

STUDY ON STABILITY OF STRUCTURE AND PROPERTIES OF TIOPC/SAN PHOTOCONDUCTIVE COMPOSITES

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Abstract The influence of the condensed structure of poly(styrene-*co*-acrylonitrile) (SAN) and traces of tetrahydrofuran (THF) that remained in titanyl phthalocyanine (TiOPc)/SAN films after fabrication on the photoconductive stability of TiOPc/SAN composites is studied. The results reveal that the existence of traces of THF results in the increase of the photoconductivity and the charging voltage. The main factors responsible for the unstable photoconductivity of the photoconductors are believed to be the relaxation of SAN and the slow volatilization of THF.

Keywords TiOPc, Stability, Solvent effect, Dynamic rheology, Organic photoconductive materials

INTRODUCTION

Owing to the importance of academic research and the widened commercial application of organic photoconductive devices^[1], the stability of the photoconductive properties of photoconductors has attracted considerable attention in recent years. It has been found that the presence of some impurities, like O₂^[2, 3], in photoconductive materials induces remarkable effects on photoconductive properties. Actually, the existence of impurities exerts some influences on the interaction between electron donors and acceptors^[4]. Moreover, studies of humidity influence on photoconductivity of titanyl phthalocyanine (TiOPc) dispersed in polymer matrix indicated that the existence of H₂O may result in increases of photosensitivity for charge generation materials, such as TiOPc^[5, 6]. More recently, it has been found by our group that the unstable photoconductive properties of titanyl phthalocyanine/poly(styrene-*co*-acrylonitrile) (TiOPc/SAN) prepared through coating are partly attributable to the residual tetrahydrofuran (THF) solvent in photoconductive films. In addition, the filled photoconductive materials of TiOPc/SAN had the character of nonequilibrium condensed state as multi-component polymer systems. The change of polymer morphology induced by the structural instability of the polymer matrix had a great effect on the properties of photoconductive materials. To our knowledge, few reports about the problems mentioned above have been found to date. This paper reports the investigation of photoconductivity change during the relaxation of SAN and the effect of traces of THF in TiOPc/SAN films on their photosensitivity ($1/t_{1/2}$) and the charging voltage (V_0) through characterization of dynamic rheological behavior combined with the measurement of photoconductivity.

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EXPERIMENTAL

Materials

Due to its high stability, non-toxicity, strong absorption in the visible spectral region and quite high photoconductivity, TiOPc was selected as the charge generation material in this study. The crystal form of TiOPc is mainly α -type according to Ref. [3]. 4-(Diethylamino) benzaldehyde 1-(1'-naphthyl)-1-phenylhydrazone (supplied by Tianjin Reprography Institute) and poly(styrene-*co*-acrylonitrile) (SAN) ($M_n = 4.5 \times 10^4$, $M_w/M_n = 2.2$, AN% = 32 wt%, Chimei Corporation, Taiwan) were used as the charge transportation material and the binder polymer, respectively. 0.05 g purified TiOPc was milled with 15 g micro quartz beads in 10 mL THF solvent for 1 h, then mixed with SAN and hydrazone. The proportions of TiOPc, SAN and hydrazone in the mixture were 1:140:140 by weight.

Dynamic Viscoelastic Measurements

Preparative mixing slurry was coated on a glass plate. With one-day evaporation of solvent beforehand at room temperature, the films were heated and dried stepwise from 60°C to 120°C in an oven for at least one day at a given temperature to ensure the complete removal of solvent.

Rectangular specimens of approximately $33 \times 12 \times 0.5$ mm were molded under pressure (150 kg/cm²) at 130°C. The slowly-cooling samples were prepared by cooling the samples from 110°C to room temperature at a rate of -1 K/min. Quenched samples were prepared by transferring samples quickly from 110°C into the ambient atmosphere. Thermally treated samples were prepared by treating the quenched samples at 70°C, 45°C and 20°C, respectively. The dynamic viscoelastic behavior of TiOPc/SAN samples was measured using an Advanced Rheometric Expansion System (ARES). A frequency of 10 rad/s and a static strain of 0.2% were used in the measurements. All dynamic mechanical data were obtained at a heating rate of 4 K/min.

Preparation and Thermal Treatment of Photoconductive Films

The mixing slurry was coated on conductive aluminum substrates, and then dried at room temperature. The thickness of the photoconductive layers was controlled to be about 25 μ m. Generally, during preparation there remains a small amount of residual THF solvent in TiOPc/SAN films. With increasing thermal treatment time and temperature, the amount of THF decreases due to volatilization. TiOPc/SAN films were treated at 35°C, 50°C, 70°C and 100°C, respectively for different periods of time in order to detect the effect of traces of THF on photoconductivity of TiOPc/SAN films. It is hypothesized that no THF exists in the film sample when its weight change, $\Delta W = W_0 - W$, under thermal treatment is less than 0.0001 g (here W_0 and W are the weight of the film before and after the treatment).

Photoconductivity Measurements of TiOPc/SAN

Measurements of photoconductive properties the treated films were conducted by using a GDT-II Photoconductive Property Measuring Apparatus. An incandescent light source from Changhong 6-8 was used, and the intensity of illumination was 30 lux. The center wavelengths of the optical filters were 450, 500, 570, 605, 678, 703 and 762 nm, respectively.

RESULTS AND DISCUSSION

Relationship Between Structure Stability and Dynamic Viscoelasticity of TiOPc/SAN

It is well-known that the dynamic viscoelastic response is very sensitive to the change of morphology/structure for multi-component polymer systems^[7, 8, 9]. In particular, taking change of dynamic viscoelastic functions with time into consideration has become a preferred method for examining whether the morphology/structure of the system has approached equilibrium or not^[10, 11]. In order to avoid test deviation, attention has been paid to the relationship between the rate of change, $dG''/dt = R$, of dynamic loss modulus (G'') and the thermal treatment time (t). Figure 1 shows this dependence at different temperatures. Comparison of Fig. 1(a) with Fig. 1(b) indicates a more obvious decrease of (dG''/dt) at 70°C than that at 45°C when t is less than 50 min. After that the R values at 70°C and 50°C become very close to each other, and almost no change of R with t is observed. These results may imply the approach to an equilibrium state. However, the case as shown in Fig. 1(c) is different from

Figs. 1(a) and 1(b). Obviously, R at 20°C is much smaller than that at higher temperatures and R continuously changes with time even at values beyond 2000 min.

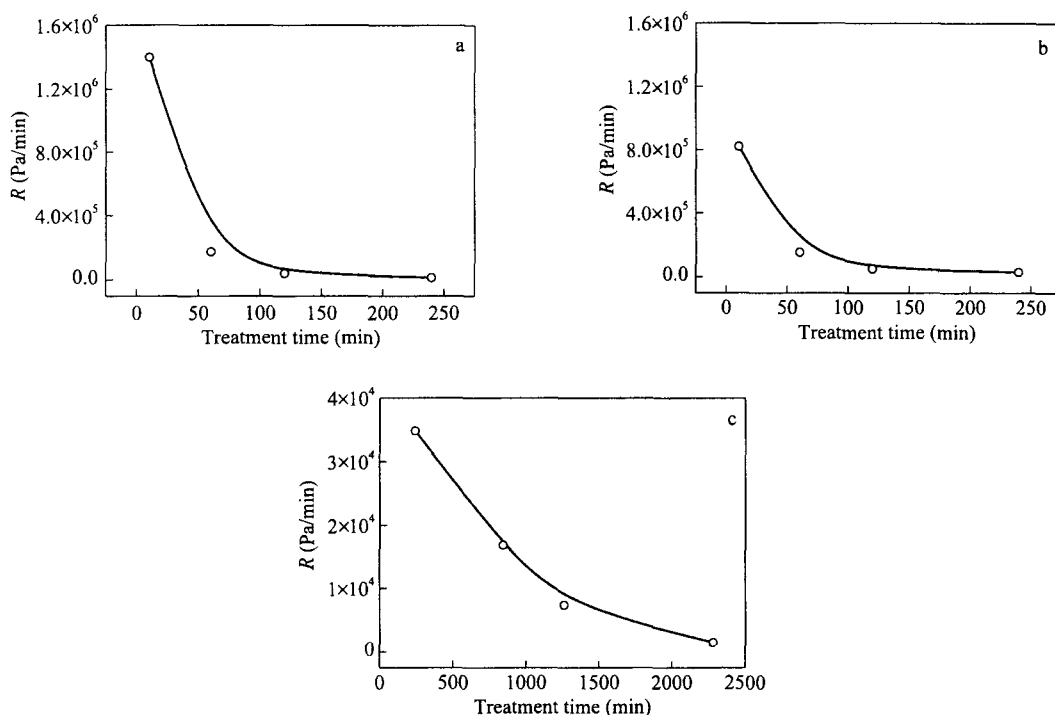


Fig. 1 Time dependence of change rate of the dynamic loss modulus (R) for samples thermally treated at different temperatures
a) 70°C; b) 45°C; c) 20°C

Figure 2 gives the temperature dependence of dynamic viscoelastic functions for TiOPc/SAN samples thermally treated at 20°C, 45°C and 70°C, respectively for different times. Also given are the results of samples obtained by quenching and slow-cooling. It can be seen that there are no discernible differences in dynamic storage modulus (G') for all the samples at three temperatures and quenched and slow-cooling conditions, but in comparison there appear remarkable differences in their dynamic loss modulus (G'') and loss tangent ($\tan \delta$). It is well known that the thermal treatment of polymers at temperatures near their glass transition temperature (T_g) is of benefit in inducing structure changes from unstable to stable states and their corresponding characteristic response is responsible for the change of free volume, namely the stability of the morphology/structure of the polymers^[10, 12]. The decrease in G'' or $\tan \delta$ values induced by exposing amorphous polymers to thermal treatment is related to the decrease of free volume corresponding to structure changes approaching a more stable state^[10, 13, 14]. It can be seen in Figs. 2(a)–2(c) that the quenched sample exhibits the highest G'' or $\tan \delta$ within the temperature range from 20°C to 80°C, as compared with those samples treated under other conditions. Hence, it is reasonable to believe that the structure of the quenched sample is unstable. In contrast, it is obvious that the slow-cooling results in a rather stable structure of the samples in view of their smallest values of G'' or $\tan \delta$. Moreover, for the thermally treated samples their G'' and $\tan \delta$ values become close to those of the slow-cooling samples with the increase of the treatment temperature as well as the corresponding time. It is noted that only G'' and $\tan \delta$ for samples treated at 45°C for 20 h and 70°C for 15 h approach to those of the slow-cooling sample, while the values of samples treated at 20°C remain considerably higher than those of the slow-cooling sample even after treatment for 96 h. According to the results mentioned above, it can be concluded that the conditions for preparing TiOPc/SAN samples of stable condensed structure are (1) slow-cooling and (2) thermal treatment

at 70°C for more than 15 h or at 45°C for more than 20 h.

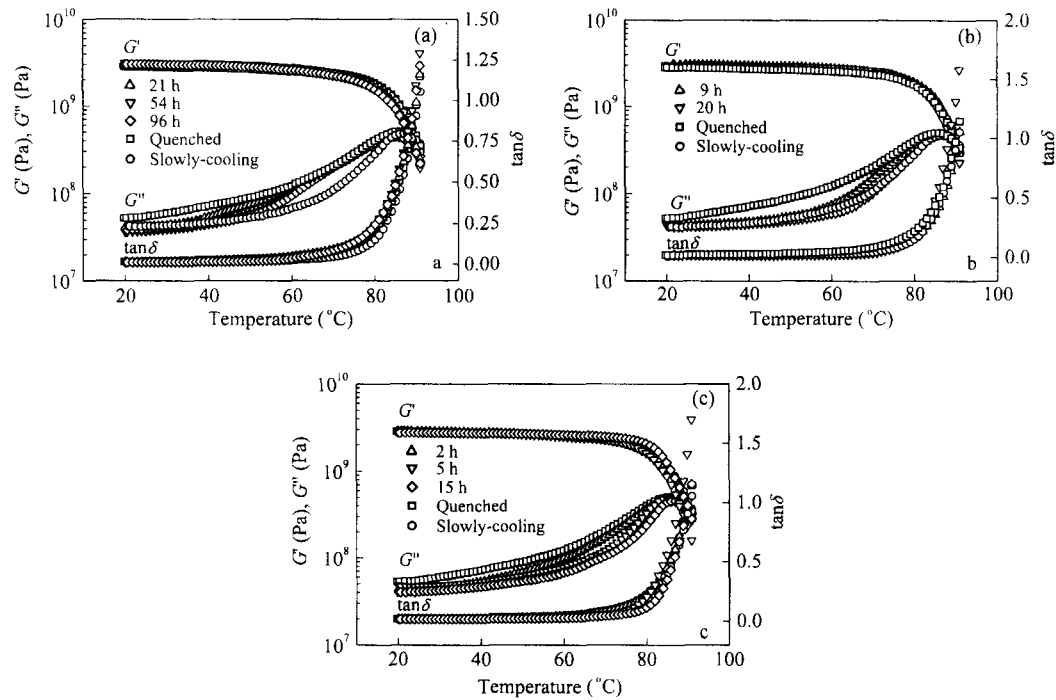


Fig. 2 Temperature dependence of dynamic viscoelastic functions for TiOPc/SAN samples thermally treated at (a) 20°C, (b) 45°C, (c) 70°C for different times compared with quenched and slowly cooling samples

Table 1 gives the photosensitive properties ($1/t_{1/2}$, $t_{1/2}$ being the half-discharge time, at 762 nm for TiOPc/SAN samples treated at different thermal conditions including quenching and slow-cooling. It is found that the thermally treated and slow-cooling samples possess better photosensitivity than the quenched ones. Moreover, the photosensitivity of samples treated at a given temperature increases with increasing treatment time. For instance, the photosensitivity of a sample treated at 70°C for 5 h is higher than that of one treated for 2 h. In addition, the photosensitivity of a sample treated at 45°C for 9 h is lower than that of one at 70°C for 5 h. Among all the samples the slow-cooling one exhibits the higher photosensitivity. On the basis of the discussion regarding Fig. 2 it is supposed that the structures of a samples treated at 45°C for 9h and at 70°C for 5 h are non-equilibrium and near equilibrium, respectively, and the stable structure of SAN is responsible for the improvement in photosensitivity of TiOPc/SAN since the other components, TiOPc and hydrazone, are thermostable in this experimental temperature range.

Table 1. Photosensitivity for TiOPc/SAN films treated at different thermal treatment conditions compared with quenched and slowly-cooling samples (762 nm)

Treatment conditions	Photosensitivity ($1/t_{1/2}$) (s^{-1})
Quenched	3.45
45°C 9h	4.55
70°C 2 h/5 h	4.55/5
Slow-cooling	5.26

Effect of traces of THF on Photoconductivity of TiOPc/SAN Films

Figure 3 shows the dependence of weight loss (wt%) on the thermal treatment time for samples prepared without treatment for solvent removal. The weight loss increases rapidly first and then approaches a limiting value. In the temperature range below the boiling temperature of THF (about 70°C) the weight loss increases with increasing

temperature. Above 70°C almost no influence of temperature on the time dependence of weight loss was observed. The weight loss behavior of three samples can be attributed to the removal of residual THF by thermal treatment. Figure 4 shows the time dependence of photoconductive parameters, photosensitivity $1/t_{1/2}$ and charging voltage V_0 , of TiOPc/SAN films measured at 762 nm (30 lux) under thermal treatment at 35°C and 70°C. It can be seen that $1/t_{1/2}$ and V_0 decrease with time of thermal treatment, and a sharp decrease is observed in the beginning. The effect of treatment temperature on $1/t_{1/2}$, V_0 and residual voltage V_r of TiOPc/SAN films is given in Table 2. Comparing the two phenomena, the weight loss and the change of photoconductivity of the samples under thermal treatment, one may suggest that the decrease of photoconductivity is related with the removal of residual THF from samples. This idea was further supported by the following experiment. When a THF-free sample, which has been treated at 100°C for 1 h, is placed in THF steam for 1 h at 70°C, it exhibits considerably higher $1/t_{1/2}$, V_0 , and V_r values, approaching those of samples treated at 35°C (Table 2). It is necessary to take into consideration that carriers of organic materials generated through an intermediate state are generally subject to a lack of satisfactory agreement on comprehensive theory describing the photoconductive mechanism of phthalocyanines. According to the photoconductive mechanism model based on charging voltage proposed by Popovic *et al.*^[5], we assume that THF not only interacts with ground state TiOPc, but also plays an important role in generation of free electron-hole and charge transfer complexes of TiOPc. These influences can

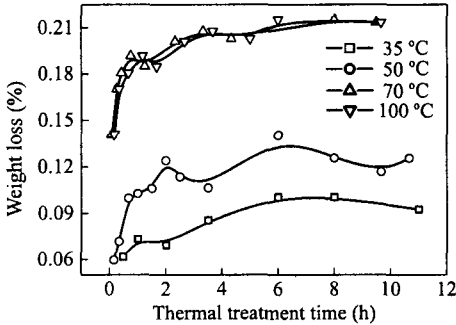


Fig. 3 Relationship between weight loss and thermal treatment time

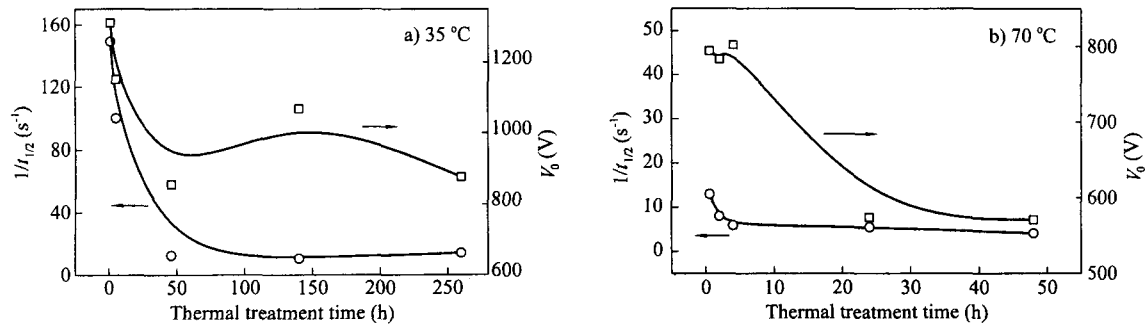


Fig. 4 Dependence of photosensitivity ($1/t_{1/2}$) and charging voltage (V_0) on thermal treatment time for TiOPc/SAN films at various temperatures

Table 2. Photoconductivity of TiOPc/SAN films treated at various temperatures for 1 h (762 nm)

Temperature (°C)	V_0 (V)	$1/t_{1/2}$ (s ⁻¹)	V_r (V)
35	1195	149	242
50	1040	100	222
70	790	11	109
100	515	4	88
Treated with THF vapor (70°C)	1120	149	294

be confirmed by the improved photosensitivity of TiOPc/SAN films in THF vapor. On the basis of these results, the attenuation of photoconductive properties or the aging of photoconductors can be partly attributed to the slow volatilization of THF solvent during use.

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