50°C, which are the polyether blocks of the copolymer. But at this time, the copolymer has not melted. The second melting peaks in the two traces are about 217°C, which are the polyamide blocks of copolymer. This is the true melting point of the copolymer. This phenomenon can be explained that the copolymer is a thermoplastic elastomer, the polyether blocks are called soft segment, and the polyamide blocks are called hard segment; the two blocks can crystallize respectively, and hydrogen bonds were formed intramolecularly and intermolecularly. When the temperature is up to about 50°C, the polyether blocks begin to melt, but the whole copolymer have not melted, because of the presence of the polyamide hard segment. When the temperature is up to about 217°C, the polyamide blocks begin to melt; at this time, the copolymer become molten polymer. Figure 2 also shows information that the melting point (T_m) of the copolymer has decreased slightly with the increasing polyether content. This behavior can be attributed to the introduction of ether bonds in the copolymer, which improves the molecular flexibility and increase mobility of the molecules.

The thermal stability of antistatic agent PEEA was studied by TGA under nitrogen atmosphere, and the TGA curve of PEEA is shown in Figure 3. It can be observed that the weight of PEEA decreases gradually before 100°C because PEEA is a hydrophilic polymer, which absorbs water from the air easily. In addition, the weight loss between 132°C and 205°C is caused by the volatilization of low-molecular-weight compounds such as sebacic acid and other impurities. The onset decomposition temperature of PEEA is 409°C, the end decomposition temperature is 477°C, and the weight of PEEA lost was 88.53%

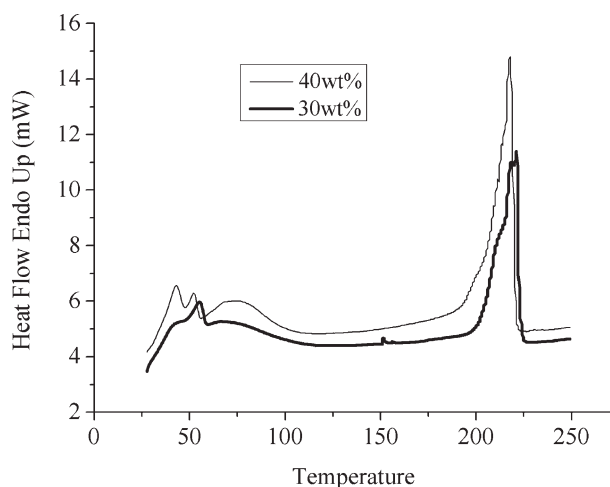


Figure 2 Differential scanning calorimetry of PEEA with different PEG content.

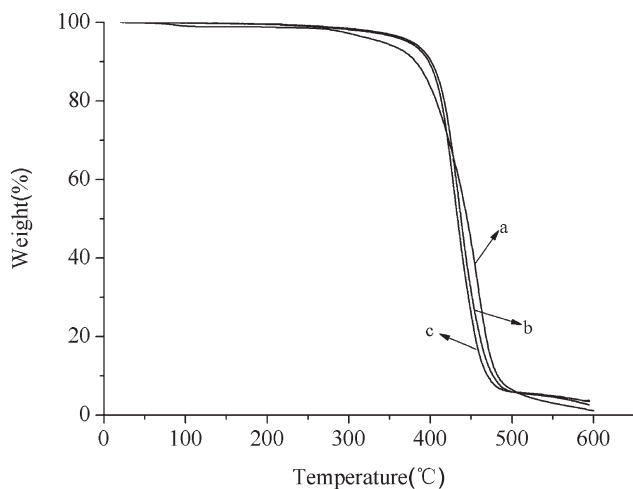


Figure 3 TGA curves of PEEA (a), ABS/PEEA blends (b), and ABS (c).

between the two temperatures. All these phenomena indicate that PEEA has an excellent thermal stability.

Thermal properties of ABS/PEEA and pure ABS were tested under the same TGA testing conditions, and the results are shown in Figure 3. The TGA curves of ABS/PEEA and pure ABS overlaps approximately. Their onset decomposition temperatures are 408.8°C and 407.6°C, and the end decomposition temperatures are about 463.7°C and 461.5°C, respectively. That is to say the so-prepared ABS/PEEA blends have excellent thermal properties, which can be compared with pure ABS resins. The corresponding thermal parameters are shown in Table I.

Surface resistivity of the ABS/PEEA antistatic materials

Figure 4 illustrates the relationship between content of PEEA and surface resistivity. It can be found that the surface resistivity of PEEA/ABS blends decrease slowly before 7 wt % of PEEA content in the ABS matrix. When the content of PEEA reach between 7 and 11 wt %, the surface resistivity have decreased rapidly from 10^{15} to 10^{11} Ω/sq . With the increase in the PEEA amount above 11 wt %, there is not an obvious decrease; the resistivity will keep a stable

TABLE I
Decomposition Temperature of PEEA, ABS/PEEA Blends, and Pure ABS

| Materials | Onset temperature (°C) | End temperature (°C) |
|-----------|------------------------|----------------------|
| PEEA | 409.7 | 477.1 |
| ABS/PEEA | 408.8 | 463.7 |
| ABS | 407.6 | 461.5 |

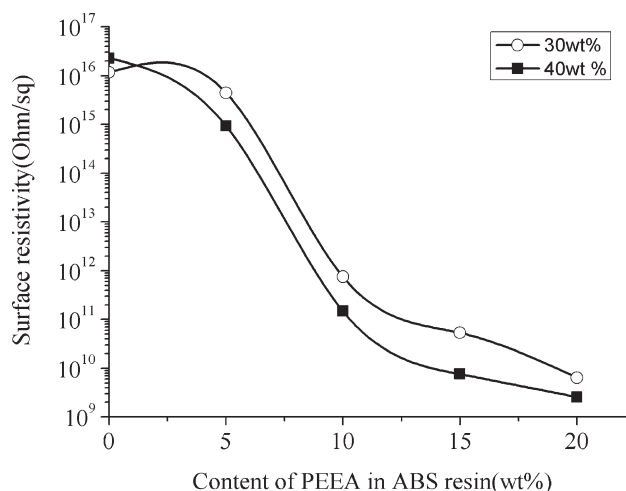


Figure 4 Relationship between content of PEEA in ABS and surface resistivity.

value 10^9 Ω/sq , even at 20% of content. The blends of PEEA/ABS show the resistivity low enough for achieving better antistatic performance. This is the feature of nonionic antistatic agent, which is decided by its structure and different antistatic mechanism.

PEEA plays a significant role in reducing the surface resistivity of polymer blends, and it is an effective antistatic agent for ABS resin materials. When a small quantity of PEEA is available in the blend, the continuous conductive network is not available in the blend, and tunneling theory¹⁹ must be taken into account. In the electron tunneling theory, the electrical conduction is described to take place by electrons jumping across a gap or tunnel through energy barriers between conducting elements in the polymer matrix. The resistivities decrease several orders compared with the matrix and reach 10^{11} $\Omega/$.

When a sufficient amount of antistatic agent is fed, the antistatic agent particles get closer to each other and form linkages, which result in continuous chains (conductive network) in the polymer matrix. There is a critical content at which the system experiences the transition from an insulator to conductor. At the critical content, the conductive network in the matrix will be formed, and a large increase in conductivity results from a minor increase in the antistatic agent in the matrix. The corresponding antistatic agent content is called the percolation threshold. When the content of antistatic agent overpasses this critical value, the conductivity of the system is mainly determined by the conductive network formed by the antistatic agent. Because the conductive network already exists, the conductivity will increase marginally against the increase of antistatic agent content.

In addition, another phenomenon can be found in Figure 4 that the surface resistivity of 40 wt % PEG in PEEA decrease more quickly than 30 wt %. The

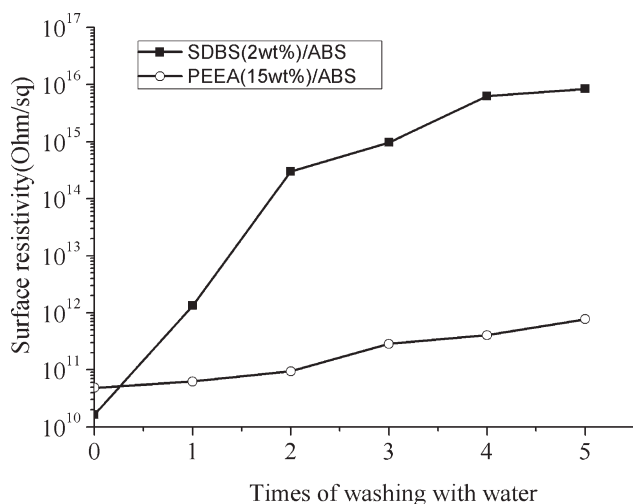


Figure 5 Influence of water-washing on surface resistivity.

reason is that the polyether section plays a main role in the antistatic agent; with the increase in the PEG in PEEA, the antistatic effect is better.

Figure 5 illustrates the influence of washing in water on surface resistivity, which is an evaluation of durability of antistatic effect. From Figure 5, it can be found that 2 wt % SDBS, which represented a conventional low-molecular-weight antistatic agent, was blended with ABS resin, and the surface resistivity of this antistatic materials increase gradually with the increase in washing times and at last have no antistatic property. On the contrary, the polymer antistatic agent PEEA (40 wt % PEG), which was blended with ABS resin with an amount of 15 wt % can keep a stable antistatic property; washing times have little influence. Different antistatic mechanisms are also certificated by these phenomena. Conventional low-molecular-weight antistatic agents immigrate to the surface of the material and are easily

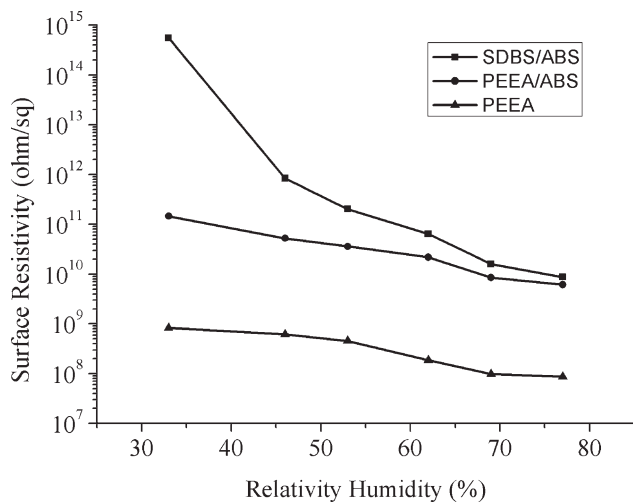


Figure 6 Influence of relative humidity on surface resistivity.

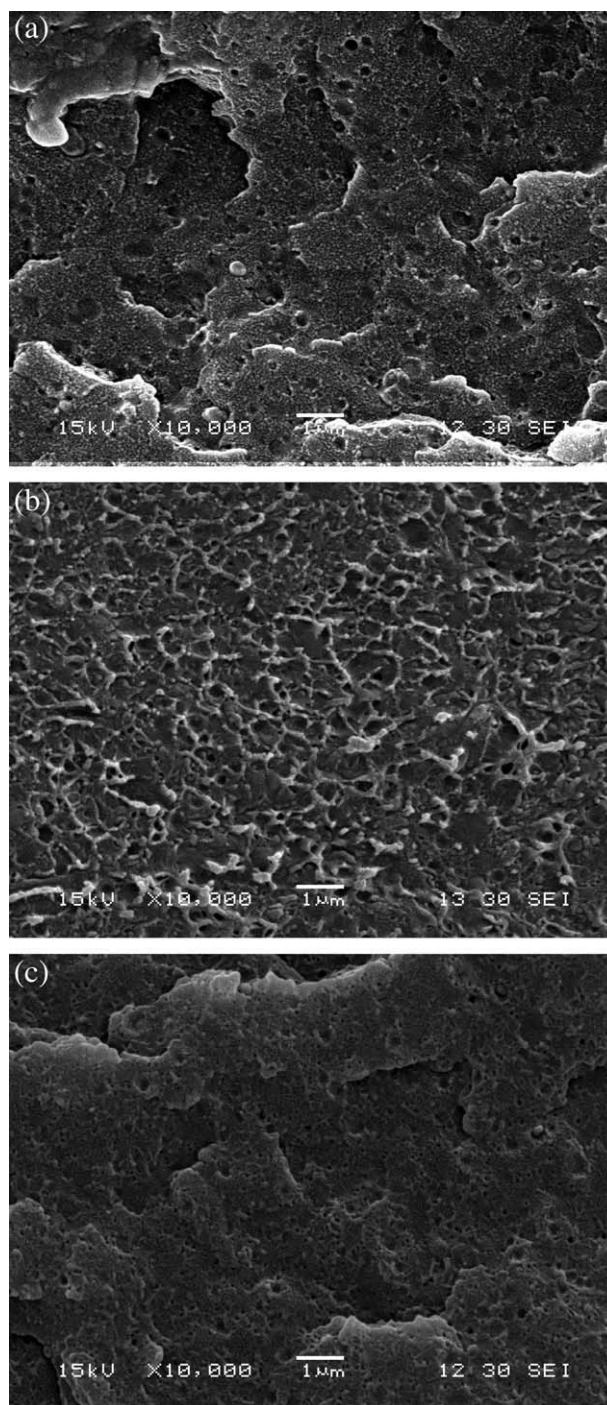


Figure 7 Scanning electron microscopy images of the dispersion of PEEA in ABS resin: (a) center distribution of PEEA in PEEA 15 wt %/ABS blends, (b) surface layer distribution of PEEA in PEEA 15 wt %/ABS blends, and (c) pure ABS resin.

removed by wiping or water-washing. Even if it is wiped and water-washed, high-molecular-weight antistatic agent remained in the materials.

Figure 6 illustrates the influence of RH on surface resistivity. One of the practical advantages of the use of high-molecular-weight antistatic agent over conventional low-molecular-weight one incorporated

TABLE II
Mechanical Properties of Various ABS/PEEA Blends

| Recipe | Tensile strength (MPa) | Elongation at break (%) | Notched impact strength (KJ/m ²) |
|--------------|------------------------|-------------------------|--|
| ABS resin | 50.3 | 22 | 23.3 |
| ABS/5% PEEA | 48.5 | 27 | 21.6 |
| ABS/10% PEEA | 46.3 | 31 | 20.8 |
| ABS/15% PEEA | 42.7 | 36 | 19.7 |
| ABS/20% PEEA | 40.2 | 43 | 18.7 |

into resin is its robust antistatic performance under various humidities, especially low humidity. From Figure 6, it is observed that SDBS/ABS antistatic material is influenced by RH seriously. The surface resistivity changes from 10^{14} to 10^9 Ω /sq when the RH increases from 32% to 77%. The antistatic test by blending with low-molecular-weight compound such as SDBS in ABS resin can be explained as the moisture absorption of the hydrophilic part on the surface of the material. In an ambient condition like 32% RH, conventional low-molecular-weight technology-based antistatic material lose antistatic performance because of lack of moisture on its surface. It is confirmed that PEEA/ABS antistatic blends have robust antistatic performance despite the larger change of the RH. All these phenomena are decided by their different structures and different antistatic mechanisms.

Morphology

Figure 7 shows the morphologies of the PEEA 15 wt %/ABS blends. From the micrographs of the samples, the ladder distribution of PEEA in ABS matrix can be seen. The black cavities or the convex particles are PEEA antistatic agent, which distribute heterogeneously in different places of the material. In the center of the antistatic material [Fig. 7(a)], there is only a little PEEA particle, despite dispersing homogeneously in a certain range. The antistatic agents distribute in the surface layer of the material mainly [Fig. 7(b)]. All these are different from pure ABS resin [Fig. 7(c)]. It was because the viscosity of PEEA synthesized in our laboratory was large enough, i.e., the PEEA had a high molecular weight. Under the injection temperature of 220°C, PEEA became dispersion phase with the high shearing force; the shearing force was higher in the center than the surface layer, and thus the ladder distribution and different size were formed. It is reported²⁰ in some literatures that the polymer antistatic agents distribute in the surface of the matrix with stripes; it is because its viscosity is larger enough than the matrix resin in the processing temperatures.

Mechanical properties of antistatic ABS blends

The mechanical properties are most important for the applications of antistatic ABS materials. Table II shows the mechanical properties such as tensile strength, elongation at break, and notched impact strength of various PEEA/ABS blends. It can be observed that the tensile strength and notched impact strength of the blends decrease with increasing PEEA content. For example, the tensile strength of pure ABS resin is 50.3 MPa, and 5, 10, 15, and 20% blending of PEEA in ABS resin are 48.5, 46.3, 42.7, and 40.2 MPa, respectively. However, the elongations at break increase relatively. These phenomena can be explained by the following theory. On the one hand, ABS resin is an amorphous polymer, but PEEA is a crystalline polymer, what is more, polyether and polyamide have different crystalline. If the compatibility of the two components can be enhanced, the mechanical performances will be excellent, despite a certain degree of compatibility is observed in scanning electron microscopy images. On the other hand, the melt viscosity or molecular weight of PEEA and the processing conditions lead to the ladder distributions in ABS matrix. If all the problems can be studied and solved, the more excellent mechanical properties can be obtained.

CONCLUSIONS

PEEA was successfully synthesized by melting polycondensation with caprolactam, PEG, and other materials. It is confirmed that PEEA has relative high melting point, sufficient thermal stability, and outstanding antistatic ability. The surface resistivity of the PEEA/ABS blends drastically decreased from 10^{16} to 10^9 Ω with increasing antistatic agent content, and was hardly influenced by times of water-washing and RH of the air. Test results show that the blends have enough antistatic properties. Fracture morphology studies reveal that the antistatic agent PEEA has a ladder distribution in ABS matrix. Under the existence of MAH-g-ABS, the two components have an adequate compatibility, which results in the excellent mechanical performances of the blends.

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