Electrolyte-Based Antistatic Plasticizer for Soft Poly(vinyl chloride) Composites

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ABSTRACT: In this study, we synthesized an aromatic ester plasticizer with ether oxygen bonds called bis[2-(2-methoxyethoxy)ethyl]phthalate (BMEP), which could dissociate sodium thiocyanate (NaSCN) by a coordination effect between the ether oxygen bond and the Na^+ cations. An antistatic plasticizer (AP) for poly(vinyl chloride) (PVC) was then prepared by the mixture of BMEP and NaSCN. The surface resistivity, tensile strength, elongation at break, and hardness of the PVC composites with AP were studied. The addition of dibutyl phthalate (DBP) was favorable for enhancing the conductivity and elongation at break of the PVC composites. The antistatic ability of the PVC composites was slightly sensitive to the relative humidity (RH). The dependence of the surface resistivity of the AP-plasticized PVC composites on temperature was in good accordance with the Arrhenius equation, and the surface resistivity of the composites effectively decreased about one order of magnitude in the temperature range 40–80°C. The surface resistivity of the antistatic PVC composites containing 40 phr DBP and 60 phr AP reached 10^8 Ω/sq orders of magnitude at an RH of 0.1%, and the corresponding tensile strength, elongation at break, and hardness reached 8.12 MPa, 416%, and 53 A, respectively. Such antistatic PVC composites, therefore, have large potential applications in corresponding antistatic fields, such as the packaging of electrical devices. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 1718–1724, 2010

Key words: additives; blends; composites

INTRODUCTION

Poly(vinyl chloride) (PVC) is a widely used kind of thermoplastic material because of its outstanding advantages, such as low cost, processability, and broad range of properties. Hence, it is extensively applied in building construction, electronics industry, and computer and automobile fields. However, its excessive electrical insulation, high surface resistivity (10^{13}–10^{16} Ω/sq), and low dielectric constant makes charges easily accumulate on the PVC surface; this leads to dust contamination during packaging, the risk of electrical shocks, and the risk of electrical discharge, which can cause fires or explosions.[1–3] Therefore, the application of PVC is restricted in some fields with special antistatic requirements, such as the coal-mining industry.

Generally, there are several common ways to improve the antistatic ability of PVC composites, for example, the addition of antistatic agents.[4–6] The addition of antistatic agents can effectively reduce the surface resistivity through the buildup of a conductive path on the surface and through the lubrication of the surface to decrease the friction factor and thus to sufficiently reduce the probability of the generation of charges. Nevertheless, this kind of antistatic ability is so strongly dependent on the relative humidity (RH) that it cannot exert antistatic ability in a quite dry environment.[2]

Another measure is the addition of conductive fillers,[2,7–11] including carbon blacks, metal fibers, and electroconductive polymers, such as acid-doped polyaniline. However, a large amount of conductive filler is needed for addition to the PVC matrix to ensure that the PVC composites possess antistatic ability. So many fillers in the matrix will greatly change the other properties of the PVC composites and will make the PVC composites nontransparent and difficult to process and will give it a deep color. These disadvantages significantly limit their greater applications.

Gel polymer electrolytes[12–15] are novel functional polymer materials that are composed of a polymer, a high-dielectric-constant solvent, and alkali metal salts. Gel polymer electrolytes are dimensionally stable and have a high conductivity in the range 10^{-3}–10^{-4} S/cm. Therefore, gel polymer electrolytes are usually able to be used to design rechargeable lithium batteries.[16–19] However, it seems that an antistatic and colorless PVC composite composed of a PVC host and an ion-conductive electrolyte has not

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been previously reported. An assumption, the introduction of an ion-conductive mechanism into the antistatic PVC field to endow the PVC matrix with excellent antistatic abilities, inspired us to explore the relevant research. We previously reported a compound antistatic plasticizer (AP) for soft PVC materials that sufficiently combined the ionic conduction of a plasticizer-based liquid electrolyte with a high boiling point with the conventional plasticizing effects of a dibutyl phthalate (DBP) plasticizer.[20] Both the bulk and surface electrostatic discharge protections of the nonblack PVC composites were able to be solved by this method, and the surface resistivity of these compounds reached 10^5 Ω/sq orders of magnitude in an ambient environment. However, the mechanical properties of the aforementioned PVC composites were relatively poor and unable to satisfy the requirements of many practical applications. In this study, we synthesized a kind of plasticizer with short ether oxygen groups that could also dissociate the alkali metal salts. The antistatic PVC composites were then obtained by the addition of the plasticizer doped with sodium thiocyanate (NaSCN) to the PVC matrix. The surface resistivity, tensile properties, and hardness of the composites were evaluated. The mechanical properties of the prepared PVC composites were found to be significantly enhanced over those of the composites in the previous study.

EXPERIMENTAL

Materials

Analytically pure dimethyl phthalate (DMP), tetrabutyl titanate, and NaSCN were purchased from Kelong Chemical Reagent Co. (Chengdu, China). Diethylene glycol monomethyl ether (DGME) was supplied by Tianjin Bodi Chemical Co. (Tianjin, China) and was used as received.

PVC powder (SG-V; average degree of polymerization = 1000–1100), DBP, compound stabilizer (Baeropan SMS 318), and nitrile butadiene rubber (NBR; XNBR820, number average degree of polymerization = 3000–3500, viscosity = 2500 Pa s at 40°C) were provided by Tianyuan Co., Ltd. (Yibing, China), Qilu Petrochemical Co., Ltd. (Zibo, China), Baerlocher Co. (Lingen, Germany), and Lanzhou Petrochemical Co., Ltd. (Lanzhou, China), respectively. All of the other chemicals used in this experiment were analytically pure.

Synthesis of bis[2-(2-methoxyethoxy)ethyl]phthalate (BMEP) by the ester-exchange reaction

Set contents of DMP and DGME were added to a three-necked flask equipped with a water segregator.
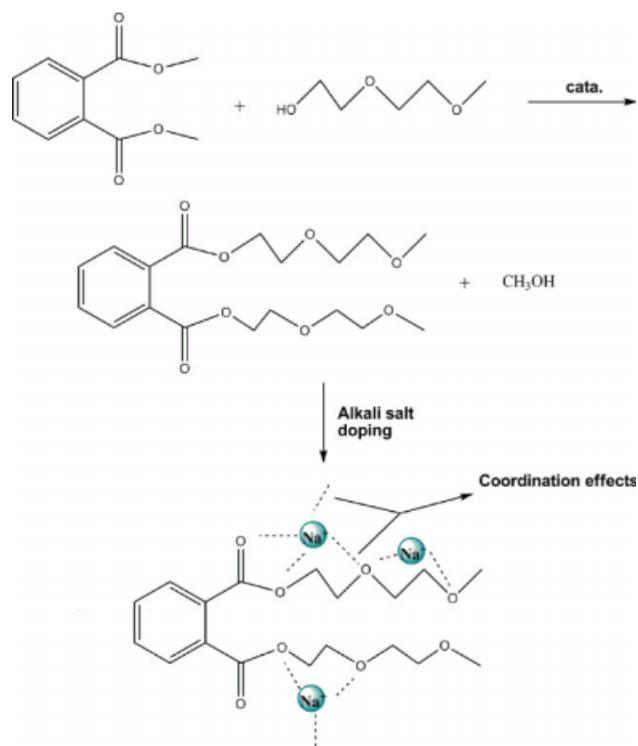
Scheme 1 Synthesis route of BMEP and preparation of AP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Tetrabutyl titanate was added as the catalyst when the temperature reached 100°C. The ester-exchange reaction was maintained for a given time at 190–195°C under the protection of nitrogen. The resulting mixture was distilled under reduced pressure, and BMEP was obtained under a pressure of 6.65 kPa at 240°C.

Preparation of AP

NaSCN was dried under a pressure of 7.98 kPa at room temperature for 4 h. Then, a set content of the dried NaSCN and BMEP were mixed under vigorous stirring for 1 h. The resulting mixture was filtered, and the filtrate was used as the end plasticizer (AP). The synthesis route of BMEP and the preparation of AP are shown in Scheme 1.

Preparation of the antistatic soft PVC composites

The PVC powder, NBR, synthesized AP, and compound stabilizer were mixed in a high-speed mixer (Yongtong SDF-400, Chengdu, China) at room temperature for 5 min; the mixing speed was 1500 rpm. The resulting mixture was dried at 60°C until AP penetrated the PVC matrix sufficiently. Then, the antistatic PVC composites were prepared in a Haake torque rheometer (Thermo Fisher Scientific, Walldorf, Germany) equipped with an electrically heated mixing head and two noninterchangeable rotors.
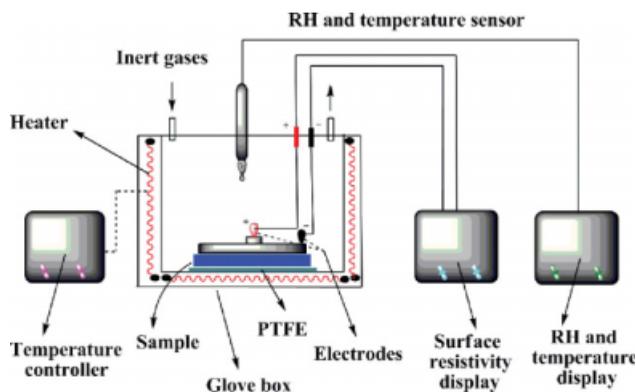
Scheme 2 Scheme of the instrument for the surface resistivity test (PTFE = polytetrafluoroethylene). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The processing temperature, rotor speed, and blending time were set at 160°C, 30 rpm, and 8 min, respectively.

Characterization

Fourier transform infrared (FTIR) analysis

DMP, BMEP, and synthesized AP were characterized with a Nicolet 560 FTIR spectrometer (Thermo Nicolet Corporation, USA) with a resolution setting of 4 cm^{-1}. The scanning range was altered from 400 to 4000 cm^{-1}.

Surface resistivity measurement

The 1-mm-thick sheets of the antistatic PVC composites were prepared by compression molding at 180°C and were then used for the conductivity measurements. A surface resistivity meter (ZC46A, Shanghai, China) was used to measure the surface resistivity of the antistatic PVC composites. The environments of different RHs and temperatures for the surface resistivity tests were obtained with a special glovebox that could be infused with high-purity nitrogen. The scheme of the instrument is shown in Scheme 2. Every environment with different RH and temperature values was stabilized for more than 2 h before testing. The RH was detected by a thermohygrometer (TRH-AZ, provided by Shinyei Co., Ltd., Tokyo, Japan).

Tensile and hardness testing

The sheets prepared for the surface resistivity measurement were also used for the tensile tests with an Instron 4302 (Instron Corporation, USA) at a tensile rate of 100 mm/min, and dumbbell samples with dimensions of 25 × 6 × 1 mm^3 were prepared for the tensile tests. The hardness of the composites was determined with a Shore hardness tester (LXA-D, Shanghai, China).

RESULTS AND DISCUSSION

FTIR results

The FTIR spectra of DGME, BMP, and BMEP are shown in Figure 1. Figure 1(a) shows the typical DGME spectra with a strong absorption band near 3430 cm^{-1}, which was the characteristic absorption band of the —OH asymmetric stretching of DGME end groups. In Figure 1(a), the vibration of —CH$_2$— around 2880 and 1358 cm^{-1} and the characteristic absorption of —C—O—C— around 1110 cm^{-1} were also observed. Figure 1(b) shows the FTIR spectra for DMP. The absorption peaks around 1729 and 1126 cm^{-1} belonged to the stretching vibration of the —C=O and —C—O—C— groups, respectively. In comparison with Figure 1(b), in addition to the stretching vibration of the —C=O and benzene ring, the characteristic absorptions of —CH$_2$— around 2881 and 1355 cm^{-1}, originating from DGME, are also shown in Figure 1(c). Furthermore, in contrast to Figure 1(b), the absorption peak of —C—O—C— around 1116 cm^{-1} broadened and strengthened in Figure 1(c), which was possibly because that of BMEP contained two —C—O—C— bonds derived from the ester group and ether oxygen group. However, the characteristic absorption band of the —OH asymmetric stretching of DGME end groups vanished. From the previous analysis, we were ensured that BMEP was successfully synthesized by the ester-exchange reaction between DGME and DMP.

Surface resistivity analysis

The effect of AP content on the surface resistivity of the PVC composites is shown in Figure 2. As shown in Figure 2, the surface resistivity of the PVC composites decreased with AP content. However, for the PVC composites containing 0 phr DBP, the surface resistivity did not change obviously when the AP
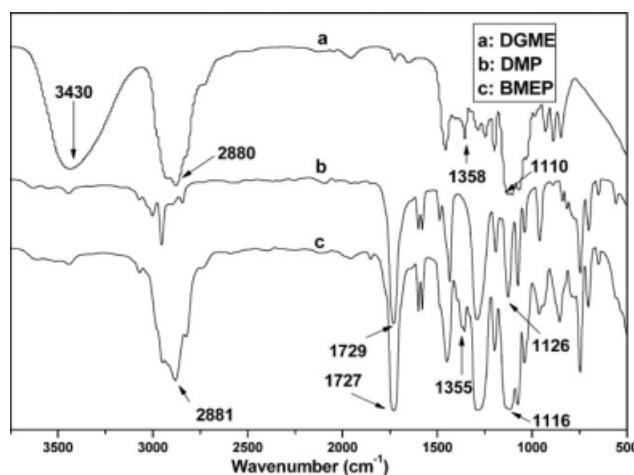
Figure 1 FTIR spectra of DGME, DMP, and BMEP.
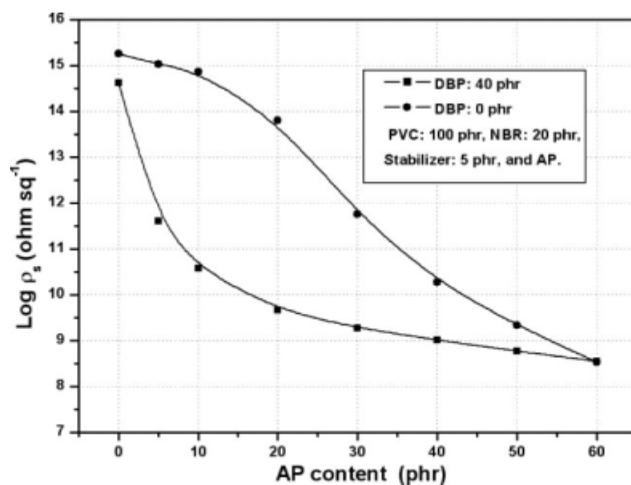
Figure 2 Effect of the AP content on the surface resistivity (ρ_s) of the PVC composites.

Figure 3 Influence of RH on the surface resistivity (ρ_s) of the prepared PVC composites.

content was less than 20 phr. With further increases in the AP content, the surface resistivity decreased sharply. Also, it was reduced by three orders of magnitude when the AP content ranged from 20 to 40 phr. It seemed that the AP content point at 20 phr was the threshold value (critical point) for ion-conductive tunnels. When the AP content was less than 20 phr, the PVC composites were rigid. Thus, the molecular chain moved with difficulty, which also resulted in the difficult transfer of the carriers. Moreover, most of the AP molecules participated in the plasticization of the PVC molecular chains when the AP content was less than 20 phr. Therefore, the mobility of AP deteriorated. Consequently, the number of effective charge carriers reduced. The fact that the curve of PVC composites containing 40 phr DBP was below that of PVC composites containing 0 phr DBP also supported that discussion. As the AP content reached 60 phr, the surface resistivity of the PVC composites decreased to 10^8 Ω/sq.

Figures 3 and 4 show the influence of RH and temperature on the surface resistivity of the prepared PVC composites, respectively. As shown in Figure 3, the surface resistivity ranged within one order of magnitude with decreasing RH; this indicated that the antistatic ability of those PVC composites had slight sensitivity to RH. Figure 4 demonstrates the dependence of the surface resistivity of the PVC composites on the temperature under an RH of 12%. The surface resistivity decreased from 10^8 to 10^7 Ω/sq as the temperature increased from 40 to 80°C; this showed a good Arrhenius relationship between the surface resistivity and the temperature. The decline in the surface resistivity with increasing temperature indicated typical features of an ion-conductive polymer.

Both of the phenomena, that the surface resistivity was slightly sensitive to the RH and that it apparently
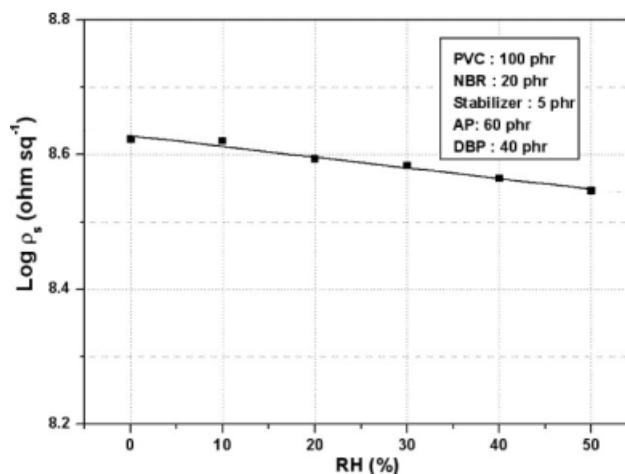
decreased with increasing temperature, could be explained by a conventional electrolyte-based ionic conduction mechanism. A sketch of the corresponding ionic conduction mechanism is shown in Scheme 3. As shown in Scheme 2, traditional antistatic agents were apt to migrate to the polymeric surface after processing and could form a conductive water film through the absorption of water in the air. However, the electrolyte-based AP developed in this study could form conductive networks or tunnels both in the polymer matrix and on the surface of the PVC composites. The PVC composites including a PVC matrix and NaSCN-doped BMEP could also be regarded as a gel polymer electrolyte based on PVC. The electrical charges both on the polymeric surface and in the bulk of the matrix were able to leak through the conductive networks or tunnels formed by the BMEP-based electrolyte in the PVC matrix, in which the alkali salt cations could easily migrate.
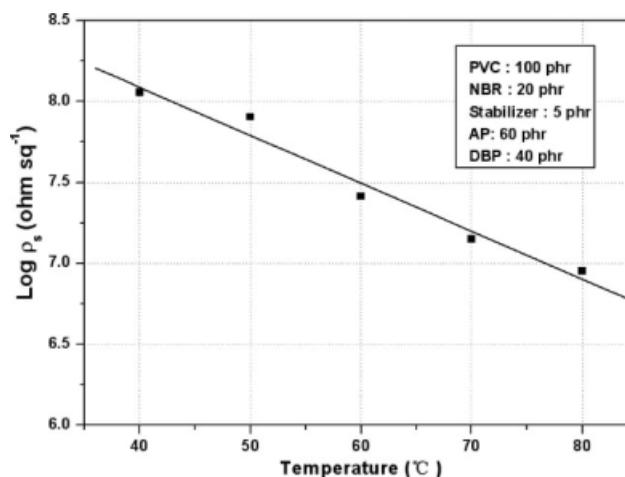
Figure 4 Influence of temperature on the surface resistivity (ρ_s) of the prepared PVC composites.
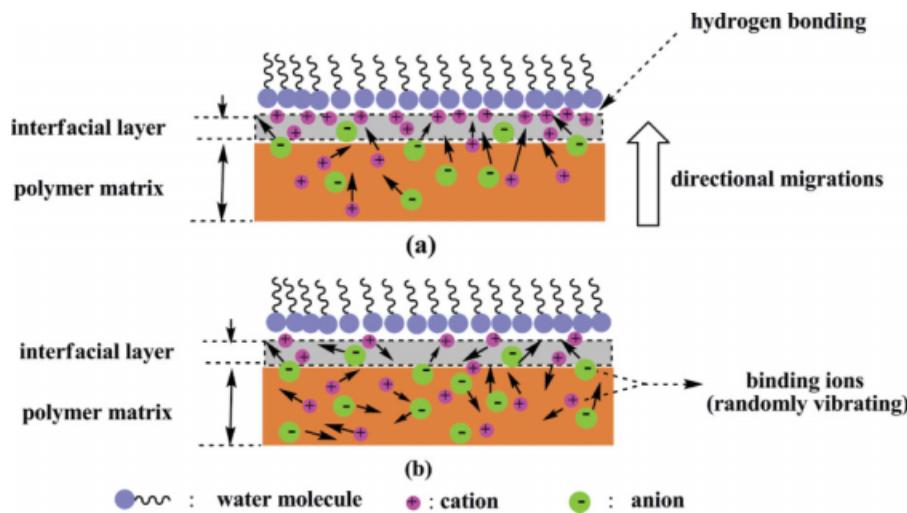
Scheme 3 Schematic antistatic mechanism of (a) the traditional antistatic agents and (b) the electrolyte-based ionic conductor. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Therefore, despite the water molecules on the surface of the composites reduced with decreasing RH, the coordination effects between the ether oxygen groups of AP and Na^+ cations were sufficient to compensate for the loss of the surface water molecules to maintain the PVC composites with a relatively high ion conductivity, even at low RH. In addition, when the temperature increased, the ions possessed more energy to easily break through the energy barrier of dissociation of the coordination effect between the ether oxygen groups and sodium cations. Meanwhile, increasing temperature enhanced the mobility of molecular chains, which was also favorable to ion migration.

Mechanical properties

Figures 5 and 6 demonstrate the effect of the AP content on the tensile strength and elongation at break of the PVC composites, respectively. In the case of the PVC composites containing 0 phr DBP, the tensile strength of the composites steeply decreased from around 35 to 12 MPa when the AP content increased from 0 to 60 phr, whereas the elongation at break sharply increased from about 110 to 250% with AP contents ranging from 0 to 10 phr. However, a further increment in the AP content slowly increased the elongation at break at the point. In the case of the PVC composites containing 60 phr DBP, the tensile strength of the composites gradually decreased from around 15 to 8 MPa when the AP content increased from 0 to 60 phr, whereas the elongation at break increased from about 280 to 418% with AP contents ranging form 0 to 60 phr. Compared with the values in Figures 5 and 6, the tensile strength and elongation at break of the PVC/DBP/AP (100/0/60) composites reached 12.1 MPa
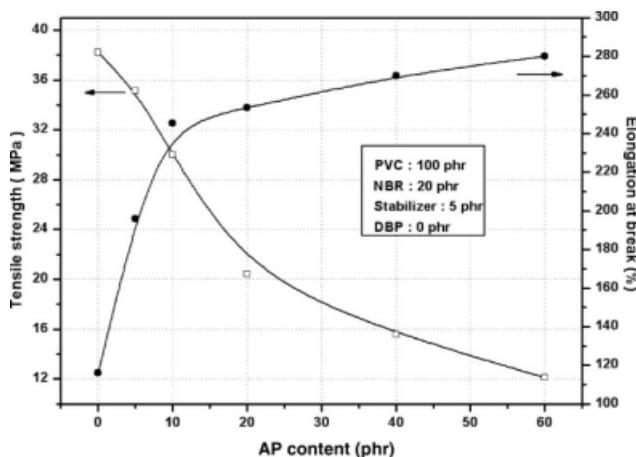
Figure 5 Effect of the AP content on the tensile strength and elongation at break of the PVC composites containing 0 phr DBP.
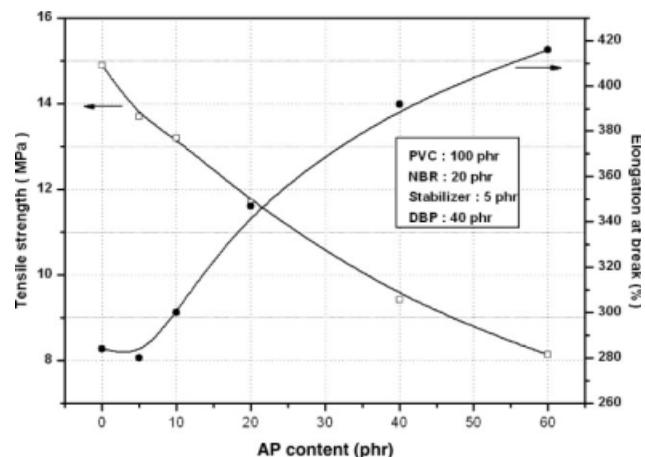
Figure 6 Effect of the AP content on the tensile strength and elongation at break of the PVC composites containing 40 phr DBP.
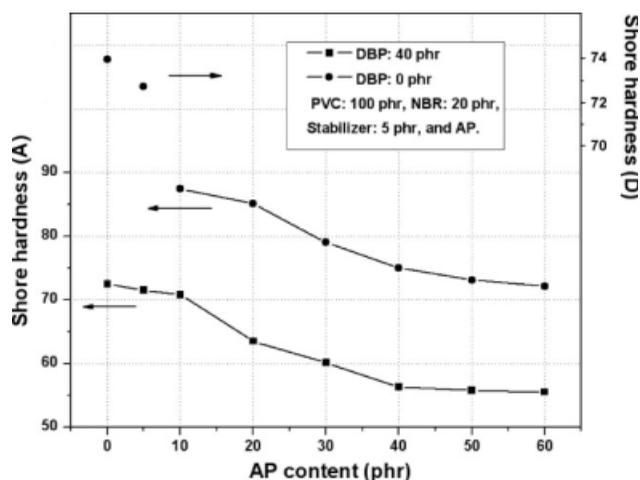
Figure 7 Effect of the AP content on the hardness of the PVC composites.

and 280%, respectively, whereas those of the PVC/DBP/AP (100/40/20) composites received 11.7 MPa and 347%, respectively. The tensile strength and elongation at break of the of the PVC composites containing 40 phr DBP and 60 phr AP reached 8.12 MPa and 416%, respectively. These behaviors indicated that the plasticizing efficiency of DBP was better than that of AP, which was partially attributed to the low molecular weight of DBP. At the same plasticizer content, there were more DBP molecules than BMEP or AP molecules to plasticize the PVC molecular chains. Moreover, the coordination effects between the ether oxygen groups and Na^+ cations in AP also partially weakened the interactions between AP and the PVC molecular chains.[15] Furthermore, as shown in Figure 2, the surface resistivity of the PVC/DBP/AP (100/40/20) composites was still able to reach 10^9 Ω/sq orders of magnitude; this showed good comprehensive properties of the composites. We could, hence, design proper proportions of DBP to AP to satisfy different requirements in various application fields.

The influence of the AP content on the hardness of the prepared PVC composites is shown in Figure 7. The hardness of the prepared composites without DBP and with 40 phr DBP continuously decreased with AP content, and the hardness of the composites without DBP was always higher than that of the composites with 40 phr DBP in the whole AP content range. In the case of the composites without DBP, the hardness decreased from 74 D to 87 A with the AP contents from 0 to 10 phr. However, further increasing the AP content from 10 to 60 phr slightly decreased the hardness from 87 to 72 A; this implied that the composites gradually turned from hard materials into semihard

materials as the AP content rose over 10 phr. Compared with AP, DBP was obviously more efficient in decreasing the hardness of the PVC composites. For the composites containing 40 phr DBP, the hardness slightly decreased from 72 to 53 A when the AP content ranged from 0 to 60 phr; this showed that there was a competitive relationship between the plasticizing effects and the dissolution of alkali salts (coordination effects) in such systems (PVC/DBP/AP composites) including AP molecules. For the PVC composites without DBP, the plasticizing effect of AP dominated in the low AP content range. Therefore, we observed that both the tensile properties and hardness of the composites changed remarkably with AP content in the previous relevant experiments (shown in Figs. 5 and 7), and the surface resistivity of the corresponding composites hardly varied with AP content (Fig. 2), especially in the lower AP content range. In the case of the composites with 40 phr DBP, DBP significantly decreased the entanglements of the PVC molecular chains, and hence, the AP molecules were also able to effectively donate to the ionic conduction by coordination with Na cations; this indicated the domination of coordination effects here. The previously discussed results are in good agreement with the variety trends of the composites in the surface resistivity, tensile strength, and elongation at break analysis and imply that the PVC/DBP/AP composites with suitable DBP/AP ratios had better comprehensive properties than the composites without DBP. Namely, the AP molecules could not sufficiently contribute to the ionic conduction in the composites without DBP, and the addition of DBP was helpful for enhancing both the flexibility of the PVC molecular chains and the mobility of free cations and, hence, improved the conductivity of the composites.

CONCLUSIONS

BMEP was successfully synthesized through an ester-exchange reaction between DMP and DGME. AP was then prepared by BMEP doped with NaSCN. The AP molecules were able to act as the plasticizer for PVC and endow the PVC composites with antistatic abilities. When the AP content was 60 phr, the corresponding elongation at break of the composites was 280%, whereas the surface resistivity of the composites reached 10^8 Ω/sq at an RH of 0.1%; this demonstrated its low sensitivity to the RH. The addition of DBP was favorable to effectively enhance the elongation at break and decrease the surface resistivity of the PVC composites. PVC composites with excellent antistatic properties and reasonable mechanical properties

could be obtained by the regulation of the content of AP and DBP.

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