ELSEVIER

Polymer 41 (2000) 1731–1739

polymer

In-situ measurement of the crystallization process of polycarbonate/epoxy resin by a photoresistor

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Received 23 March 1999; received in revised form 12 May 1999; accepted 19 May 1999

Abstract

The PC crystallization process is measured by the photoresistor, by which the reciprocal relationship is obtained between the illumination of transmission light and the resistance. In the beginning of annealing the change of resistance is insignificant when the crystallization is still at the induction stage. Then the increasing number and size of spherulites scatter the incoming light and the resistance increases quickly. Finally the concentration of amorphous PC decreases and the increasing rate of resistance slows down. The X-ray pattern shows an ordered PC structure of $2\theta = 11^\circ$ in the induction period, then converts to amorphous (broad peak at 20°) and spherulite (17.2°) structure. The dissolving heat of PC spherulite, analyzed by differential scanning calorimetry, shows a linear relationship to the resistance. Thus the relative crystallinity can be obtained by measuring the resistance of the photoresistor from both primary and secondary crystallization. The experimental results show good correlation to the Avrami model and the highest crystallization rate is obtained at 80°C. The thermodynamic factor controls the crystallization rate at higher annealing temperature while the kinetic factor dominates the crystallization rate at lower annealing temperatures.

Keywords: Polycarbonate; Epoxy; Photoresistor

1. Introduction

The crystallization rate of bisphenol-A polycarbonate is very slow. Tomikawa [1] studied the 0.1 mm thick PC film and reported that the crystallization process is completed after 10 days at 190°C. Von Falkai and Rellensmann [2] studied thinner film (50 μm) and reported that the induction time for nucleation is 25 h. The crystallization rate can be accelerated by introducing a plasticizer or a solvent into the system to increase the chain mobility [3, Chapter 7]. Jonza and Porter [4] added acetone in polycarbonate and reported a 22% crystallinity by differential scanning calorimetry (DSC) analysis.

The crystallization phenomenon of polymer has been analyzed mostly by DSC [4–6], X-ray diffraction [4–7] and light scattering [7,8]. The relative crystallinity can be measured by the DSC analysis, while the size of spherulite can be measured by the light scattering. The light scattering method is widely used to trace the in-situ crystallization process of small molecules and polymers. However, the light scattering method requires complicated instruments and highly purified materials thus it is not suitable for industry usage.

The polymer crystallization rate can be predicted by the Avrami model [3, Chapter 6] which describes the crystallization process by a raindrop. The spreading of a raindrop wavefront can be used to simulate the growth of the spherulite. Since the spherulites cannot cross over with each other as the raindrop wavefront, the Avrami model can only describe the early stage of crystallization behavior. The crystallization behavior of polymers after the spherulites are connected to its neighbor can be expressed by a modified Avrami model.

In this study, the polycarbonate crystallization process of the polycarbonate/epoxy resin system is investigated by a photoresistor. Unlike the conventional light scattering method by measuring the diffracted patterns and intensity of light, this photoresistor is used to measure only the illumination of the transmission light. Since the measurement of the diffracted light is ignored, the required instrumentation and technique of this photoresistor method are relatively simpler and easier than the conventional light scattering method.

In an earlier report [9], the transesterification occurs between the hydroxyl groups of the epoxy and the carbonate groups of the polycarbonate. This side reaction causes PC

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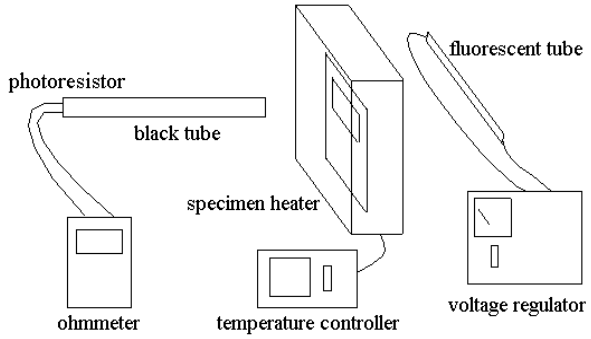
0032-3861/00/$ - see front matter
PII: S0032-3861(99)00352-3



Scheme 1.

chain scission and crosslinking and therefore retards the PC crystallization in the epoxy resin. In this study a purified epoxy resin, to eliminate the influence by the hydroxyl group, is employed to avoid transesterification and maintains the original molecular weight of the PC. The X-ray diffractor is used to confirm the appearance of PC spherulites. The relative PC crystallinity is measured by the DSC exotherm profile, which is then compared with the resistance of the photoresistor. The correlation between the resistance profile of the crystallization process and the Avrami model is studied. The effect of annealing temperature on the crystallization rate is also studied.

2. Experimental

2.1. Materials

A DGEBA type epoxy resin DER 332, with epoxide equivalent weight of 170, was purchased from Dow Chemical Company, USA. The Calibre 201-15, a nature grade polycarbonate was also supplied by the Dow Chemical Company, USA. Dichloromethane was supplied by the Union Chemical Works Ltd., Taiwan.

2.2. Procedures and instrumentation

2.2.1. Experimental techniques

The mixture of 10 g polycarbonate, 40 g dichloromethane and 40 g epoxy resin was stirred until the system became completely homogeneous at ambient condition. The system is then heated to 200°C under vacuum to remove dichloromethane. The final product is a clear and viscous liquid at 200°C and becomes opaque gradually after steady cooling to about 100°C due to the appearance of the PC spherulites.

The specimen cell dimension for the photoresistor test is $20 \times 16 \times 2\ mm^3$. The specimen cell holder and the PC/epoxy mixture was heated at 200°C until a homogeneous solution was obtained, then the PC/epoxy solution was poured into the cell holder. This holder is then immersed into a cold water bath to prevent polycarbonate crystallization. The following photoresistor test has to be carried out immediately after quenching the holder because this homogeneous mixture gradually turns opaque after seven days under room temperature, an indication of polycarbonate crystallization even under the ambient conditions.

2.2.2. Photoresistor method

The photoresistor, a light-sensitive electronic device which is made from CdS or CdSe, was purchased from Feedback Instruments Ltd., UK. The resistance of the photoresistor was changed based on the illumination of light. The lower resistance was obtained when a stronger incident light was employed.

Since the resistance of the photoresistor is a function of the incoming light, the environmental background must be totally eliminated. This study uses a black tube with length of 150 mm and radius of 10 mm in front of the resistor to make sure that the environmental light will not affect the resistor. To obtain a stable light source, a fluorescent tube connected with a voltage regulator has been used. The specimen holder was placed in a mold with a pre-determined annealing temperature. Then the mold was placed between the light source and the photoresistor, and the resistance of the photoresistor measured by a digital ohmmeter from 0 to 200 kΩ (upper limit of the ohmmeter). The instrument setup is shown in Scheme 1.

2.2.3. Differential scanning calorimetry

A TA Instrument DSC 910 with heating rates of 10°C/min was used to analyze the relative crystallinity of the PC. The dissolving heat of the PC spherulite in epoxy resin was calculated by integrating the endotherm profile with the sigmoidal baseline.

2.2.4. X-ray diffraction

A Inel CPS 120 X-ray diffractor was used to analyze the PC spherulite. The scanning 2θ ranged from 5 to 30°.

3. Results and discussion

3.1. Calibration of the photoresistor

The photoresistor changes its resistance when the intensity of incident light is changed. Normally the intensity of incident light can be controlled by the following two methods. The first method is to control the intensity of the incident light by changing the voltage of electric bulb by a transformer and the input electric work is proportional to the illumination of light. However, the input electric work does not correspond to the illumination of the light produced because the bulb itself also consumes energy in generating heat. Therefore, the exact energy transformed into light cannot be determined precisely. Besides, this technique is applicable only for the electric bulb, not for the fluorescent system. The second method uses two polarized lenses between the light source and a photoresistor to control and quantify the strength of the incident light. When the degree

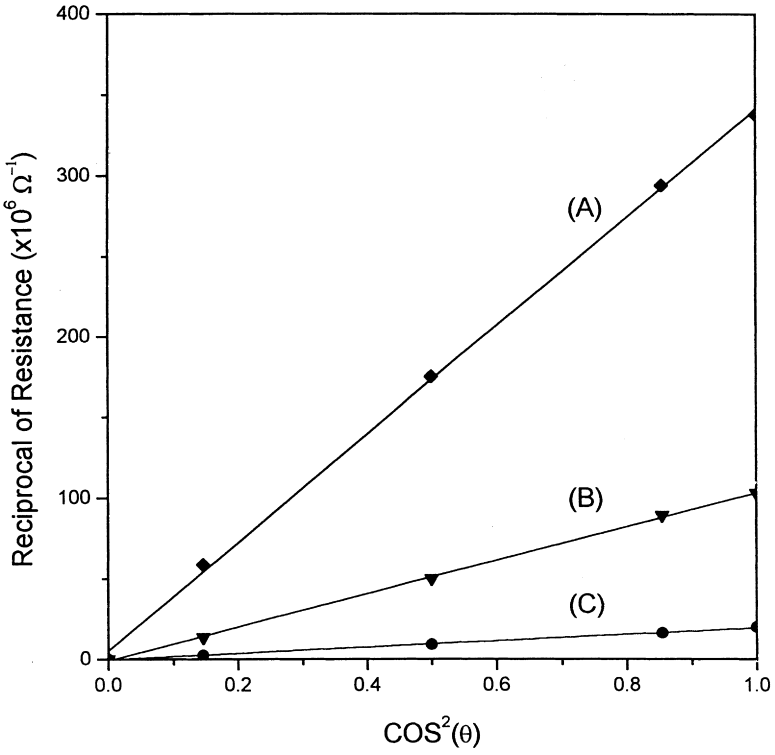


Fig. 1. Reciprocal of resistance (Ω^{-1}) versus $\cos^2(\theta)$. Light source: (A) electric bulb; (B) double fluorescent tube; and (C) single fluorescent tube.

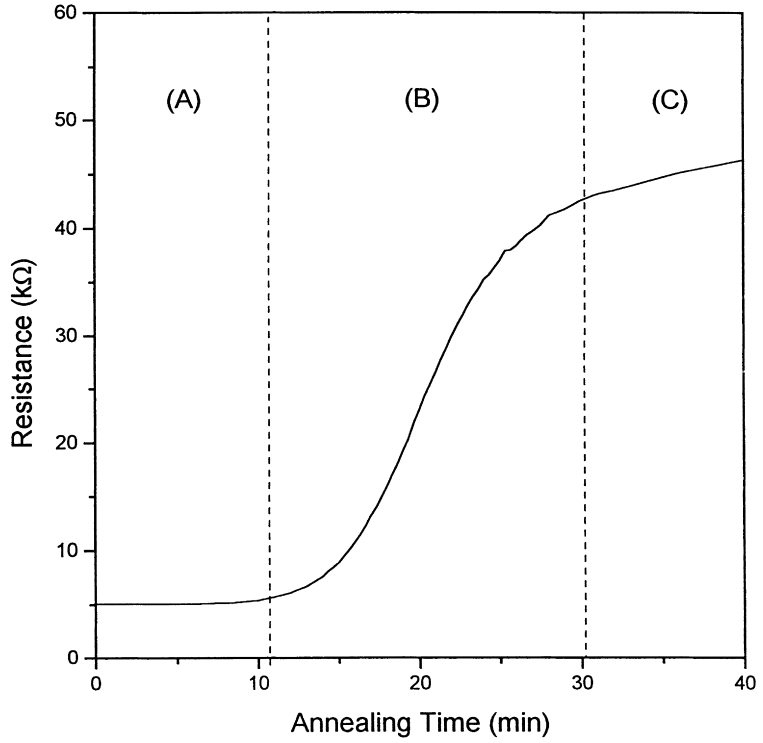


Fig. 2. Resistance (kΩ) versus annealing time (min) at 80°C annealing of PC 20 wt.% system.

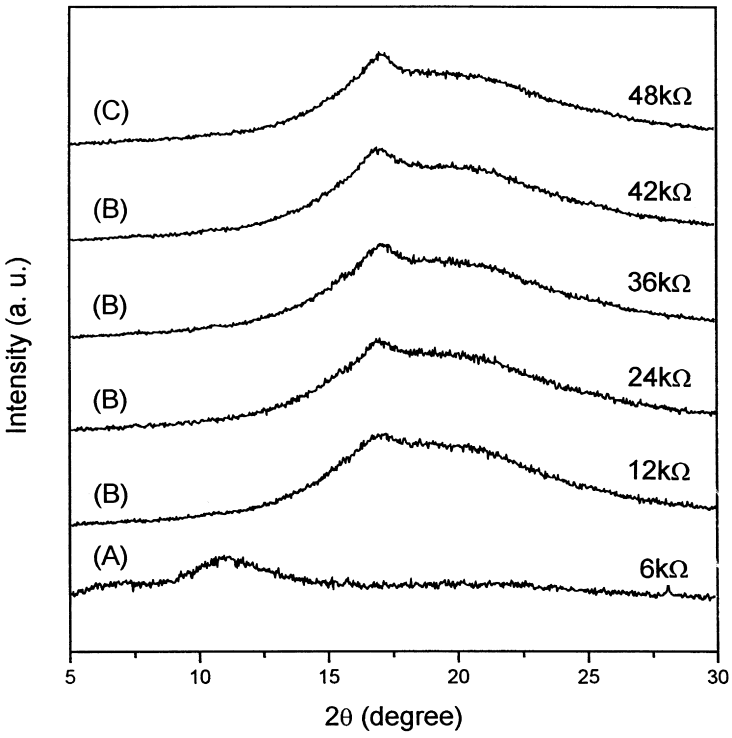


Fig. 3. X-ray diffraction pattern of PC 20 wt.% system at 80°C annealing.

of the polarized lenses is varied, the transmission light is also changed because a fraction of the incident light is eliminated by interference. The strength of transmission light can be expressed by the following equation:

$$E_t = E_0 \cos(\theta)$$

where E_t is the strength of transmission light, E_0 the strength of incident light and θ the angle between two polarized lenses. The illumination of transmission light I_t can be represented by the following equation:

$$I_t = E_t E_t^* = E_0^2 \cos^2(\theta)$$

where E_t^* is the conjugate of E_t.

E_0 is a constant for a fixed input voltage. Thus the illumination of light can be controlled by changing θ. This method has an additional advantage that there is no limitation on the light source. In this study a fluorescent tube is employed for the white crystals of polycarbonate which has better efficiency on scattering the white light.

The characteristics of the photoresistor is that a stronger incident light results in a lower resistance. The simplest way to express the relationship between them is the reciprocal:

$$\Omega = \frac{1}{I_t} \propto \frac{1}{\cos^2(\theta)} \qquad \text{or} \qquad \Omega^{-1} = I_t \propto \cos^2(\theta).$$

Fig. 1 shows the diagram of Ω^{-1} versus $\cos^2(\theta)$ where a high linearity is obtained from different light sources and different illuminations of the incoming light. The obtained result confirms the above prediction, i.e. the resistance is reciprocal to the illumination of incident light. The data range is from 5×10^{-6} to $3.3 \times 10^{-4}\,\Omega^{-1}$, which means the linear relationship is obtained from 3 to 200 kΩ.

3.2. Crystallization of polycarbonate in epoxy resin

Fig. 2 shows the plot of resistance versus annealing time of PC 20 wt.% system at an annealing temperature of 80°C. The curve can be divided into three parts. In region (A), the resistance increases slowly and the specimen is still transparent visually. In region (B), the resistance increases rapidly and results in an opaque specimen. In region (C), the resistance increase is slowed down. Fig. 3 shows the X-ray diffraction patterns of the PC 20 wt.% system at the annealing temperature of 80°C. Similar to the Fig. 2, these diffraction patterns can also divided into three groups, (A)–(C). Scattering of the incoming light by the PC spherulites is responsible for the increase of the resistance. Group (A) can be considered, as during the induction period the light scattering by the PC spherulites is not seen. However, the X-ray diffraction pattern does shows a larger scale of chain ordering as shown at 11°. In group (B), the PC spherulites are formed corresponding to the characteristic peak [10] at 17.2°, and a broad peak at 20° corresponding to the amorphous region of the PC. Both the number and the size of spherulites are growing in region (B) and result in a rapid increase of resistance and a related characteristic peak of 17.2° in the X-ray pattern. In the later region (B) (Fig. 2), the rate of resistance increment starts to slow down because the growth of spherulites is retarded by the neighbor spherulites. The secondary crystallization may also appear and further

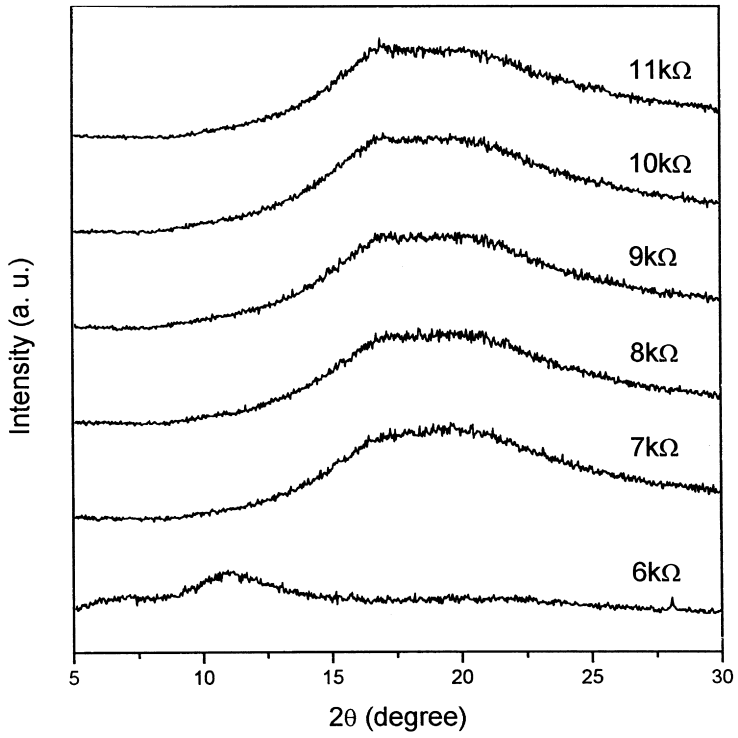


Fig. 4. X-ray diffraction pattern of PC 20 wt.% system from 6 to 11 kΩ.

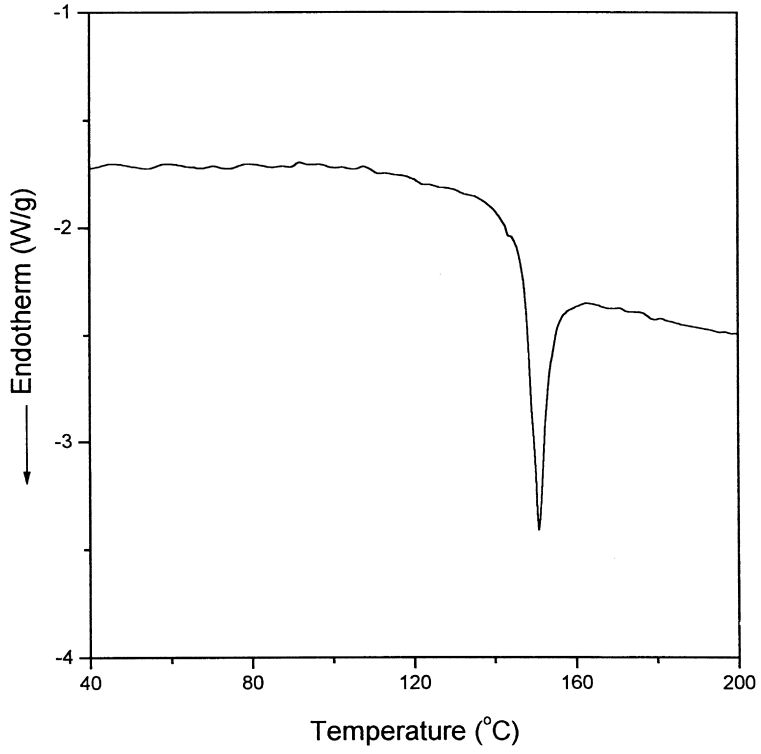


Fig. 5. DSC thermogram of PC 20 wt.% system at 80°C annealing for 22 min. Dissolving heat: 15.94 J/g.

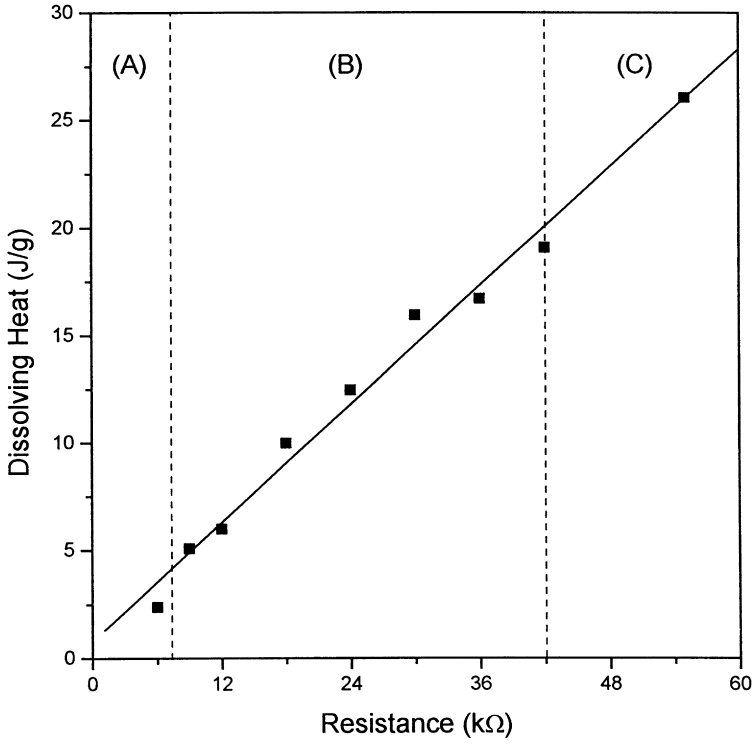


Fig. 6. Dissolving heat (J/g) of polycarbonate in DER 332 epoxy resin versus resistance of photoresistor (kΩ).

scatters the incoming light. In region (C) the main crystallization mechanism is the spherulite-inside secondary crystallization, where the crystallization rate is lower and the increase in resistance is also slowed down. Since the X-ray diffractor can only detect the surface structure of the PC spherulites, the secondary crystallization structure is unable to increase the 17.2° peak significantly.

Fig. 4 shows the X-ray patterns from 6 to 11 kΩ

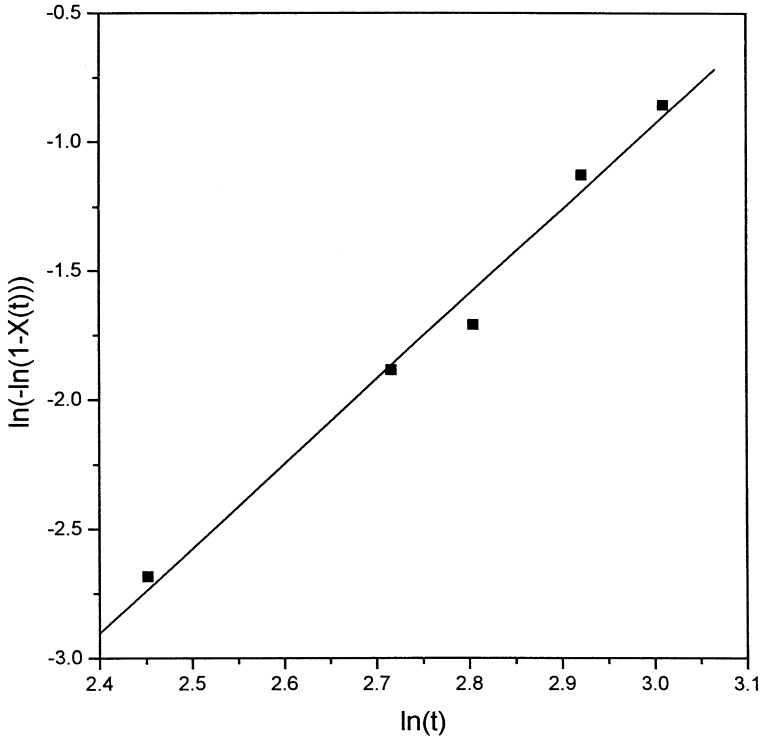
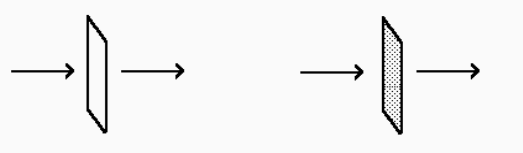


Fig. 7. Avrami constant of PC 20 wt.% system at 80°C annealing temperature. Regression slope $n_1 = 3.28$.



amorphous totally crystalline

I_1 I_2

Scheme 2.

corresponding to the induction mechanism of the PC spherulites. The larger chain ordering peak at 11° disappears when the resistance is 7 kΩ, and a broad peak appears in the range of 16–22°. Since the annealing time from 6 to 7 kΩ is only about 1 min, the disappearance of the 11° peak implies that the chain ordering structure is very unstable as a transition state. Further rearrangement of these PC ordering chains takes place rapidly with the combination of the amorphous structure (a broad peak near 20°) and the PC crystallites at 17.2°. This 17.2° peak becomes better defined with the increase of the resistance, as an indication of the growth of PC spherulites with annealing time.

Fig. 5 shows the DSC thermogram of the PC 20 wt.% system at an annealing temperature of 80°C for 22 min, corresponding to the resistance of the system of 30 kΩ (Fig. 2). Although the melting point of the PC spherulites is near 240°C, the epoxy resin is able to act as an effective solvent in this system and thus the observed endothermic peak near 150°C corresponds to the heat of dissolving of PC spherulites in the epoxy resin. Further, the purified epoxy resin with a melting point of 50°C [11] does not crystallize in this study because no endothermic peak is detected in Fig. 5. Fig. 6 shows the relationship between the dissolving heat of the PC spherulites and the corresponding resistance. Fig. 6 shows good linearity even in region (C). Such a linear relationship means the primary crystallization and secondary crystallization of PC have the same effect in scattering the incoming light. Thus the relative crystallinity and rate of crystallization can be obtained by measuring the resistance of the photoresistor.

3.3. Avrami model

The crystallization process of polymer is normally simulated by a two-stage crystallization [3, Chapter 6]. The first stage follows the Avrami equation. When the spherulites begin to connect to their neighboring spherulites ($t = \tau$), the second stage crystallization begins and follows a modified Avrami equation. The equations are presented as follows:

$$X(t) = 1 - \exp(-k_1 t^{n_1}) \quad \text{when } t < \tau,$$

$$X(t) = \omega_{\mathrm{I}}(1 - \exp(-k_1 t^{n_1})) + \omega_{\mathrm{II}}(1 - \exp(-k_2(t-\tau)^{n_2})) \quad \text{when } t > \tau$$

where X is the relative crystallinity, k_1 the growth rate constant of the spherulites, n_1 the Avrami constant, ω_{I} the ratio of the Avrami model, k_2 the growth rate constant of the

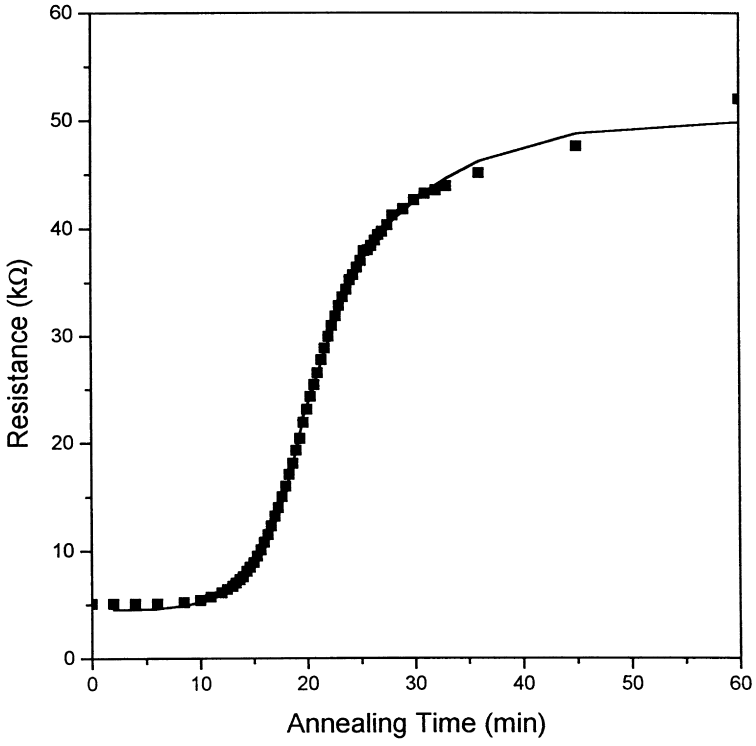


Fig. 8. Experimental data [■] of PC 20 wt.% system and the Avrami model prediction (solid line) at 80°C annealing.

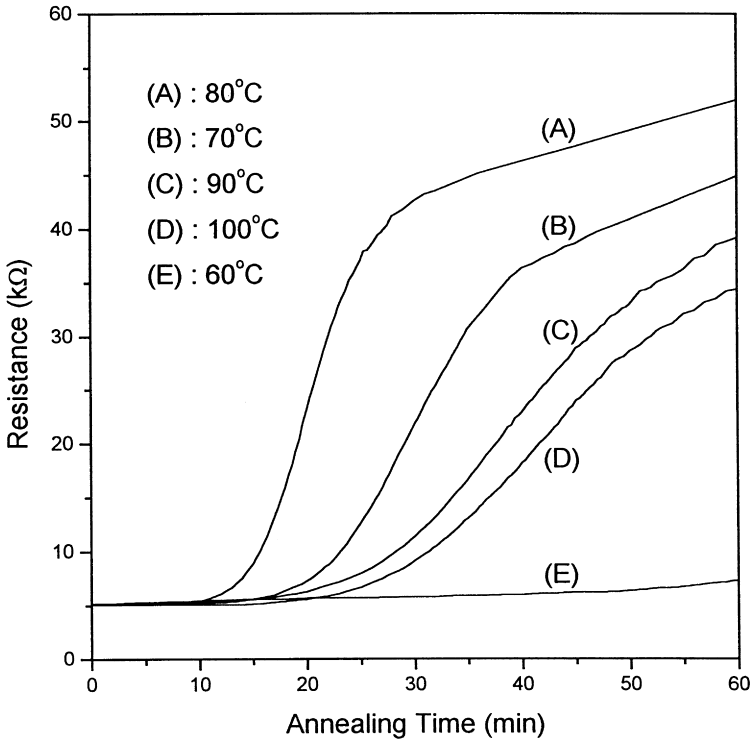


Fig. 9. Resistance (kΩ) of photoresistor versus annealing time (min) of PC 20 wt.% system at different annealing temperature (°C).

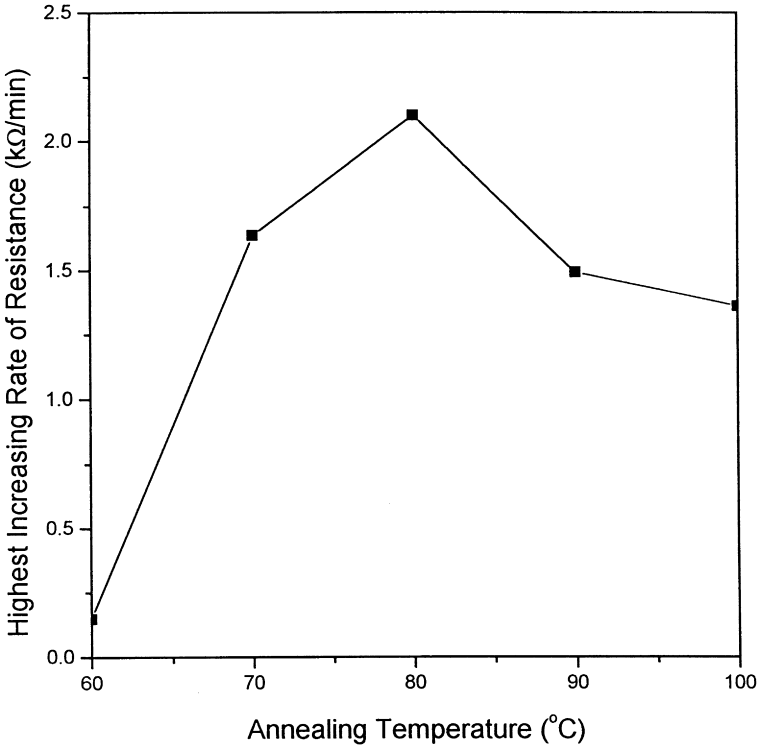


Fig. 10. Highest increasing rate of resistance (kΩ/min) of PC 20 wt.% system versus annealing temperature (°C).

spherulites in restricted condition, n_2 the Avrami constant in restricted condition ($n_2 = 1$ in this study) and ω_{II} the ratio of the modified Avrami model ($\omega_{II} = 1 - \omega_I$).

The Avrami number can be calculated by the following equation:

$$\ln(-\ln(1 - X(t))) = \ln k_1 + n_1 \ln t.$$

Fig. 7 shows the plot of $\ln(-\ln(1 - X(t)))$ versus $\ln t$ of the PC 20 wt.% system during the first stage crystallization ($t < \tau$). This plot shows good regression and the slope of n_1 is between 3 and 4 (3.28 for this study), which is usually observed in the PC crystallization [12].

The system can be divided into amorphous and crystalline regions (including the secondary crystalline). As shown in Scheme 2, the illumination of the transmission light of the amorphous specimen is defined as I_1 and that for the totally crystalline specimen is defined as I_2. The overall illumination of light (I) can be represented as $I = I_1[1 - X(t)] + I_2X(t)$. Since the resistance is reciprocal to the illumination of light, the resistance can be expressed as follows:

$$\Omega = I^{-1} = \{I_1[1 - X(t)] + I_2X(t)\}^{-1}$$

where I_1 is the reciprocal of the resistance at the beginning of annealing and I_2 the reciprocal of the resistance at the end of annealing.

Fig. 8 shows the experimental data by annealing at 80°C and the model predicted line in the study. The n_2 value is set as 1 here under the assumption of the highly restricted secondary crystallization environment in the PC spherulites [3, Chapter 6]. The experimental results fit well with the Avrami model, which confirms that the photoresistor is an appropriate method in tracing the PC crystallization process.

3.4. Effect of annealing temperature

Fig. 9 shows the resistance of photoresistor versus the annealing time at different annealing temperatures (60–100°C) of the PC 20 wt.% system. Fig. 10 shows the plots of the highest increasing rate of resistance versus annealing temperature. The highest increasing rate of resistance corresponds to the highest PC crystallization rate at 80°C. The slower crystallization rate at higher temperature can be attributed to the lower thermodynamic driving force. In contrast, the slower crystallization rate at lower temperature is due to lower kinetic driving force.

4. Conclusions

The photoresistor is a convenient instrument for analyzing the in-situ crystallization process of polymers and other chemical products. The relationship between the measured resistance and the illumination of incoming light is reciprocal, from 3 to 200 kΩ. The incoming light illumination can be determined by measuring the resistance of the photoresistor. The crystallization process of polycarbonate in the epoxy resin has been used as an example which is divided into three regions by the measurement of the photoresistor. In the first region the change of resistance is insignificant because the crystallization is at the induction stage. The measured resistance increases rapidly in the second region when both the size and the number of spherulites increases. When the PC spherulites begin to connect with others, the crystallization rate and the rate of resistance increase slow down. The X-ray diffraction patterns shows a larger chain ordering structure of PC in the first stage induction period with characteristic peak at 11°. This ordered structure is unstable and rearranges into PC amorphous (a broad peak at 20°) and spherulites (17.2°) quickly. The secondary crystallization in the final stage cannot be adequately detected by the X-ray diffractor because the crystallization happens within spherulites. However, the measured resistance does show linear relationship with the dissolving heat of PC spherulites, an indication that the primary crystallization and the secondary crystallization have the same effect on scattering the incoming light. Therefore, the relative degree of crystallinity of the PC can be adequately determined by the resistance of the photoresistor. The crystallization process measured by the photoresistor shows good correlation with the Avrami equation. The highest crystallization rate is observed at 80°C. The thermodynamics controls crystallization rate for annealing at higher temperature while the kinetics controls crystallization rate at lower temperatures. This study demonstrates that a simple photoresistor device is an adequate tool in tracing the crystallization process of the polymer solution.

Acknowledgements

This research was financially supported by the National Science Council, Taiwan, Republic of China, under contract No. NSC 87-2216-E-009-007. We also thank to the Epolab Chemical Co., Taiwan, for materials donation.

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