Polymer 40 (1999) 5513–5522

polymer

Hygrothermal effects of epoxy resin. Part II: variations of glass transition temperature

Jiming Zhou*, James P. Lucas

Department of Materials Science and Mechanics, Michigan State University, East Lansing, MI 48824, USA

Received 8 July 1998; received in revised form 30 October 1998; accepted 3 November 1998

Abstract

Three epoxy systems (DGEBA + mPDA, TGDDM + DDS, and Fiberite 934^{TM}) were used to investigate glass transition temperature (T_g) variation of epoxy under hygrothermal environment exposure. Materials were immersed in distilled water at constant temperatures of 45°C, 60°C, 75°C, and 90°C for water absorption and then desorbed at different temperatures. Thermomechanical analysis (TMA) and differential scanning calorimetry (DSC) were employed to determine T_g changes at different hygrothermal stages. The investigations revealed the following results: i) the change of T_g does not depend solely on the water content absorbed in epoxy resins, ii) T_g depends on the hygrothermal history of the materials, iii) for a given epoxy system, higher values of T_g resulted for longer immersion time and higher exposure temperature, and iv) the water/resin interaction characteristics (Type I and Type II bound water) have quite different influence on T_g variation. A sorption model and collateral evidence introduced in Part I of the series were used to interpret and explain T_g variation in epoxy resin systems. Both Type I and Type II bound water influence T_g variations, albeit in different ways. Type I bound water disrupts the initial interchain Van der Waals force and hydrogen bonds resulting in increased chain segment mobility. So Type I bound water acts as a plasticizer and decreases T_g. In contrast, Type II bound water contributes, comparatively, to an increase in T_g in water saturated epoxy resin by forming a secondary crosslink network. The experimental T_g values encompass the combined effect of the two water-resin interaction mechanisms described briefly in the preceding text and in detail in Part I of this paper series. The often-cited polymer-diluent model used to predict T_g variation of polymers exposed diluent media is lacking when a dual sorption mechanism is involved during hygrothermal exposure process. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxy; Hygrothermal effects; Glass transition temperature

1. Introduction

The glass transition temperature (T_g) is a very important parameter of epoxy resin and epoxy matrix composites because the T_g establishes the service environment for the materials' usage. In most applications, the epoxy is used at a temperature well below T_g (i.e., in the glassy state). Usually, when the material is exposed in a hygrothermal environment the T_g decreases and, therefore, the service temperature of the material changes. This modification in T_g reflects the degree of resin plasticization and water/resin interactions occurring in the material. Identifying mechanisms responsible for T_g change and being able to predict T_g depression are critical for material applications and engineering design.

Frequently, the so-called ''polymer-diluent'' model introduced by Kelly and Bueche is used for predicting T_g of polymers exposed hygrothermally [1]. Kelley assumed that the diluent media diffusing in polymers do not enter pre-existing free volume, but, rather, resided in the free volume created by the diffused media. In accordance with their model [1] the depression in T_g is simply the function of diffusing media content in the material and is independent on exposure temperature and time. This model has been applied by others [2,3] to predict the T_g depression of hygrothermally exposed epoxy resins with limited success.

Recent studies have revealed that T_g variation in epoxy resins differed significantly from the T_g values calculated by using the polymer-diluent model [4–9]. DeIasi [10] found sorbed water in epoxy resins had different bonding states. The suggestion was that sorbed water molecules that disrupt the interchain hydrogen bonds depressed T_g, whereas, water that formed clusters or hydroxyl-water groupings had no measurable effect on T_g. Mijovic and Weinstein [11] found that sorbed water induced depression of T_g in a Gr/Ep composite was strongly dependent on the temperature during the water absorption process. The authors' previous

---

* Corresponding author. Present Address: Delphi Delco Electronics Systems, Advanced Processes, Packaging, and Materials, P.O. Box 9005, MS D-16, Kokomo, IN 46904-9005, USA.

0032-3861/99/$ - see front matter
PII: S0032-3861(98)00791-5

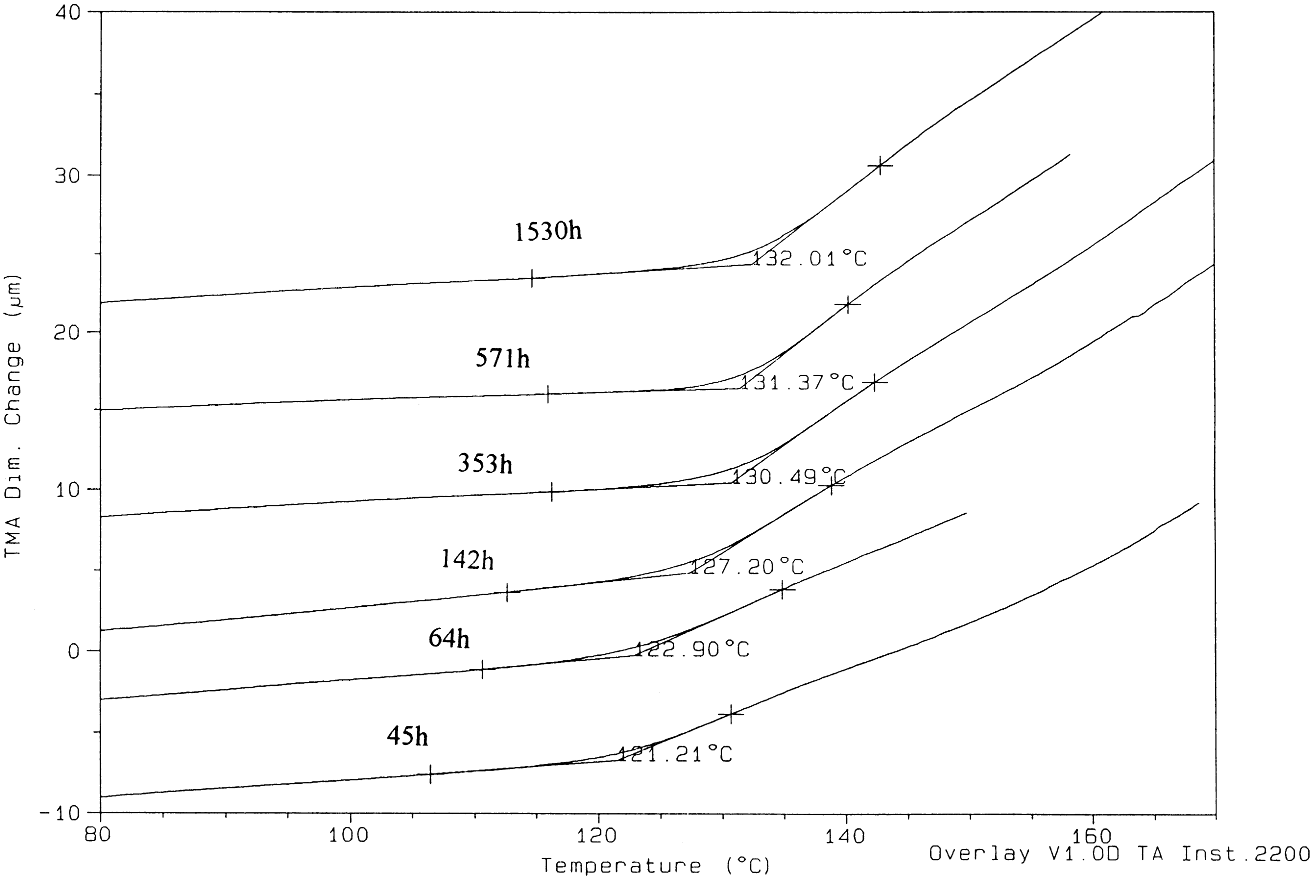

Fig. 1. T_g change of TGDDM + DDS with exposure time, the exposure temperature was 90°C.

work [12] reported that graphite/epoxy (Gr/Ep) composites exposed at different temperatures ranging between 45°C and 90°C show a large T_g variation ($>$ 35°C) when fully saturated with water.

Reported data of T_g values in the technical literature exhibit a rather wide scatter band [2,13] for a given epoxy system. Frequently, the variation in T_g is explained by differences associated with material preparation. However, from experimental data of others [10–12] and from results of Part I of this paper, the effects of hygrothermal history (i.e., exposure time and temperature) on T_g variation is indeed exhibited. To further investigate the variation of T_g in hygrothermal environments, a comprehensive study was conducted employing the three epoxy systems identified in Part I. T_g was measured at different hygrothermal stages by thermomechanical analysis (TMA). This paper series (Part I) provides an alternative viewpoint of the T_g variation of epoxy in hygrothermal environments.

2. Materials and experimental

The materials used in this study are the same as in Part I. The materials are: (i) tetraglycidyl-4, 4’-diaminodiphenyl methane (TGDDM, Ciba Geigy MY720) resin with a 4,4’-diaminodiphenyl sulfone (DDS, DuPont) hardener; (ii) diglycidyl ether of bisphenol-A resin (DGEBA, Shell Epon 828) with a metaphenylene diamine (mPDA) epoxy system; and (iii) a Fiberite 934 (TGDDM resin) epoxy system. Material preparation details were described in Part I.

Generally, two methods were used to determine T_g, differential-scanning calorimetry (DSC), thermomechanical analysis (TMA). DSC testing is based on the measurement of the change in specific heat. The sample size is small, usually $\backsim$ 20 mg. Reliable T_g values of dry samples are easily determined by DSC. However, accurate T_g values of moisture saturated samples are inherently more difficult to obtain since the output signal is small and often mixed superposed with other phase transition signals. Being aware of the potential for ambiguity in DSC test results, TMA testing was conducted to corroborate T_g results in this study.

TMA testing determines the change in T_g via measurement of dimensional variation in the sample with temperature. T_g is determined from the intersection of two tangential lines drawn along discontinuities in the dimensional change vs. temperature profiles. During testing, partial water desorption is unavoidable, but the loss is minimized by using a fast temperature ramp rate, usually 10°C–20°C/min. Detailed methodology for determining T_g by TMA were

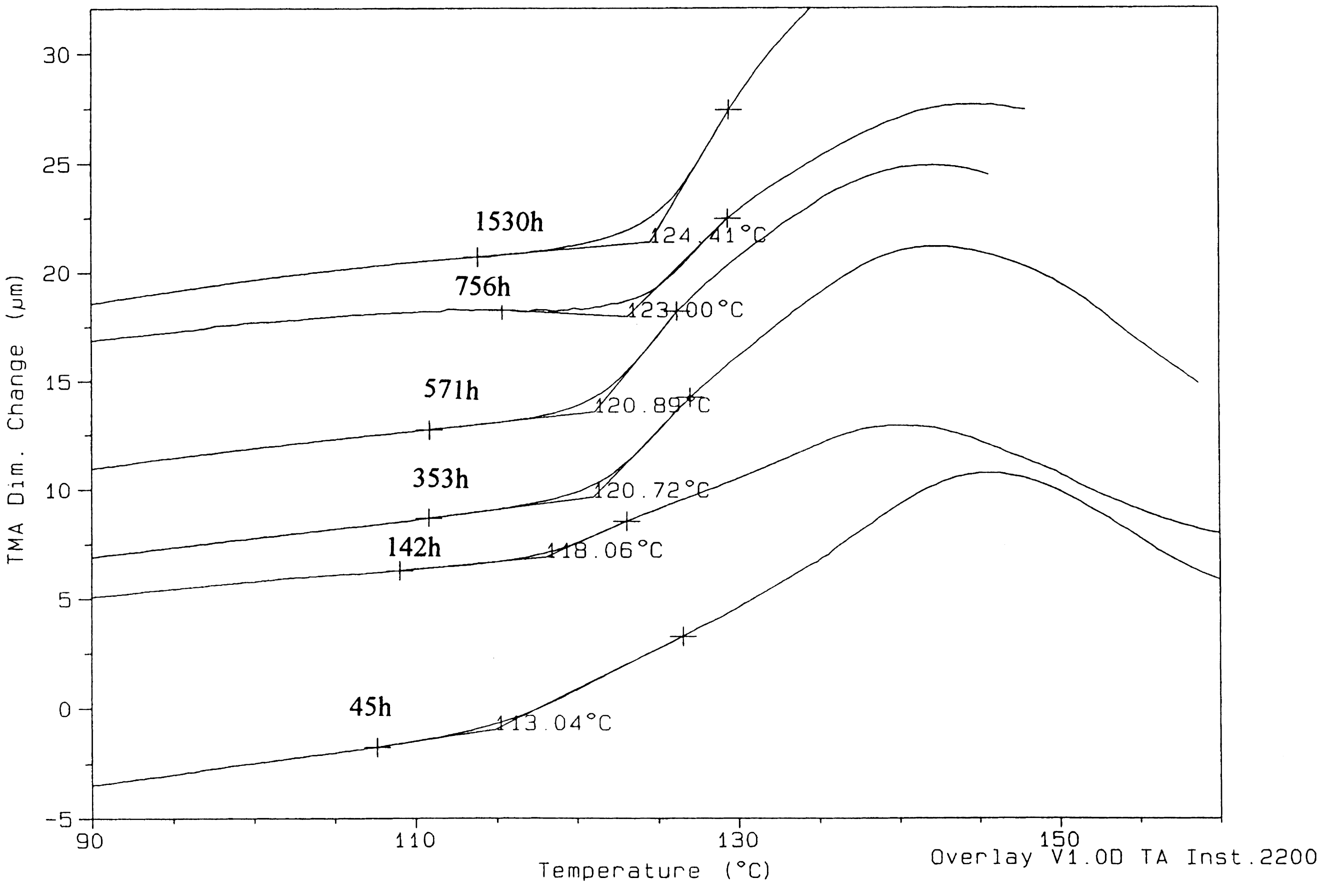

Fig. 2. T_g change of DGEBA + mPDA with exposure time, the exposure temperature was 90°C.

reported by Carter [14] and McKague [15]. In this study, 7 x 7 x 2 mm test were immersed in distilled water at constant temperatures of 45°C, 60°C, 75°C, and 90°C for 1530 h and then desorbed at different temperatures.

3. Results

3.1. T_g change with exposure time

The change in T_g with time for the three epoxy resins hygrothermally exposed at 90°C are shown in Figs.1,2, and Fig. 3. The materials were immersed in water at 90°C for up to 1530 h. After a 45 h exposure, TGDDM + DDS samples saturated and the observed T_g value was 121°C. Under similar hygrothermal conditions, however, at 1500 h the T_g value observed was 132°C (Fig. 1). For the DGEBA + mPDA resin, the change in T_g ranged from 113°C–124°C over the same temperature and time duration (Fig. 2). Fiberite 934 shows T_g variations ranging from 113°C–126°C (Fig. 3). T_g change with exposure time was observed at lower exposure temperatures (i.e., 60°C and 75°C). Figs. 4 and 5 show the T_g change with exposure time at 90°C and 60°C for the three epoxy resins, respectively. The upper figures (Fig. 4a and Fig. 5a) show corresponding water absorption data. Both Figs. 4 and 5 indicate sharp T_g depression during the initial stages of water uptake in the materials. The minimum value of T_g (or the maximum degree of T_g depression) occurs when the resins first saturate. Afterwards, T_g increases with exposure time under isothermal and fixed saturation conditions. On average, the increase in T_g is about 15°C after hygrothermal exposure for 1530 h. The effect of exposure time on the T_g variation (i. e., T_g increase) is well exemplified in Figs. 4 and 5.

3.2. T_g change with exposure temperatures

Comparing Figs. 4 and 5 it follows that T_g depression of materials exposed at 90°C is always less than materials similar exposed at 60°C. These similar trends were observed in all epoxy systems investigated. This indicates that the extent of T_g depression is influenced by exposure temperatures. To verify the influence of temperature on T_g variation, tests were conducted under fixed exposure time at different temperatures.

After immersion in water at 45°C, 60°C, 75°C and 90°C for 1530 h, T_g was measured and the results are shown in Fig. 6, Fig. 7 and Fig. 8. Samples exposed at higher immersion temperature exhibit higher T_g values (less T_g depression) even though the maximum water uptake for exposed

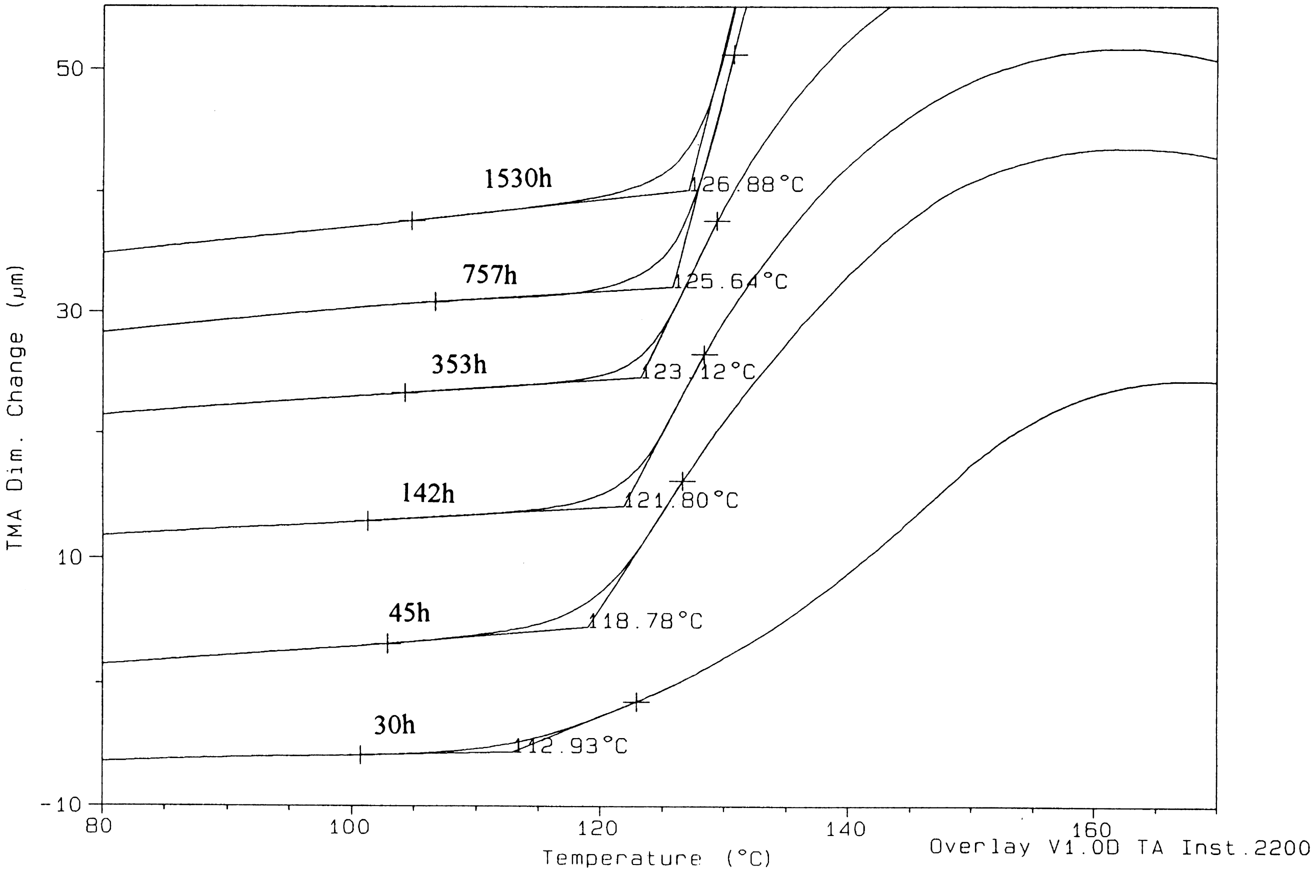

Fig. 3. T_g change of Fiberite 934 with exposure time, the exposure temperature was 90°C.

samples were essentially the same ($M_{max} = 6.8$ wt% for TGDDM + DDS, 3.3 wt% for DGEBA + mPDA, and 6.9 wt% for Fiberite 934).

The effect of thermal history on the extent of T_g depression is appreciable and readily apparent. The range of difference in the T_g values is 45°C for TGDDM + DDS, 43°C for DGEBA + mPDA, and 39°C for Fiberite 934 epoxy system. Similar effects of exposure temperature on the extent of T_g depression were demonstrated in a previous study [12] for carbon fiber composites, Fiberite T300/934.

Fig. 9 shows the T_g values of the DGEBA + mPDA determined by TMA and DSC. Consistent T_g values were obtained using DSC and TMA test.

3.3. *T_g change at various desorption stages*

After exposure for 1530 h, all water-saturated samples were placed in a dry environmental chamber at 60°C to begin the water desorption process. Water desorption was allowed to take place over 1430 h. Although most of the sorbed water diffused out of the material at the 60°C desorption temperature, a much smaller amount of residual water could not be removed until the desorption temperature was raised to 140°C for 240 h. T_g was measured after each of the desorption process schedules described above. Table 1 contains T_g values of the materials obtained at various hygrothermal conditions which include the following: i) as-prepared dry, ii) water-saturated at 60°C after 1530 h, iii) semi-dried (60°C desorption), and iv) re-dried (140°C desorption) samples. It is interesting to note that under the semi-dried condition T_g is recovered despite a small amount of residual water still persisting in the resins (see Part I Table 2). That suggests that the residual water is not acting as a plasticizer. After bake-out at 140°C for 240 h, the materials were fully dried. For the fully dried materials, the T_g has completely recovered to the initial value and there is essentially no change compared with the T_g of semi-dried samples. That is no depression of T_g.

4. Discussions

The experimental results indicate that the T_g of a water-saturated epoxy depends strongly on exposure time and temperature. At the time when the hygrothermally-exposed materials first reach saturation, the depression of T_g is greatest. However, T_g begins to gradually recover with time post saturation. Higher immersion temperature and longer time induce a greater degree of recovery of T_g. The results are quite different from the traditional point of view, which proposes that T_g variation is simply a matter of the amount of water uptake of the material. Some previous experimental

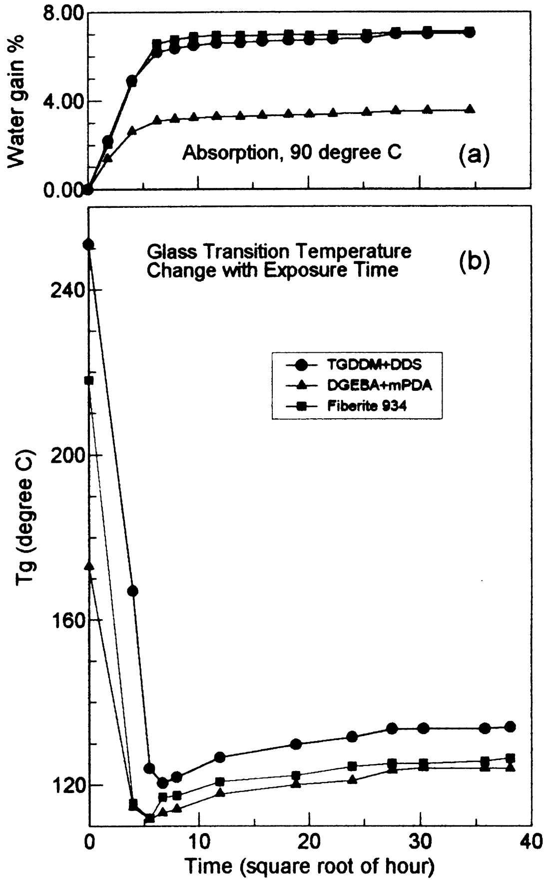

Fig. 4. T_g change with exposure time. Samples were immersed in water at 90°C for 1530 h. The upper figure is the corresponding water absorption profiles at the same temperature.

results that will be discussed later in this paper supported the viewpoint. Other researchers [2,3] used a polymer-diluent model for theoretical prediction of T_g variation. This model was introduced by Kelley et al. [1] to predict T_g change associated with diluent media diffusion in a polymer.

According to the polymer-diluent model, the glass transition value of water saturated epoxy T_{gwet} can be calculated by using the two equations below [1]:

$$T_{gwet} = \frac{\alpha_e V_e T_{ge} + \alpha_w (1 - V_e) T_{gw}}{\alpha_e V_e + \alpha_w (1 - V_e)} \tag{1}$$

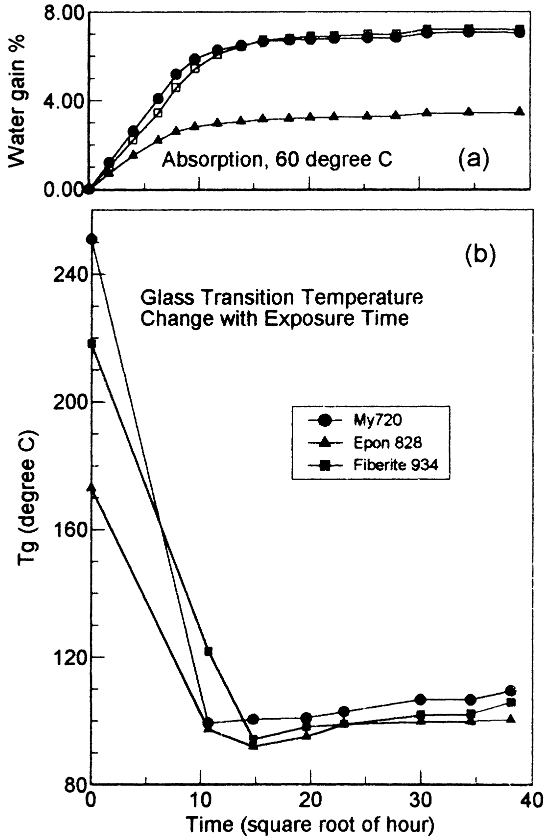

Fig. 5. T_g change with exposure time. Samples were immersed in water at 60°C for 1530 h. The upper figure is the corresponding water absorption profiles at the same temperature.

$$V_e = \frac{1}{1 + 0.01 M_m (\rho_e / \rho_w)} \tag{2}$$

Here, ρ_e = density of dry epoxy; M_m = equilibrium water content; V_e = volume fraction of epoxy; α_{re} and α_{ge} are rubbery and glassy linear thermal expansion coefficient respectively determined by TMA dimensional change trace; epoxy volumetric expansion coefficient $\alpha_e = 3(\alpha_{re}\text{-}\alpha_{ge})$; T_g of water $T_{gw} = 4^{\circ}\mathrm{C}$; water expansion coefficient $\alpha_w = 4 \times 10^{-3}/^{\circ}\mathrm{C}$; and density of water $\rho_w = 1\ \mathrm{g/cm^3}$. From the two expressions it is apparent that the predicted T_g values for the materials will be the same provided the amount of water uptake is the similar, regardless of the exposure temperatures and time.

Table 1
T_g change of the three epoxies in different hygrothermal stages

	T_g of dry as-prepared sample (°C)	T_g of sample saturated at 60°C 1530 h (°C)	T_g of sample desorbed at 60°C for 1450 h (°C)	T_g of sample desorbed at 60°C 1450 h & then 140°C 240 h (°C)
TGDDM + DDS	251	108.5	250	251.5
DGEBA + mPDA	173	98	173	173
Fiberite 934	218	106	218	219

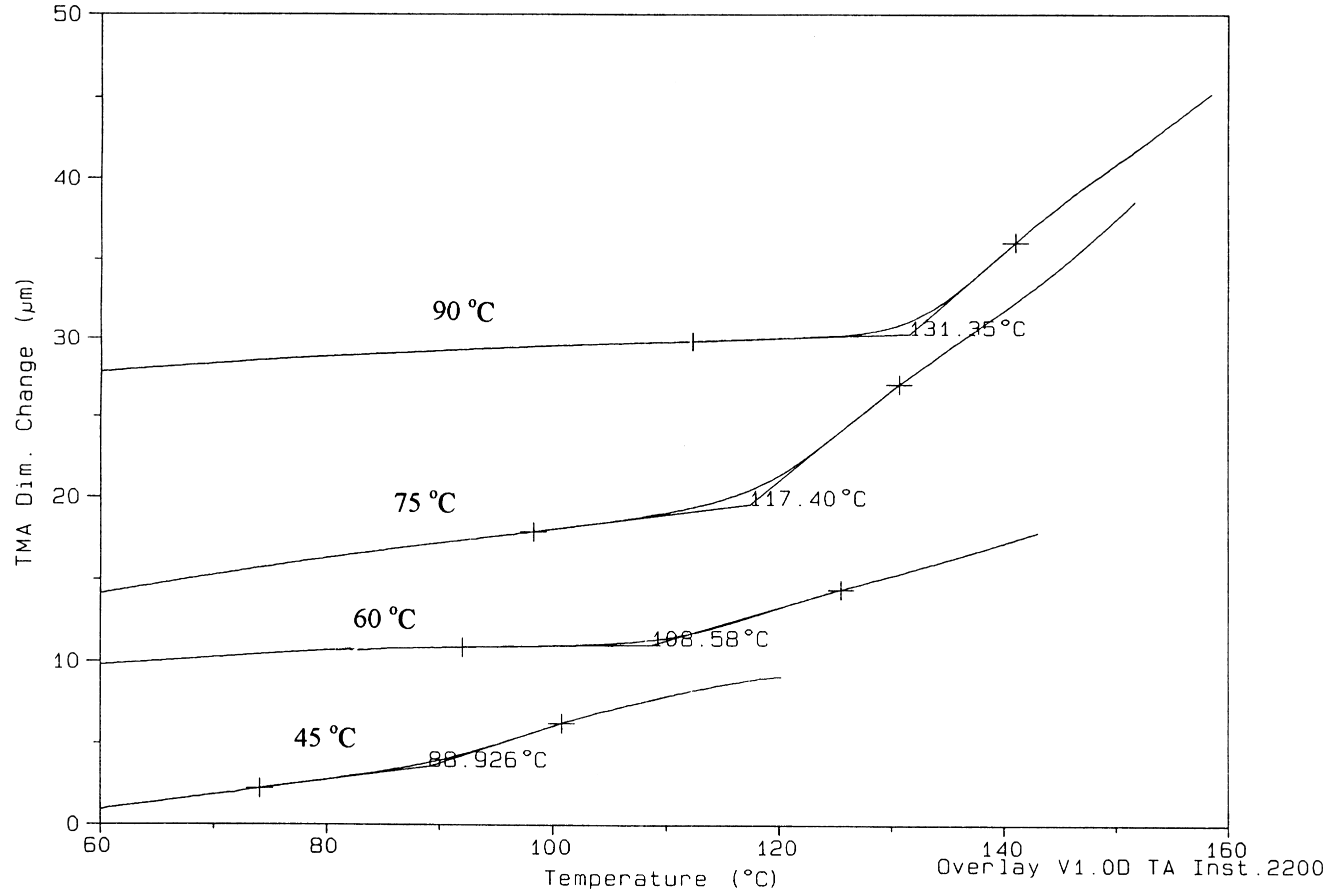

Fig. 6. T_g change of TGDDM + DDS with bath temperatures after immersion in water for 1530 h.

Since all epoxy resin parameters needed to determine the T_{gwet} can be obtained conveniently by experiment or from cited literature, T_{gwet} of the three resins was calculated by Kelly-Bueche model. All material data experimentally obtained in this study are listed in Table 2. The calculated and experimental T_g results of the three epoxies are shown in Table 3. Quite apparent is the difference in the predicted glass transition temperature, which is based on the ‘‘polymer-diluent’’ model and the experimentally determined T_g. It appears that this model is not appropriate for some polymers with strong polar groups such as hydroxyls. The model is incapable of predicting the T_g of water saturated epoxy resin where a dual-mechanism governs the nature of T_g as proposed here.

Since the previous models do not provide satisfactory explanation and prediction of the T_g variations observed for hygrothermally exposed epoxy resins, a new interpretation is proposed in this study according to the experimentally-determined T_g results and the nature of water interaction in epoxy described in the Part I. Water molecules diffuse into the material and, effectively, disturb the interchain bonding established by Van der Waals force and initial hydrogen bonds in the epoxy resin. As a consequence of this disturbance, so-called Type I bonded water forms with the chain network. The net effect of this interchain

Table 2
Experimental data of the three epoxies. T_g of dry epoxy T_{ge}; density of epoxy ρ_e; equilibrium water content M_m; volume fraction of epoxy V_e; rubbery and glassy thermal expansion coefficient α_{re} and α_{ge}; epoxy volumetric expansion coefficient $\alpha_e = 3(\alpha_{re}\text{-}\alpha_{ge})$

	TGDDM + DDS	DGEBA + mPDA	Fiberite 934
T_g (°C) (dry, as prepared)	251	173	218
ρ_e (g/cm^3)	1.26	1.19	1.28
M_m (%)	6.8	3.35	6.95
V_e	0.9211	0.9617	0.9183
α_{re} (cm/cm°C)	6.7×10^{-5}	1.45×10^{-4}	8.4×10^{-5}
α_{ge} (cm/cm°C)	1.86×10^{-5}	2.8×10^{-5}	2.4×10^{-5}
α_e (cm^3/cm$^{3\circ}$C)	4.5×10^{-4}	6.1×10^{-4}	5.4×10^{-4}

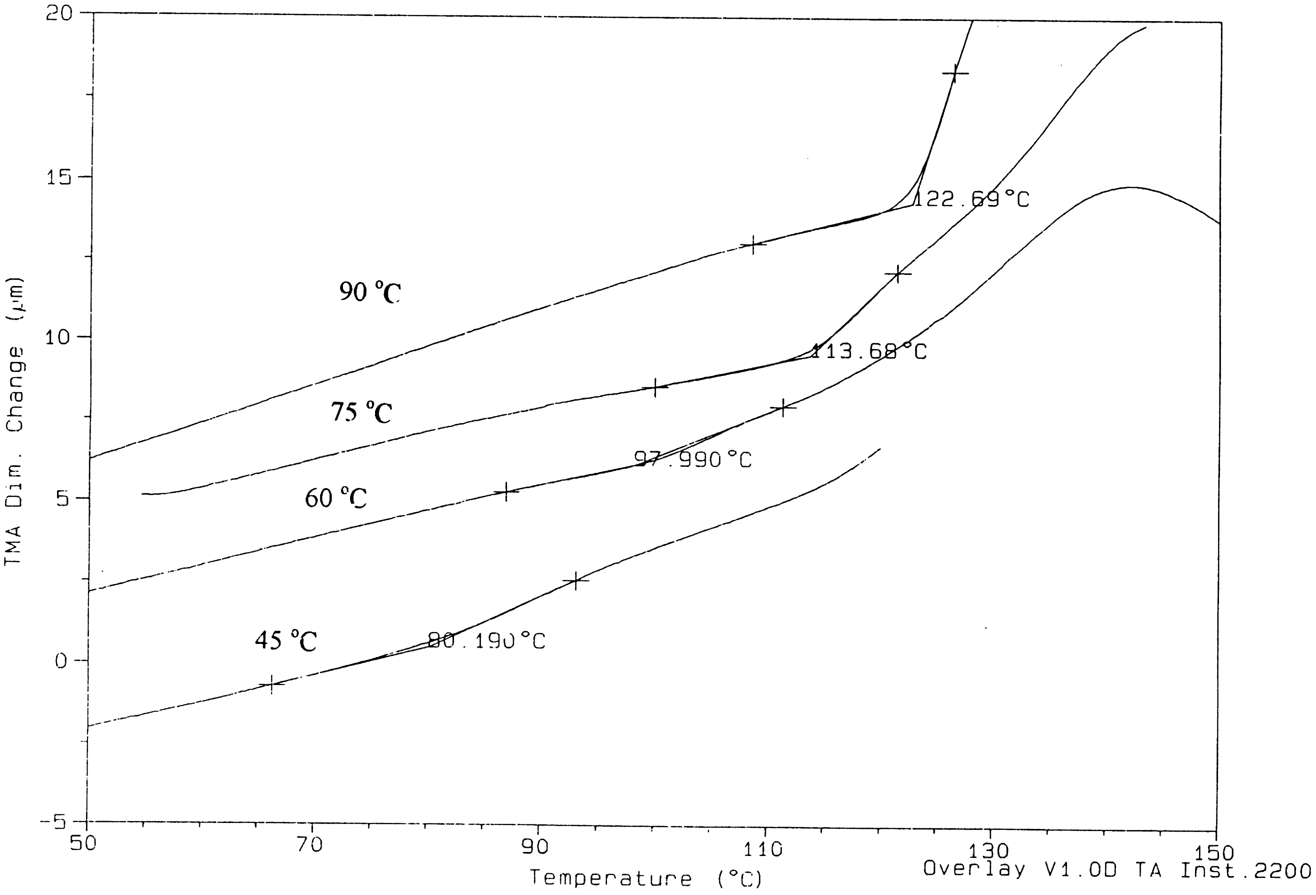

Fig. 7. T_g change of DGEBA + mPDA with bath temperatures after immersion in water for 1530 h.

bond breakage is the increase in chain mobility that contributes to T_g depression. With increasing water absorption, more interchain bond breakage occurs resulting in a precipitous drop in T_g. Assuming that T_g is affected solely by just the amount of water diffused into the resin, the ensuing rationalization can be made. If only Type I bound water existed in the resin materials, the T_g of the resin system would be independent of hygrothermal-exposure conditions, since, previous models and experimental results suggest that only the amount of water uptake matters. This implies that T_g, determined experimentally, will be unaffected by exposure temperature and exposure time duration. The observed T_g results from the current study refute this.

In previous studies [2,3] the nature of water absorbed in the resin is described singly by Type I bound water. However, this study suggests that Type II bound water also exists as a viable resin/water-binding complex in epoxy resins. As described in Part I of the study, the amount of Type II bound water increases with immersion time and higher immersion temperature. Since the extent of T_g depression decreases and the quantity of Type II bound water increases with higher hygrothermal temperature and time, this indicates that Type II bound water has a significantly functional role in affecting T_g. Type II bound water promotes secondary crosslinking with hydrophilic groups such as hydroxyls and amines in the epoxy network [13]. This increased crosslink density contributes to the lowering of T_g depression in epoxy resins. We contend that T_g value is influenced by a dual-mechanism process. That is, Type I bound water causes a steep drop in T_g owing to breakage of interchain bonds and Type II bound water lessens the

Table 3
Comparison of the experimental and the calculated T_g of water-saturated epoxy resins. The calculation was based on the polymer-diluent model. The experiment results were tested by TMA and vary from different immersion temperatures and exposure time

	TGDDM + DDS	DGEBA + mPDA	Fiberite 934
T_g (°C) (dry, as prepared)	251	173	218
T_{gwet} (°C) (calculated)	144	120	133
T_{gwet} (°C) (experimental)	81–132	80–124	87–127

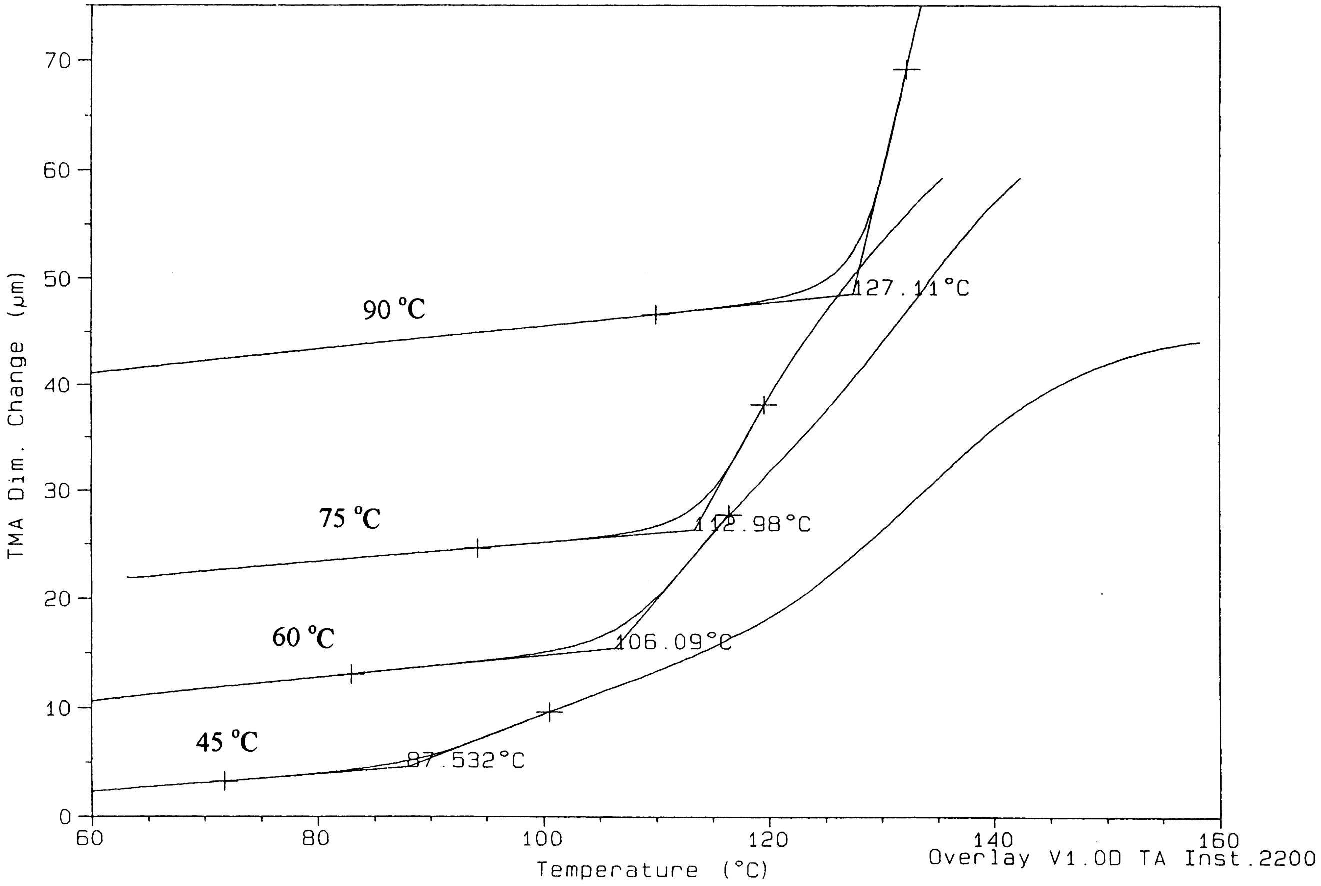

Fig. 8. T_g change of Fiberite 934 with bath temperatures after immersion in water for 1530 h.

drop in T_g via secondary crosslinking resulting from water-resin network interaction. In a succinct summary, the T_g variation can be described as follows. When the epoxy resins initially saturate with T_g depression is greatest. Also, we contend that the sorbed water is partitioned such that the amount of Type I bound water is much more prevalent that Type II bound water. With exposure time and temperatures, however, more Type II bound water persists and correspondingly there is a lessening T_g in depression.

When Type I bound water is removed under conditions where the desorption temperature is comparable to the absorption temperature, Type II bound water is still retained in the resin and the T_g is completely recovered. This observation indicates the dominance of Type I bound water on influencing T_g depression. The removal Type I bound water in turn restores interchain Van der Waals bonding and T_g quickly recovers. The secondary crosslink effect on T_g is relatively weak and masked by the recovery of interchain bonding. An increase in T_g induced by Type II bound water has been observed at the semi-dried desorption stage [12].

This interpretation can be applied reasonably well to explain previous works [4,10,13]. DeIasi [10], Moy [4], and DeNeve [13] reported T_g test results for epoxy resin. Their experiments were carried out at constant exposure temperature with varying relative humidity. They found that T_g was proportional to water uptake in the material. The rational for this observation is that for specimens tested at the same exposure temperature and time but different relative humidity, all of the specimens should have the same amount of Type II bound water since Type II bound water is controlled by exposure temperature and time. The only difference is the amount of Type I bound water since the maximum moisture level is determined solely by relative humidity. Higher relative humidity creates conditions for more water uptake in the resin and, thus, this increases T_g depression.

5. Summary and conclusions

The variation in T_g of epoxy exposed to a hygrothermal environment is rationalized as follows: i) the change in T_g does not depend solely on the water content alone in epoxy resins, ii) T_g is influenced by the hygrothermal history of the materials, iii) for a given epoxy system longer time and higher exposure temperature result in higher value of T_g, and iv) Type I and Type II bound water influences on T_g variation by quite different mechanisms and in opposing ways. Type I bound water breaks the initial interchain Van der Waals force and hydrogen bonds resulting in the

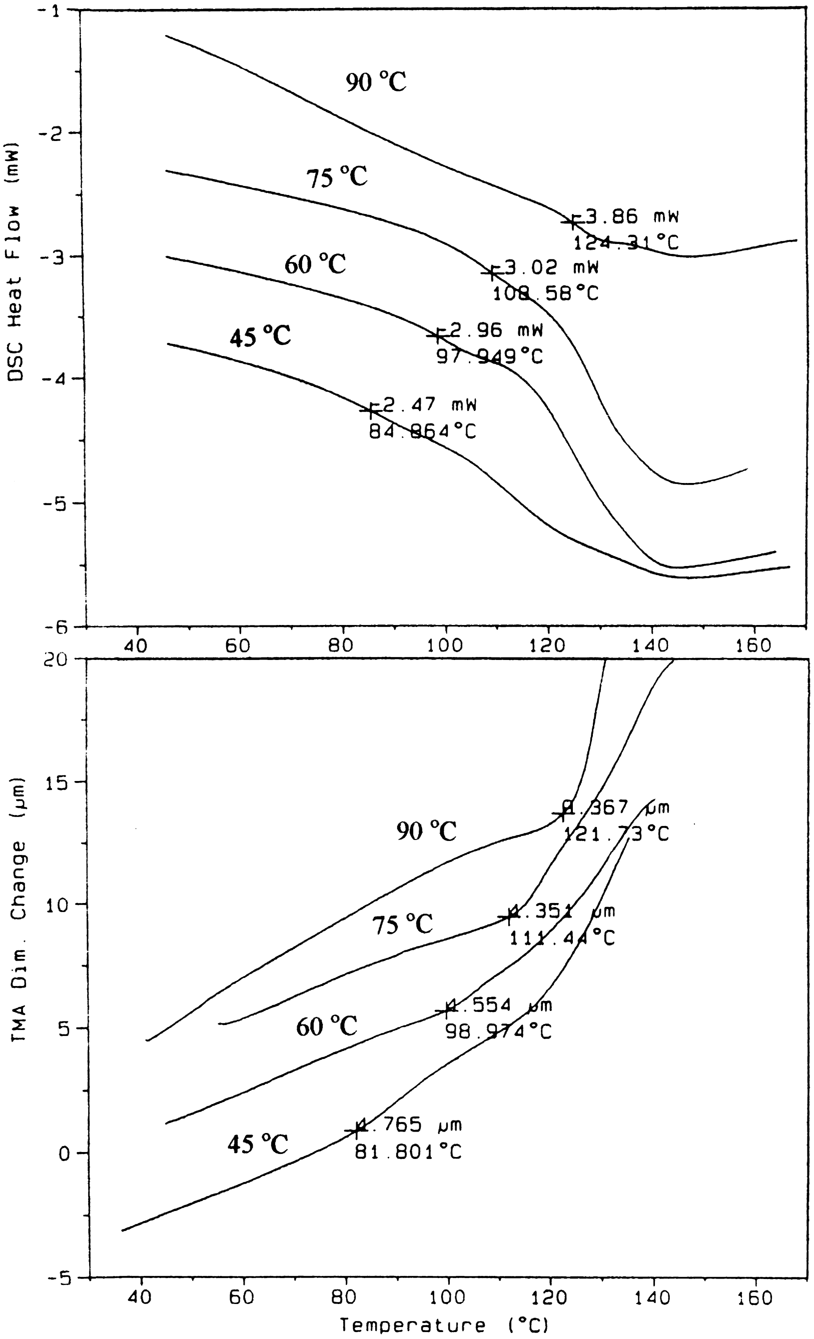

Fig. 9. T_g test results of DSC and TMA. The material is DGEBA + mPDA immersion in water for 1530 h at different temperatures.

increase of chain segment mobility. So, it acts as a plasticizer causing large depression in T_g. In contrast, Type II bound water lessens the extent of T_g depression in the water saturated materials as a result of secondary crosslinking. Experimentally determined T_g values represent the combined effect of the two mechanisms. The popular polymer-diluent model used to predict T_g is insufficient when dual-sorption mechanisms are operative under hygrothermal conditions.

References

[1] Kelley FN, Bueche F. J Polymer Science 1961;L:549.
[2] Browning CE. Polymer Engineering and Science 1978;18(1):16.
[3] Wright WW. Composites 1981;201.
[4] Moy P, Karasz FE. Polymer Eng and Sci 1980;20:315.
[5] Apicella A, Tessieri R, de Cataldis C. J Membrane Science 1984;18:211.
[6] Adamson MJ. J Mat Sci 1980;15:1736.
[7] Bellenger V, Verdu J. J Mat Sci 1989;24:63.

[8] Barrie P, Sagoo PS, Johncock P. J Membrane Science 1984;18:197.
[9] Jelinski LW, Dumais JJ, Cholli AL, Ellis TS, Karasz FE. Macromolecules 1985;18:1091.
[10] DeIasi R, Whiteside JB. In: Vinson JR, editor. Advanced composite materials–environmental effects. ASTM STP 658, American Society for Testing and Materials 1978:2.
[11] Mijovic J, Weinstein SA. Polym Commun 1985;26:237.
[12] Zhou J, Lucas JP. Proc of the 9th Conf of the ASC, p. 1213, Technomic Publishing, 1994.
[13] DeNeve, Shanahan MER, Reynolds JD. Polymer 1993;34:5099.
[14] Carter HG, Kibler KG, Reynolds JD. In: Vinson JR, editor. Advanced composite materials–environmental effects. ASTM STP 658,1978:84.
[15] McKague Jr. EL, Reynolds JD, Halkias J. J Appl Polymer Sci 1977;22:1643.