Low Environmental Sensitive Antistatic Material Based on Poly(vinyl chloride)/Quaternary Ammonium Salt by Blending with Poly(ethylene oxide)

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ABSTRACT: A quaternary ammonium salt (QAS) was synthesized and characterized by ^{1}H NMR. A low environmental sensitive antistatic plasticized poly(vinyl chloride) (PPVC) was prepared by blending with QAS and poly(ethylene oxide) (PEO). The structure and properties of PPVC/QAS/PEO blend were studied by scanning electronic microscope (SEM), surface resistivity, and mechanical properties tests. The results show that the surface resistivity of PPVC/QAS/PEO (100/4.5/0) blend without PEO component can be reduced to less than 3.0×10^{8} Ω at 65% environmental humidity, which satisfied the antistatic property requirement related to MT113-1995 of China. However, QAS, similar to other commercial antistatic agents, is much sensitive to environmental humidity. When a small amount of PEO is added, the surface resistivity of PPVC/QAS/PEO blend has a quite low sensitivity to environmental humidity and further reduces. An excellent antistatic property of PPVC/QAS/PEO blend under low humidity can be achieved. Its tensile strength and elongation at break are also improved with PEO addition. J Appl Polym Sci 109: 3887–3891, 2008

Key words: quaternary ammonium salt; plasticized poly (vinyl chloride); surface resistivity; antistatic; poly(ethylene oxide)

INTRODUCTION

Because of its low cost and ease of process, plasticized poly(vinyl chloride) (PPVC) is widely used as thermoplastic elastomer in many fields as a substitution for traditional rubber materials. However, PPVC have high surface resistivity in the range of 10^{14}–10^{17} Ω. The static charge on its surface easily forms and accumulates by contacting or rubbing with other materials during storage, transport, and usage stages, which may lead to semiconductor devices damage or gas explosion in coal mine,[1] etc. To overcome these problems, antistatic agent is often incorporated into the PPVC. One kind of the classical antistatic agents is amphiphilic molecule with a hydrophobic tail, which entraps into the polymer matrix, and a hydrophilic head, which migrates to the surface and absorbs a conductive layer of water. This absorbed water benefits to leak the static charge formed on the PPVC surface.[2–5] Such antistatic agents are easy to prepare and purchase, but their antistatic property depends on moisture strongly and they have no enough antistatic effect under the low environmental humidity. How to reduce the environmental humidity sensitivity of the traditional antistatic agents is very important for their application under all environmental conditions. It is regrettable that no concerned literature has been found.

In this study, poly(ethylene oxide) (PEO) were introduced into PPVC together with the synthesized quaternary ammonium (QAS). The PPVC/QAS/PEO blends with low environmental sensitivity of the antistatic property were prepared. The structure and properties of PPVC/QAS/PEO blends were studied by scanning electronic microscope (SEM), surface resistivity, and mechanical property tests.

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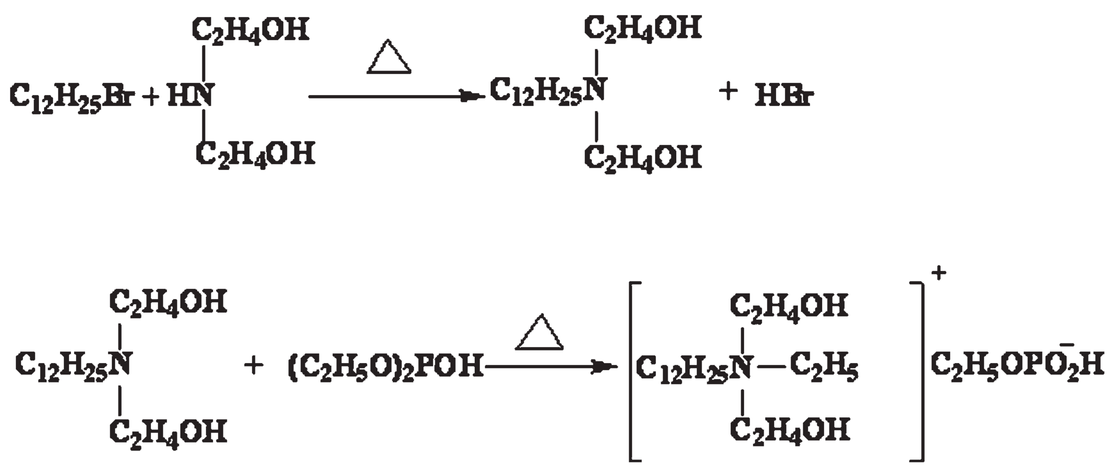
EXPERIMENTAL

Materials

PVC (SG-2) used in this work as a matrix material were manufactured by Sichuan Province Jinlu Resin, Sichuan, China.

PEO (average number molecular weight: 1×10^{5}) was supplied by Shanghai Jichen, Shanghai, China. DOP was supplied by SINOPEC Qilu Co., Sandong, China. Stabilizer was supplied by Chongqing Assistant Factory, Chongqing, China. 1-Bromododecane was purchased from Shanghai Reagent, Shanghai, China. Diethyl phosphite was purchased from Fine Chemical Lab of Nankai University (Tianjing, China). Diethanol amine was purchased from Chengdu Kelong Reagent, Chengdu, China. All the



Scheme 1 Synthesis of quaternary ammonium salt (QAS).

polymers and chemicals were used as received without further purification.

Synthesis of quaternary ammonium salt

1-Bromododecane, diethanol amine, and solvent were added into a three-necked flask equipped with a stir bar and a thermometer. The reaction mixture was stirred at reflux temperature for a certain time before it was cooled to room temperature. Following completion of the reaction, diethyl phosphite was introduced into the flask and then heated to reflux temperature again. A few minutes later, the reaction was completed and the reaction mixture was cooled to room temperature. The proposed reactions are described in Scheme 1.

Preparation of PPVC/QAS/PEO blend

PVC powder, DOP, and stabilizer with set contents were mixed in a high-speed stirrer until all DOP was absorbed into PVC powder, by which the PPVC powder was prepared.

The PPVC powder, QAS synthesized as earlier, and PEO with set contents were mixed by a twin-roll miller (SK-160R, Shanghai Rubber Machinery, China) at 145°C ± 5°C for 10 min. The weight proportion of each raw material component is showed in Table I. Then the PPVC/QAS/PEO blend sheets about 1 mm in thickness and 20 mm in both width and length were prepared by compression molding machine (HP63, Shanghai Zimmerli Weili Rubber and Plastic Machinery, Shanghai, China) at 160°C.

TABLE I
The Weight Proportion of Each Component in PPVC/QAS/PEO Blends

PVC	PEO	QAS	DOP	Stabilizer
100	0, 5, or 10	4.5	55	4

Measurement and characterization

^{1}H NMR spectra were recorded on a INOVA-40 spectrometer (Varian Inc., Palo Alto, CA) operated in $CDCl_3$ with tetramethylsilane.

Surface resistivity was measured at room temperature using a ZC-90 insulation measurement instrument (Shanghai Yuanzhong Electronic Meter Plant, Shanghai, China) at 250 V. They were performed according to the China Industry standard MT113-1995. Before testing, the specimens were dried under vacuum at 40°C for 24 h and then conditioned at 65% relative humidity (RH) or 50% RH at 23°C ± 2°C for 2 h. The same conditions were maintained during the measurements.

SEM investigation

The cross section of PPVC/QAS/PEO blends were sputtered with a silver film and then examined by SEM using a JEOLJSM-5900LV microscope made in Jeol Ltd., Tokyo, Japan, at 20 KV accelerating voltage.

Tensile strength and elongation at break measurement

PPVC/QAS/PEO blends and pristine PPVC (PPVC/QAS/PEO = 100/4.5/0) blend were tested by universal tensile testing machine using Instron 4320 (Instron Co., Norwood, MA) at a crosshead speed of 100 mm/min.

RESULTS AND DISCUSSION

^{1}H NMR spectra

Figure 1 shows the ^{1}H NMR spectra of the synthesized QAS antistatic agent. The signals of the ethyl

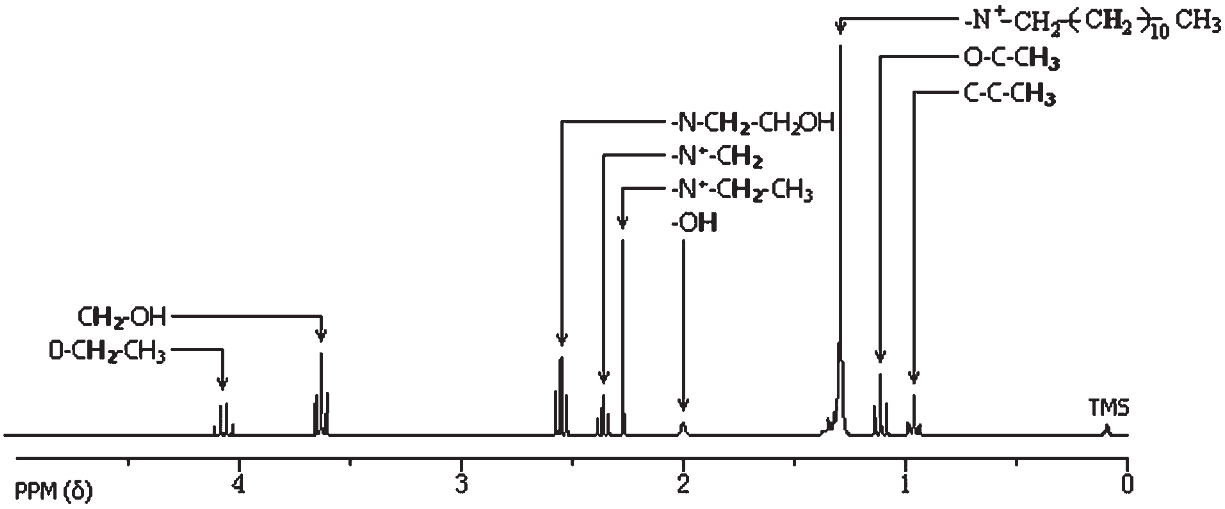


Figure 1 ^{1}H NMR of quaternary ammonium salt (QAS).

protons in diethyl phosphite molecule at about 3.57 ppm (m, 2H, O—$\mathbf{CH_2}$—CH_3) has not been detected. However, two new peaks which cannot occur in all reactants at 4.07 ppm (m, 2H, O—$\mathbf{CH_2}$—CH_3) and 2.27 ppm (s, 2H, N^+—$\mathbf{CH_2}$—CH_3) is shown in Figure 1. This confirms that the chemical reaction between diethyl phosphite and docecyldiethanolamine has taken place, and the designed QAS has successfully been synthesized.

Surface resistivity

Figure 2 indicates that with the increase of PEO content, the surface resistivity of PPVC/QAS/PEO blend decreases. The surface resistivity of PPVC/QAS/PEO blends with the weight proportion of 100/4.5/5 and 100/4.5/10 decrease to 1.5×10^8 Ω and 1.2×10^8 Ω, whereas that of PPVC/QAS/PEO blend with the weight proportion of 100/4.5/0 is 1.9×10^8 Ω. This result suggests that PEO added in PPVC/QAS enhances the antistatic ability. This is probably because of the unique hydrophilic effect of the PEO, which is well recognized as an excellent water-soluble polymer. PEO dispersed in PPVC matrix can also absorb moisture from air to improve conductivity. Therefore, it is a benefit to electrostatic discharge. Figure 2 also shows that as the storage time increases, the surface resistivity of PPVC/QAS/PEO blend decreases and finally tends toward an equilibrium value. It is because of the fact that QAS antistatic agent migrates from PPVC matrix to its surface to generate a conductive layer during storage, and the surface resistivity of PPVC/QAS/PEO blend gradually reduces to a minimum as the QAS conductive surface layer completely forms.

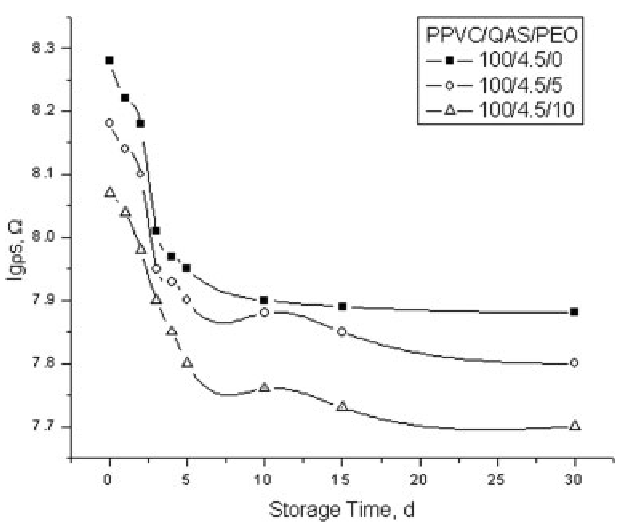


Figure 2 Surface resistivity of PPVC/QAS/PEO (100/4.5/×) blend with different PEO content versus storage time under 65% humidity.

Effect of environmental humidity on surface resistivity

From Table II we can see that at a high humidity condition like 65% RH, the surface resistivity of PPVC/QAS/PEO (100/4.5/0) blend could reach 1.9×10^8 Ω, which satisfied the antistatic technical request related to MT113-1995 standard of China.

TABLE II
Effect of PEO Content on Surface Resistivity of PPVC/QAS/PEO Blends (100/4.5/×) at 50 or 60% Humidity, Respectively

PPVC/QAS/PEO	100/4.5/0	100/4.5/5	100/4.5/10
Surface resistivity (Ω) at 65% RH	1.9×10^8 Ω	1.5×10^8 Ω	1.0×10^8 Ω
Surface resistivity (Ω) at 50% RH	5.0×10^8 Ω	2.0×10^8 Ω	1.2×10^8 Ω

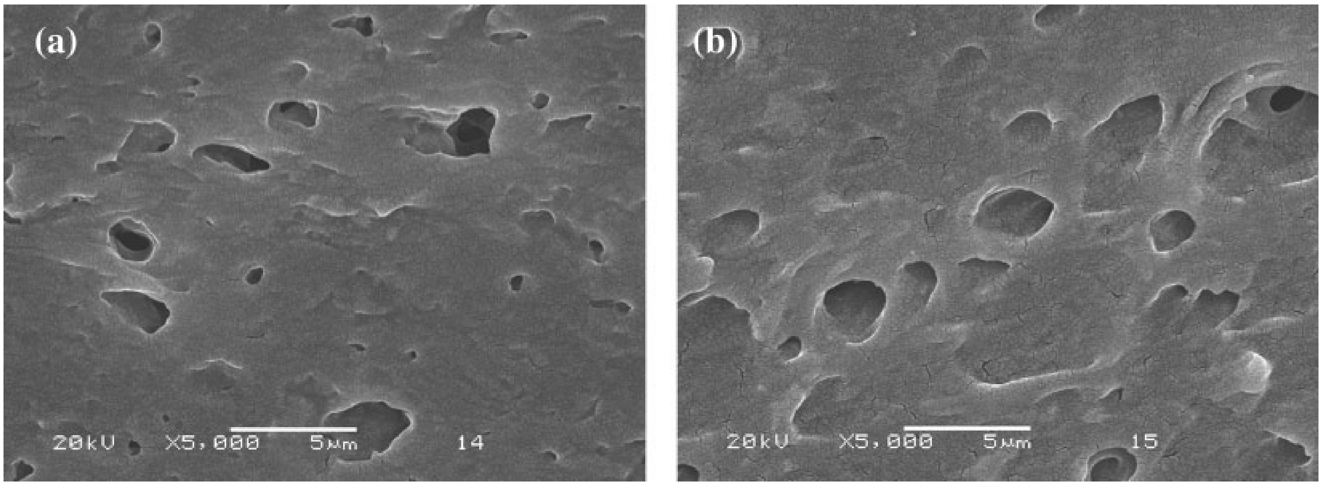


Figure 3 SEM of PPVC/QAS/PEO blends with different PEO content (×5000): (a) 100/4.5/5 and (b) 100/4.5/10.

The MT113-1995 standard of China require the surface resistivity of polymer materials to be less than 3.0×10^8 Ω. But at a lower humidity condition like 50% RH, the surface resistivity of pristine PPVC (PPVC/QAS/PEO = 100/4.5/0) blend increases to 5.0×10^8 Ω, which unsatisfied the antistatic property requirement related to MT113-1995. This is due to the fact that insufficient moisture can be absorbed onto the surface of the blend to form a conductive water layer under low humidity condition. However, as a small content of PEO is introduced, the surface resistivity of the PPVC/QAS/PEO blend with the weight proportion of 100/4.5/5 and 100/4.5/10 reduces to 2.0×10^8 Ω and 1.0×10^8 Ω at 50% RH. PEO particles dispersed in PPVC matrix absorb moisture from the air at high environmental humidity to form some water sources similar to some pools, and slowly release the H_2O molecules as the environmental humidity decreases, which guarantees QAS migrated onto the surface of PPVC/QAS/PEO blend can absorb enough moisture to form a conductive water layer even at low environmental humidity. Therefore, the humidity sensitivity of the ionic antistatic agent of QAS can be restrained by the addition of PEO.

Morphology

Figure 3 shows that PEO in PPVC/QAS/PEO (100/4.5/×) blend forms a similarly spherical structure and homogeneously disperse in matrix. The spaces between the dispersed PEO particles in PPVC matrix for PPVC/QAS/PEO (100/4.5/10) blend [Fig. 3(b)] become narrower as compared with that of PPVC/QAS/PEO (100/4.5/5) blend [Fig. 3(a)]. Some parts of PEO particles assemble together as PEO content in PPVC/QAS/PEO blend increase to 100/4.5/10, which is shown in Figure 3(b). Therefore the ability of moisture absorption become stronger, which corresponds to the surface resistivity data tested as earlier.

Mechanical properties

The data listed in Table III show that the pristine PPVC (PPVC/QAS/PEO = 100/4.5/0) blend have 8.2 MPa of tensile strength and 140.0% of elongation at break. The tensile strength and the elongation at break of PPVC/QAS/PEO blend increase with PEO content. As PEO content in PPVC/QAS/PEO blend increases to 100/4.5/10, its tensile strength and elongation at break increase to 11.3 MPa and 249.1%, 1.3 times and 1.7 times, respectively, as compared with those of PPVC/QAS/PEO (100/4.5/0) blend.

CONCLUSIONS

The synthesized QAS can effectively promote the antistatic performance of PPVC. When a small amount (less than 4.5% by weight) of such synthesized antistatic agent is introduced, the surface resistivity of PPVC can be reduced below 3.0×10^8 Ω, which satisfied the antistatic property requirement related to MT113-1995 of China. However, similar to other commercial antistatic agents, this synthesized antistatic agent is much sensitive to environmental humidity. When a small amount of PEO is added,

TABLE III
Effect of PEO Content on Mechanical Properties of PPVC/QAS/PEO (100/4.5/×) Blends

PPVC/QAS/PEO	100/4.5/0	100/4.5/5	100/4.5/10
Tensile strength (MPa)	8.2	8.3	11.3
Elongation at break (%)	140.0	157.7	249.1

the surface resistivity of PPVC/QAS/PEO blend has a quite low sensitivity to environmental humidity and further reduces. An excellent antistatic property of PPVC/QAS/PEO blend under low humidity can be achieved. The mechanical properties (tensile strength and elongation at break) of the PPVC can also be improved by the addition of PEO.

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