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Application of TRIZ to Develop New Antistatic Materials

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In this paper, the existing methods to increase the electrical conductivity of the materials were analyzed. Then the technical conflict solution derived from TRIZ was used to realize the innovation of the antistatic agent. According to the invention principles, DEP with high boiling point, low volatility, good compatibility with PVC and a good solubility of alkali metal salts has been designed and successfully synthesized. Then an antistatic agent with high electrical conductivity was obtained by doping alkali metal perchlorates to DEP. After using DEP/$NaClO_4$ as a new plasticizer, the PVC/DEMP/$NaClO_4$ composite was obtained. Whose surface resistivity was decreased sharply with the increase of the DEP/$NaClO_4$ content. The surface resistivity can drop to $10^{7.6}$ Ωsq^{-1} (25 ºC, 0.1 % RH) when the DEP/$NaClO_4$ content was 60 phr.

Key Words: TRIZ, Anti-static, DEP, $NaClO_4$, PVC.

INTRODUCTION

In recent years, antistatic materials have been developed to be an important part in polymer field. Currently, antistatic materials could show more properties such as high dielectric constant, high electrical conductivity and low surface resistivity by adding external antistatic agents to PVC[1-3]. The existing antistatic agents can form conductive water film *via* adsorption of environmental water to realize antistatic purpose[4-6]. However, their antistatic abilities are strongly influenced by the relative humidity (RH)[7]. In the case of dry environment (low humidity), the surface resistivity will rise to one or several orders of magnitude, which has seriously affected the antistatic ability of the polymer materials[1,8]. The electrostatic accumulation will also cause explosion or fire[9], so we should take strict precautions against economic loss or casualties caused by accumulation of the electrostatic charges. Therefore, developing an environmentally non-sensitive antistatic agent will have great significance.

When problems in material or engineering appear, engineers and material designers always have access to company employees, company files and open literatures. These resources provide helpful leads to specific problems, as well as information about related products. However, these processes only depend on the experiences of process engineers and take too much time and cost as well, systematic solutions can not be obtained. Therefore, new methods should be studied to overcome these limitations. In this paper, we proposed an alternative approach based on TRIZ method. TRIZ is a problem solving method based on logic and data, not intuition. Based on analysis over ten thousands of patents, TRIZ was created by Genrich Altshuller in the former USSR in 1946, which has been developed from then on. Nowadays, TRIZ has being developed and practiced throughout the world[10]. TRIZ consists of patterns of problems-solutions, patterns of technical evolution and methods of using scientific effects. The core of TRIZ is to use originally 39 parameters and 40 inventive principles for solving contradictions without compromising on conflicting features of technical system. General TRIZ patterns to the specific situation are shown in Fig. 1. The solid arrows represent analysis of the problems and the striped arrow represents the analogy thought for developing the specific solution.

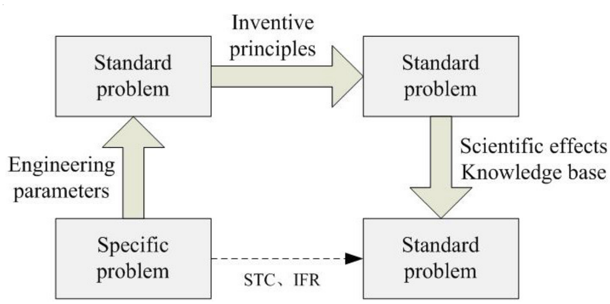

Fig. 1. General principle of the application of TRIZ

In recent researches, TRIZ has been applied to the fields of chemical engineering and materials. Grierson *et al.*[11]

analyzed the symmetry and asymmetry of 40 inventive principles for use in the chemical field. Srinivasan and Kraslwaski[12] illustrated the application of the modified TRIZ to the design of inherently safer chemical processes. Kim *et al.*[13] developed a modified method of TRIZ to improve safety in chemical process design.

In this paper, the existing problems were analyzed by TRIZ first. Then we derived the invention principles according to the conflict matrix. Finally, according to the invention principles, we designed and synthesized a new compound DEP, after doping alkali metal salts, high electrical conductivity can be obtained. As a new type of plasticizer, it was mixed it with PVC in order to prepare new antistatic materials.

TRIZ-based design of new anti-static PVC materials

Technical contradiction solution system: The main goal is to increase reliability of PVC and prevent the explosion. The existing antistatic agents can form conductive water film *via* adsorption of environmental water to realize antistatic purpose. Their antistatic abilities are strongly influenced by relative humidity. In case of dry environment (low humidity), the surface resistivity will rise one or several orders of magnitude, it has seriously affected the anti-static ability of the polymer materials.

Therefore, the existing technical contradiction is: Characteristics to be improved: Antistatic abilities under the dry conditions. Improve the reliability of the material.

Characteristics that are getting worse: Harmful factors acting on PVC. In the low humidity condition (dry environment), the surface resistivity will rise one or several orders of magnitude.

According to the characteristics to be improved: Reliability and the corresponding characteristics that are getting worse: Harmful factors acting on an object from outside, we found out the appropriate lines and columns in the matrix: No. 2 extraction, No. 27 dispose, No. 35 transformation of properties, No. 40 composite materials.

Selection of the innovative solution: Extraction means extracting the disturbing part or property from an object. Dispose means replacing an expensive object with a cheap one and compromising other properties. Transformation of properties means changing the physical or chemical state of the system. Composite materials means replacing homogeneous materials with composite ones. After analyzing the suggested principles, we have chosen No. 30: 'Composite materials' as the best suggestion.

The most commonly used plasticizers for PVC, such as DOP, DBP, dimethyl phthalate, have a series of characteristics: good compatibility, high melting point and low volatile[14,15]. Electrolyte plasticizers, such as EC, PC, DME, DGDE, have high dielectric constant, strong ability of dissociating alkali metal salts, but low boiling point and high volatile are their disadvantages[16-18]. After combining the advantages of these two types of plasticizers, we obtained the optimal solution. In this work, we first designed and synthesized a new plasticizer DEP with both adjacent benzene side chain from dimethyl phthalate and polar ether oxygen bond from DGDE. It had not only advantages such as high boiling point, low volatility and good compatibility with PVC, but also had a strong ability to dissociate alkali metal salts. Then we doped alkali metal salts to improve its electrical conductivity. Finally, DEP/$NaClO_4$ was mixed with PVC in order to prepare antistatic composite material.

EXPERIMENTAL

Dimethyl phthalate (DMP) and diethylene glycol ether (DGDE) were supplied by Changzheng Chemical Co. (Chengdu, China). $LiClO_4$, $NaClO_4$, $KClO_4$ were provided by Xilong Chemical Co. (Shantou, China). PVC powder (average degree of polymerization 1000-1100) was provided by Qilu Petrochemical Co. Ltd. (Zibo, China). All the other chemicals used in this experiment were analytically pure.

Synthesis of DEP: DEP was synthesized using a ester-exchange reaction, as shown in Fig. 2. Briefly, calculated amounts of dimethyl phthalate and DGDE (2.2 : 1 molar ratio) were added to a three-necked flask equipped with thermometer and condenser and heating with constant stirring. Tetrabutyl titanate catalyst was added when the temperature reached 80 ºC. The mixture was allowed to react at 190-195 ºC for 6 h under nitrogen protection. Then it was distilled under vacuum, DEP was obtained under a pressure of 40 mm Hg at 240 ºC.

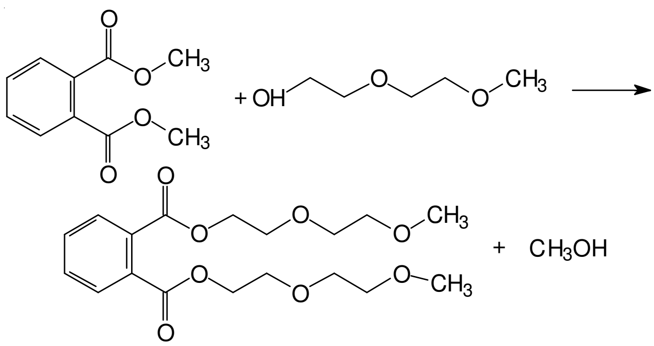

Fig. 2. Synthesis route of DEP

Alkali metal salt doping DEP: Alkali metal salt was first dried under a pressure of 60 mm Hg at room temperature for 4 h and then dried at 60 ºC under atmospheric pressure for 12 h. Subsequently, certain amounts of dried alkali metal salt and DEP were added to a three-necked flask. After stirring for 1 h, the mixture was dehydrated under a pressure of 10 mm Hg at 100 ºC for 10 min. The resulting compound liquid was the antistatic plasticizer.

Preparation of the antistatic PVC composite: The PVC powder, alkali metal salt doped DEP and compound stabilizer were mixed in a high-speed mixer and dried at 75 ºC for 2 h. Then, the antistatic PVC composite was prepared in a Haake torque rheometer (RC-90, Thermo Fisher Scientific, Walldorf, Germany). The processing temperature was 170 ºC and rotor speed was set at 30 rpm for 8 min. The 1-mm-thick sheets of the antistatic PVC composite samples were prepared by compression molding at 180 ºC.

Electrical conductivity and surface resistivity measurement: Volume electrical conductivity σ (S cm^{-1}) of the alkali metal salt doped DEP and antistatic PVC composite were calculated by the following formula (1):

$$\sigma = \frac{d}{R_v \cdot S} \quad (1)$$

In the formula, d (m) was the distance between the electrodes, S(m^2) was the electrode area, RV (Ω) was the surface resistivity, which was measured by a surface resistance meter (ZC-70 Shanghai, China). The relative humidity was detected by a thermo hygrometer (TH602).

RESULTS AND DISCUSSION

Effect of salt content and type on the electrical conductivity of the plasticizer: Different alkali metal perchlorates such as $NaClO_4$, $LiClO_4$ and $KClO_4$ were chosen to dope DEP. Fig. 3 shows the effect of salt content on the electrical conductivity for $LiClO_4$, $NaClO_4$ and $KClO_4$ doped DEP, respectively.

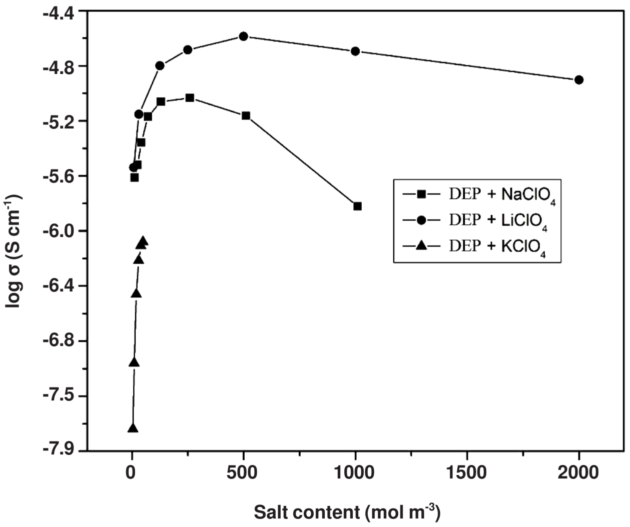

Fig. 3. Electrical conductivity of $NaClO_4$, $LiClO_4$, $KClO_4$ droped DEP with different salt content at 25 ºC

Fig. 3 showed that at the same salt concentration, electrical conductivity of the antistatic plasticizer decreases with $LiClO_4$, $NaClO_4$, $KClO_4$. Among them, electrical conductivity of DEP/$LiClO_4$ and DEP/$NaClO_4$ first increases and then decreases with increasing salt concentration. Their maximum conductivity reach $10^{-4.59}$ S cm^{-1} (500 mol/m^3) and $10^{-5.03}$ S cm^{-1} (290 mol/m^3), respectively. However, electrical conductivity of DEP/$KClO_4$ increases with the salt concentration increases. When the $KClO_4$ content reaches 50 mol/m^3, the electrical conductivity becomes $10^{-6.72}$ S cm^{-1}. Further increase of $KClO_4$ can not raise electrical conductivity for the salt solution was saturated. Among three samples, DEP/$LiClO_4$ has the highest electrical conductivity. $NaClO_4$ doped DEP has both relatively high conductivity and cheap price. So we used this new plasticizer $NaClO_4$/DEP to modify PVC.

Effect of plasticizer content on the surface resistivity of the PVC/DEP/$NaClO_4$ composite: PVC/DEP/$NaClO_4$ composites with different plasticizer contents were prepared (100 phr PVC/0-60 phr plasticizer/5 phr stabilizer). $NaClO_4$ concentration in DEP/$NaClO_4$ plasticizer was unified as 300 mol/m^3. Fig. 4 shows the surface resistivity of PVC/DEP/$NaClO_4$ composite with the plasticizer content changes at 25 ºC, 0.1 % relative humidity. As the plasticizer content increases, the surface resistivity of the composite decreases. The surface resistivity of the pure PVC without any plasticizer adding is higher than 10^{15} Ωsq^{-1}. With increasing in the plasticizer content, the surface resistivity decreases rapidly. The value reduces to about $10^{9.9}$ Ωsq^{-1} for 30 phr plasticizer content, which has a certain degree of antistatic capability. When the plasticizer content further increases to 60 phr, the resistivity value of the PVC composite decreases to $10^{7.6}$ Ωsq^{-1}. The results indicate that DEP/$NaClO_4$ plasticizer can reduce surface resistivity of the PVC materials effectively, for the purpose of antistatic.

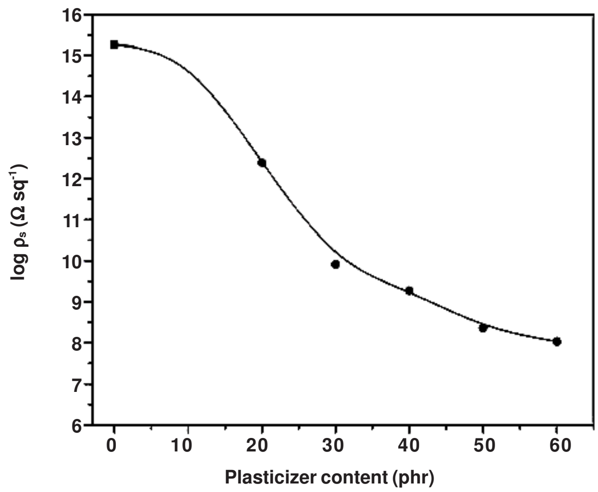

Fig. 4. Surface resistivity of PVC/DEP/$NaClO_4$ composite with different plasticizer content

Effect of relative humidity on the surface resistivity of the PVC/DEP/$NaClO_4$ composite: In order to investigate effect of relative humidity on the surface resistivity of the PVC/DEP/$NaClO_4$ composite. A sample with 30 phr plasticizer and 300 mol/m^3 $NaClO_4$. was determined at various relative humidity, as shown in Fig. 5. As the relative humidity increases (from 0.1 % to 60 %), surface resistivity of the PVC composite decreases from $10^{9.9}$ Ωsq^{-1} to $10^{9.5}$ Ωsq^{-1} slightly. Moreover, when the relative humidity exceeds 20 %, the surface resistivity

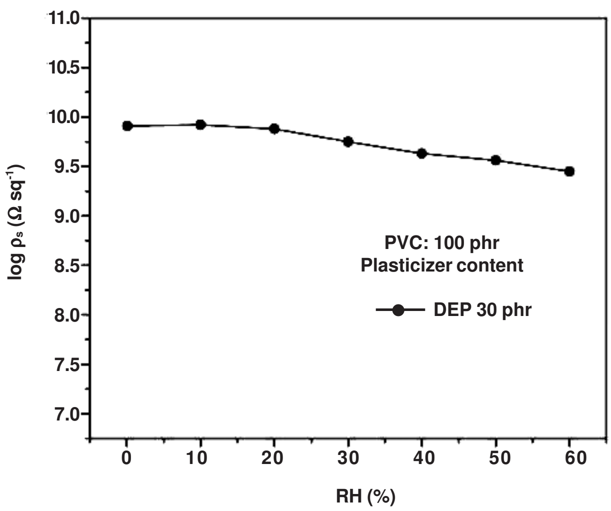

Fig. 5. Surface resistivity of PVC/DEP/$NaClO_4$ composite under different relative humidity

value decreases slowly with the increasing relative humidity. When the relative humidity is below 20 %, the surface resistivity does not change much with decreasing relative humidity. This indicates that the antistatic ability of those PVC composite is slightly sensitive to relative humidity, especially in dry conditon.

Conclusion

With the help of TRIZ, we have designed and successfully synthesized a new plasticizer DEP, after doping alkali metal salts, high electrical conductivity was obtained. $NaClO_4$ doped DEP as a new type of plasticizer was mixed with PVC to prepare a new antistatic material, The surface resistivity decreased sharply from 10^{15} Ωsq^{-1} to $10^{7.6}$ Ωsq^{-1} after adding 60 phr DEP/$NaClO_4$ to PVC. Also, the anti-static ability was slightly sensitive to the environment relative humidity.

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