

Determination of the Glass Transition Temperature of Polymeric Photorefractive Composite from Photo-charge Generation Efficiency Measurements

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Introduction

The photorefractive (PR) effect arises when charge carriers, generated by a spatially modulated light intensity, are separated by the mechanisms of drift or diffusion, and are trapped to produce a nonuniform space charge distribution,¹ which consequently modulates the refractive index of materials via reorientation of nonlinear-optical (NLO) chromophore. Since optical nonlinearity of PR composites is based on the alignment of the rod-like chromophores towards electric field within the composite, it should be sensitive to the temperature, especially the temperature difference with the glass transition temperature (T_g) of the composites.^{2,3} Therefore, determining the accurate T_g of polymeric PR composite and understanding its role in each of the relevant processes involved in the PR effect are essential to optimizing the PR response.^{4,6}

Generally, the glass transition temperatures are determined by differential scanning calorimetry (DSC). However, the application of DSC to polymeric PR composites is often ineffective, since the transitions observed in the DSC curves are weak and relatively broad.⁴ Recently, Quintana *et al.* proposed an alternative method that consisted of analyzing the temperature dependence of the photoconductivity (σ_{ph}); the T_g corresponds to the temperature at which a clear change in slope (break point) in the Arrhenius representation of σ_{ph} (i.e., σ_{ph} versus $1000/T$, where T is temperature).⁴

In this work, we proposed a new method to determine the glass transition temperature of polymeric PR composites from xerographic discharge techniques. This method consists of analyzing the temperature dependence of photo-charge generation efficiency (ϕ), so the T_g corresponds to the temperature at which the tendency of photo-charge generation

efficiency has reversed. In order to confirm our method, we also determined the T_g of PR composites from photoconductivity measurements at the same applied electric field.

Experimental

Materials. In this work, polymeric PR composites were prepared by doping NLO chromophore, 2-{3-[(*E*)-2-(dibutylamino)-1-ethenyl]-5,5-dimethyl-2-cyclohexenylidene} malononitrile (DB-IP-DC), into photoconducting polymer matrix, poly[methyl-3-(9-carbazolyl) propylsiloxane] (PSX-Cz) sensitized by 2,4,7-trinitro-9-fluorenone (TNF). PSX-Cz and DB-IP-DC were synthesized using previously described methods.⁷ TNF was obtained from Kanto Chemistry Co. and was used after purification.

Sample Fabrication and Measurements. The photo-charge generation efficiency of PR composites was evaluated using the standard photoinduced discharge technique, which is the basis of the xerographic process in the photocopying systems.⁸ Polymer composites (PSX-Cz: DB-IP-DC: TNF=69: 30: 1 wt% and 79: 20: 1 wt%) are dissolved in a 1,1,2,2 tetra chloroethane (TCE) solvent and the films are fabricated by doctor-blade technique on a 2.5×2.5 cm² ITO (indium tin-oxide) glass substrate to determine the photo-charge generation efficiency. Layer thickness (in the 3.5 μm range) is measured by Metricon 2010. Xerographic discharge experiments were performed with a wavelength of 632.8 nm ($I=3.6$ mw/cm²). Under emission-limited conditions, the photo-charge generation efficiency was independent of the charge drift velocity and was determined only by the generation rate of free charges. The photo-charge generation efficiency was calculated from the slope of the discharge rate as follows:

$$\phi = -\frac{C}{eI_0} \left(\frac{dV}{dt} \right)_{vi} = -\frac{\varepsilon\varepsilon_0}{deI} \left(\frac{dV}{dt} \right)_{vi} \quad (1)$$

where C is the capacitance per unit area, dV/dt is the rate of change of the surface potential, I_0 is the absorbed photon flux (I : photon flux density), e is the elementary charge, ε is the dielectric constant (measured at 632.8 nm by Metricon 2010 which was based on the prism coupling method), ε_0 is the vacuum permittivity, and d is the thickness.

The measurement temperature of the PR device was carefully controlled with a device holder designed in our laboratory which can be adjusted from 15 to 50 °C with error range of ± 0.2 °C. There was a 1.5 cm diameter hole at the center of the heating plate of the device holder. The laser beams illuminating the device passed through this hole. The sample temperature was monitored using a thermometer (Fluke 50S), whose probe was placed in contact with the glass plate of the device.

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Results and Discussion

The T_g of polymeric PR composites is usually attributed to the existence of phase separation or to motions of different components of the polymer, i.e., backbone and side chains.^{9,10} Figure 1 represents glass transition curves for PR composites of the type PSX-Cz (79%)/DB-IP-DC (20%)/TNF (1%) (composite 1, thin line) and PSX-Cz (69%)/DB-IP-DC (30%)/TNF (1%) (composite 2, thick line). The T_g was determined by differential scanning calorimetry (Perkin-Elmer DSC7) at heating rate of 10 °C/min under nitrogen atmosphere.¹¹ The T_g of PSX-Cz is approximately 51 °C; and the T_g of PR composites is substantially decreased due to the presence of the large amount of NLO chromophore that can act as a plasticizer. As shown Figure 1, the glass transition region of PR composite 1 was from 26 to 38 °C. When the amount of chromophore was increased, the transition was observed at lower temperature, reaching region from 20 to 32 °C for composite 2 (thick line, Figure 1). However, all DSC curves of composites had broad transition region, so we could not indicate a precision T_g .

Figure 2 shows the temperature dependences of photo-charge generation efficiency of PR composites 1 and 2 in the temperature region 18–36 °C at an external electric field of 30 V/ μ m. For composites 1 and 2, the photo-charge generation efficiency had the maximum value at 32 and 26 °C, respectively, and then decreased with an increase in the temperature. We believe that this temperature corresponds to the T_g of the composites 1 and 2 under these experimental conditions. In general, the photo-charge generation efficiency exhibits thermally activated behavior below T_g but abruptly decreases and then becomes temperature independent above T_g .¹² This observation can be explained by Williams-Lan-

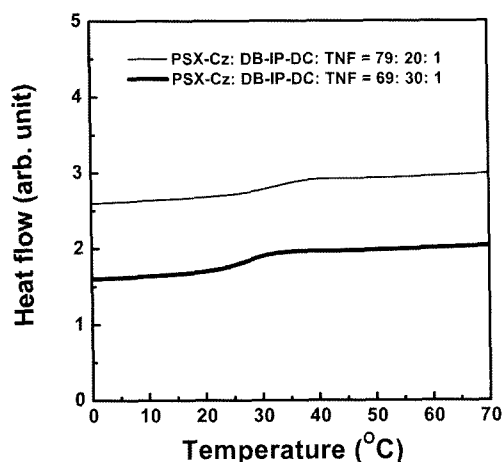


Figure 1. Glass transition curves for PR composites of the type PSX-Cz (79%)/DB-IP-DC (20%)/TNF (1%) (composite 1, thin line) and PSX-Cz (69%)/DB-IP-DC (30%)/TNF (1%) (composite 2, thick line) at the cooling rate of 10 °C/min under a nitrogen atmosphere.

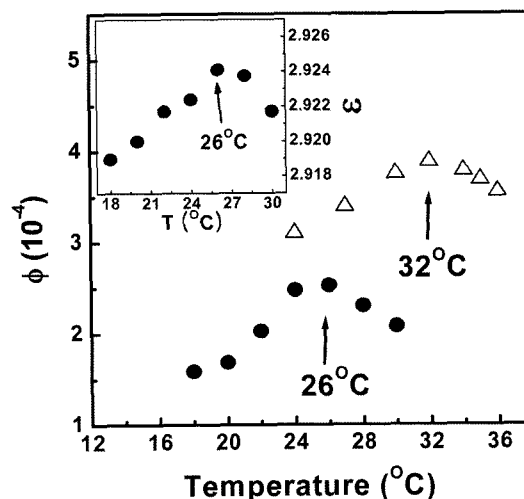


Figure 2. Temperature dependence of the photo-charge generation efficiency (ϕ) for PR composites 1 (open triangles) and 2 (closed circles) at an external electric field of 30 V/ μ m. Inset shows dielectric constant (ϕ) for PR composite 1 as a function of temperature.

del-Ferry (WLF) model which describes the temperature dependence of various parameters such as viscosity, elasticity, and characteristic relaxation times.¹³ Inset of Figure 2 shows the dielectric transitions of PR composite 2 measured over the temperature range 18 °C < T < 30 °C. According to the WLF model, dielectric constant which determines the photo-charge generation efficiency (eq. (1)) is abruptly changed around glass transition temperature.¹⁴ The dielectric constants reached the maximum value at 26 °C and then decreased during further heating. The transition behavior reflects the glass transition region of PR composite. In the glass transition region the amorphous PR composite rapidly gains the freedom to undergo structural relaxation toward a thermodynamic state given by the extrapolated equilibrium-liquid curve. At the same time the molecules of the amorphous PR composite become free to participate in a collective type of persistent micro-Brownian motion the Fourier components of which can in part be resolved in dynamic mechanical measurements and dielectric constant.¹²

In order to confirm that the maximum values of photo-charge generation efficiency as a function of temperature are T_g , we also determined the T_g of PR composites 1 and 2 from photoconductivity measurements⁴ at the same external electric field (30 V/ μ m). Figure 3 shows the temperature dependence of the photoconductivity, in an Arrhenius representation for PR composites. In agreement with photo-charge generation efficiency, changes in the photoconductivity, at a temperature interpreted as the T_g of PR composites, were obtained.

For PR composites 1 and 2, a clear change in slope is observed for σ_{ph} at around 32 and 26 °C, respectively. This indicates that at these temperatures a change in the mechanism dominating σ_{ph} takes place, getting different activation

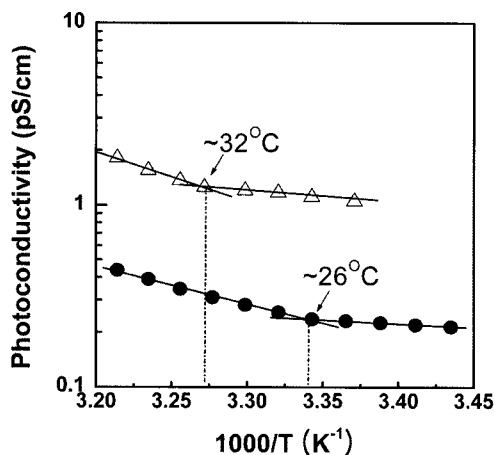


Figure 3. Photoconductivity (σ_{ph}) for PR composites of the type PSX-Cz (79%)/DB-IP-DC (20%)/TNF (1%) (open triangles) and PSX-Cz (69%)/DB-IP-DC (30%)/TNF (1%) (closed circles) at an electric field of 30 V/ μm , as a function of temperature in an Arrhenius representation.

energies in each regime of temperature.⁴ From these results, we have evidence that photo-charge generation efficiency measurements as a function of temperature are a realizable method to determine an accurate T_g of polymeric PR composites.

Conclusions

In summary, it has been shown that DSC is not an appropriate technique for determining the T_g of polymeric PR composite, since the transitions observed in the DSC curves are weak and relatively broad. Thus, an alternative method has been proposed, consisting on studying the temperature dependence of photo-charge generation efficiency and iden-

tifying T_g with the temperature at which tendency of photo-charge generation efficiency has reversed.

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