

Effects of Moisture on Properties of Epoxy Molding Compounds

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Received 10 June 2000; accepted 2 December 2000

ABSTRACT: In this article the effects of moisture on a novel epoxy molding compound, including the mechanical properties, temperature transition, and thermal degradation behavior, are studied. The experimental results reveal that the absorbed water acts predominantly as a crazing agent, continuously decreasing the mechanical strength with the time in water. The glass-transition temperature decreases at the early stage and is finally equilibrated. The thermal degradation behavior of the materials is not greatly influenced by the hydrothermal age. The decomposition of samples in oxygen is composed of two independent steps: the thermal degradation and oxidation at high temperature. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2253–2259, 2001

Key words: hydrothermal age; water absorption; epoxy molding compound; glass-transition temperature; mechanical property

INTRODUCTION

Electrical and electronic devices have been encapsulated in a variety of resinous materials, including epoxy, silicone, and phenolic materials. Epoxy molding compounds for the encapsulation of electronic components are considered a specialty market by the epoxy manufacturers. The worldwide consumption of electronic grade molding compounds was approximately 100,000,000 metric tons in 1997 and is still growing. The amount of epoxy resin used in these compounds is approximately 10% of that figure. Electronic grade epoxy resins must have a higher degree of purity than

the commodity epoxy resins. The halogen content of these resins is usually less than 800 ppm and they are much more difficult to manufacture than the standard resins.¹

Polymeric materials differ from other structural materials in that, at ambient temperatures, low molecular weight substances can easily migrate in them freely. Early studies of the adsorption mechanisms and diffusion of small molecules in plastic materials arose from the desire to prepare barrier materials, mainly against gases and moisture.

Over the years, a few aspects of the moisture transport process in epoxies have become clear.^{2–5} The most significant development was realizing the role of polarity in determining the ultimate moisture uptake. Water is a polar molecule and capable of hydrogen bonding with other polar species such as hydroxyls and amines in the epoxy.

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Contract grant sponsor: Sang Jin Silicone Co., Ltd., Korea.

Journal of Applied Polymer Science, Vol. 81, 2253–2259 (2001)
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Empirical, linear-additive relations based on the polar group concentration describe the equilibrium moisture uptake in linear thermoplastics and thermoset resins. In addition to polar interactions, chain topology must be considered in a discussion on the absorption process. Different molecular configurations can result in a more "open" structure, which should influence how much moisture is absorbed.⁶⁻⁸ The essence of this idea of openness is captured by the free-volume arguments. Researchers have tried to relate both the equilibrium uptake and diffusion coefficient to the free-volume content of the materials. The fact that properties differences between desiccated and soaked samples exist supports the concept that physical modifications are introduced into the polymer network by the moisture-temperature aging. Although the exact nature of this change has not been completely identified, previous investigations offered explanations related to the microvoiding and crazing of the polymer or by assuming a dual state of the water in the cured epoxies.^{9,10}

The environmental degradation of the mechanical properties of epoxy polymers is associated with the plasticization and micromechanical damage induced by the absorbed moisture.^{11,12} Water molecules reportedly act as plasticizers or crazing agents for the epoxides, strongly influencing the properties of the materials subjected to temperature, humidity, and stress fatigue tests.¹³⁻¹⁵

In this article a novel epoxy molding compound for application in the electronics industry is used to conduct hydrothermal aging tests. The effects of water molecules on the mechanical properties, glass-transition temperature (T_g), and degradation behavior of epoxy molding compounds are studied. The experimental data from aged and unaged samples in water are compared.

EXPERIMENTAL

The resin used in this study was a commercial mineral filled diglycidyl ether of bisphenol A based epoxy compound (MG6-0330, The Dexter Corporation), which contains acid anhydride hardeners and a filler content of 72%. The samples for the mechanical property and water-resistance tests were processed by transfer molding at 135-177°C and postcured at 150°C for 2 h.

A group of specimens was soaked in a water bath at 30°C. The moisture intake in the speci-

Table I Physical Properties of Dry and Water Equilibrated Epoxy Molding Compounds at 30°C

Time in Water (h)	σ (MPa)	ϵ (%)	Water Uptake (%)	T_g (°C)
0	7.62	1.08	0	101.3
24	7.66	1.16	0.014	95.8
72	7.06	1.05	0.047	92.5
120	6.66	1.27	0.044	92.7
168	5.74	0.87	0.035	91.2

mens was observed by periodically recording the mass of the specimens. The tensile strength measurements were conducted with an Instron mechanical testing machine (Shimadzu) according to the procedures described by ASTM D543 and D1259 for the original and water soaked samples, after which they were weighed immediately. An Instrumental Specialists TGA-1000 thermogravimetric (TG) analyzer was used to obtain weight loss data for original samples and samples after the water-resistance tests. Water equilibrated samples were dried in a vacuum at ambient temperature before the TG analysis (TGA) measurements. For the dynamic thermal degradative runs the samples were purged with nitrogen gas at a flow rate of 50 mL/min. Constant heating rates of 5, 10, 20, and 50 °C/min were used. Isothermal TGA was performed under an oxygen atmosphere at different temperatures. The sample weights were in the range of 20-50 mg in all cases. The glass-transition temperature was measured by DSC at a heating rate of 10 K/min under a nitrogen atmosphere. More details about the calibration procedure and thermal conditions can be found elsewhere.^{16,17}

RESULTS AND DISCUSSION

The mechanical properties and water uptake of epoxy molding compounds before and after soaking in water are listed in Table I and plotted in Figure 1. It is clear that the apparent water uptakes in the materials were saturated in 3 days, and then they slightly decreased. The low moisture adsorption in epoxy molding compounds is related to the low resin component, which also affects the other properties mentioned above, and the application of acid anhydride curing agent. The curing agent lowers the polarity of cured

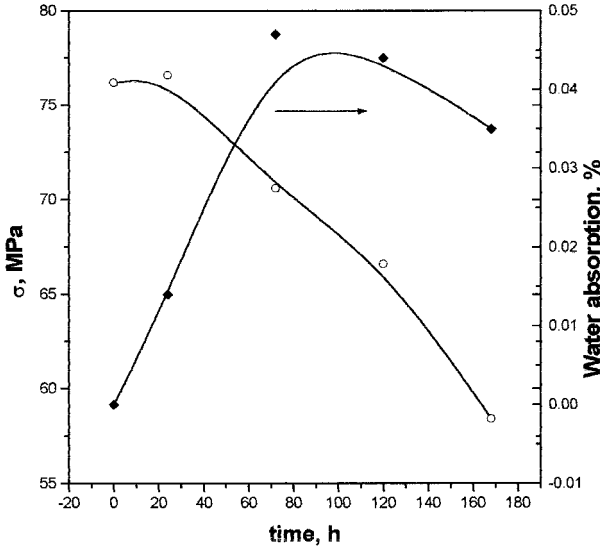


Figure 1 The mechanical property change and water absorption with the time in water.

materials and decreases the formation of hydrogen bonds as in amine-cured epoxy systems, where moisture uptakes of 2–5% can be easily reached under environmental conditions, leading to a significant drop of T_g , even well below the application limits of most of the epoxy materials. It was also reported that at lower temperatures the translational freedom of the water molecules was strongly hindered by the stiffness of the polymer chain segments, and the formation of clusters was kinetically unfavored and was usually not observed in short-term experiments.¹⁸ Otherwise, the high-pressure processing of samples is also advantageous to decrease the “holes” generated during the vitrification and to lower the absorption of moisture due to the dense molecule packing in cured materials, where very little room exists for a penetrant molecule. The slight drop in water uptakes with time may be associated with the progressively greater damage developed in these inhomogeneous materials or with the solution of some additives in the compositions. The change of the glass-transition temperatures with time is given in Figure 2. As the water was absorbed the tendency of the glass-transition temperature to decrease was terminated after 72 h because it was mainly caused by the plasticization of the sorbed water. Thus, the glass-transition temperature of this compound was not greatly depressed by the absorption of moisture as were the amine-cured systems because of its low polarity and hydrogen bond concentration.

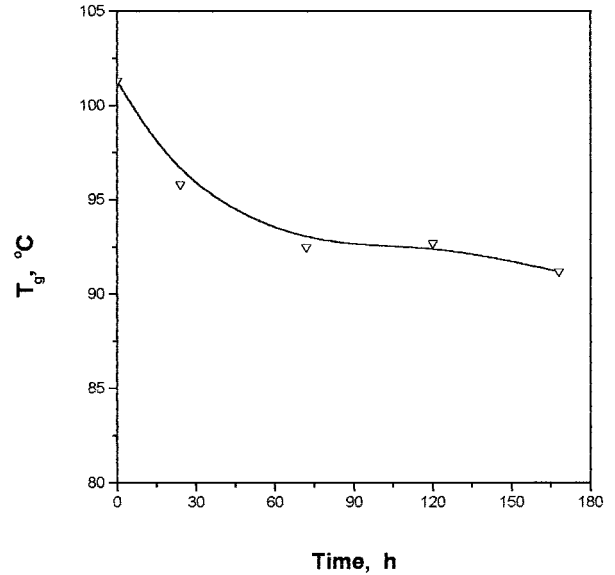


Figure 2 The glass-transition temperature change as a function of time for epoxy molding compounds.

The unaged epoxy molding compounds had an average tensile strength of 7.62 MPa, an elongation at break of 1.08%, and a Young’s modulus of 6.64 GPa. The tensile strength decreased with increasing time. However, as shown in Table I, the elongation at break did not seem to be markedly changed and the glass-transition temperature also did not decrease further with time and was practically equilibrated after 72 h. Thus, the decrease in mechanical strength could be attrib-

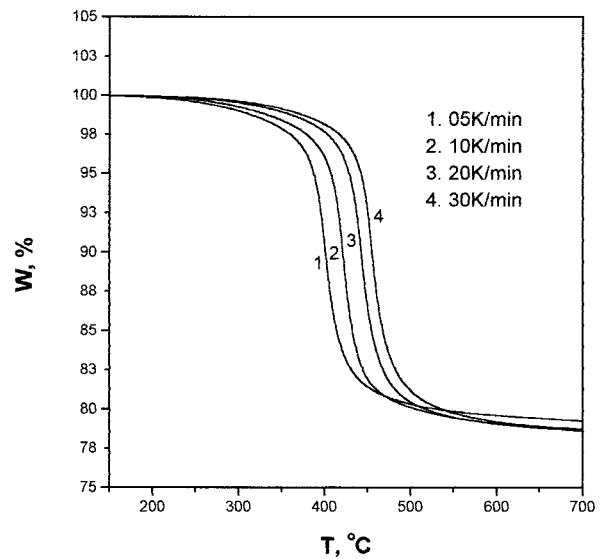


Figure 3 TG thermograms of epoxy molding compounds at various heating rates.

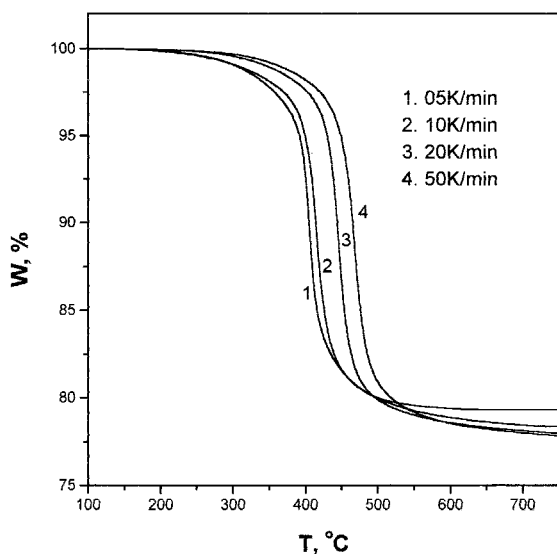


Figure 4 TG thermograms of samples in water for 120 h at various heating rates.

uted to the crazing effect of water; in other words, water acted predominantly as a crazing agent for this observed system, thus resulting in a continued decrease in the mechanical strength with time (Fig. 1).

Figures 3 and 4 show the TG curves of the original and aged samples at heating rates from 5 to 50 °C/min. For a thermal degradation analysis a number of experimental indices are often used to characterize the process of thermal decomposition, including the onset temperature of decomposition (T_{onset}), the temperature of the maximum rate of decomposition ($T_{d,\text{max}}$), and the average energy of activation (E_d).

These indices, especially the characteristic temperatures, are dependent on the heating rate applied during pyrolysis (Table II). The thermograms shifted to higher temperatures as the heating rate increased. The shift of the onset to a higher temperature with increasing heating rate

was due to the shorter time required for a sample to reach a given temperature at the faster heating rates.

Comparing the data in Table II makes it clear that the degradation behavior of epoxy molding compounds was not drastically affected by water and showed excellent temperature resistance, although their glass-transition temperature (101.3°C) was much lower than that of aromatic amine-cured systems. This may be attributed to the high content of inorganic filler and the high quality resin used in these compounds.

Although there are several methods for calculating kinetic parameters, it is commonly believed that nonisothermal methods describe the degradation process better.^{19,20} In our previous work we observed that the kinetic analyses that involved multiple constant heating rates, such as the Osawa and Kissinger methods, were superior to other methods,¹⁷ a summary of which follows.

Osawa used a linear empirical approximation given by Doyle to approximate the integral form of the basic rate-conversion relation.²¹ The resulting equation is

$$\log \beta = -0.4567 \frac{E_d}{RT} + \left[\log \frac{ZE_d}{R} - \log g(\alpha) - 2.315 \right] \quad (1)$$

Thus, at the same conversion, a plot of $\log \beta$ versus $-1/T$ should be a straight line with a slope of $0.4567E_d/R$. If E_d does not change with conversion, α (weight of polymer volatilized/initial weight), a series of parallel straight lines are obtained. The $\log Z$ can be calculated from the intersection of the Y axis as

$$\log Z = \log \beta + \frac{0.457}{RT} + 2.315 - \log E_d + \log R + \log g(\alpha) \quad (2)$$

Table II Characteristic Temperatures of Materials by TGA

Heating Rate (K/min)	T_{onset} (°C)		T_{max} (°C)		Residual (%)	
	Original	120 h in Water	Original	120 h in Water	Original	120 h in Water
5	312.3	292.7	402.5	396.1	79.04	79.16
10	339.3	318.9	412.7	417	78.39	78.37
20	325.3	355.1	431.6	427.4	78.27	77.97
50	412.6	425.8	471.7	460.1	78.29	77.58

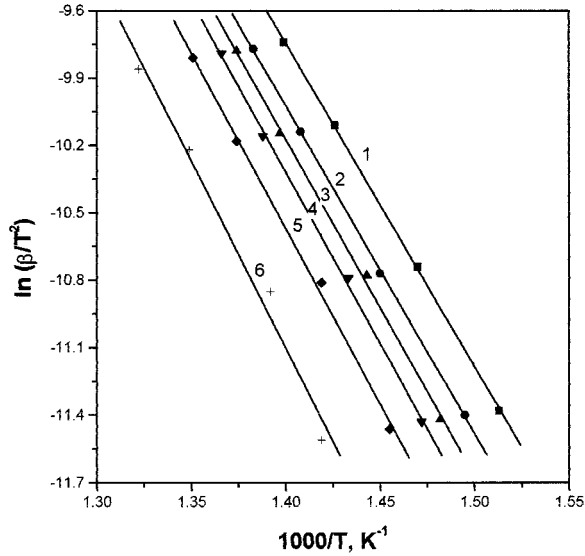


Figure 5 Kissinger plots for epoxy molding compounds at different conversions.

where $\log g(\alpha)$ is a function of conversion.

Kissinger, however, used an approximation based on successive integration by parts and then retaining only the first term in a rapidly converging series.²² The final expression is

$$\ln\left(\frac{\beta}{T^2}\right) = -\frac{E_d}{RT} + \left[\ln \frac{ZR}{E_d} - \ln g(\alpha) \right] \quad (3)$$

Thus, a plot of $\ln(\beta/T^2)$ versus $-1/T$ at constant conversion should be a straight line of slope

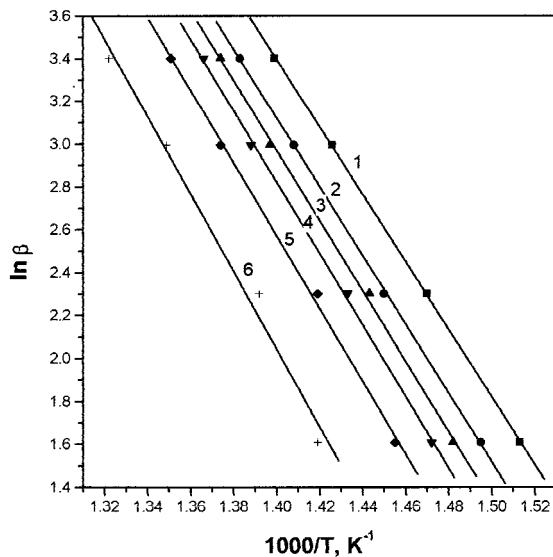


Figure 6 Osawa plots for epoxy molding compounds at different conversions.

Table III Activation Energy at Different Conversions for Original and Aged Samples

Conversion (%)	E_d (kJ/mol)			
	Original		Aged in Water	
	Kissinger	Osawa	Kissinger	Osawa
5	119.7	124.4	136.5	140.7
7.5	121.3	126.8	133.8	138.5
10	124.5	129.4	136.3	141.0
12.5	126.8	131.9	136.4	141.2
15	129.8	134.1	138.1	143.0
17.5	134.2	137.3	138.6	147.5

$-E_d/R$. This expression is also given by the American Society for Testing and Materials (ASTM).

Figures 5 and 6 show the Kissinger and Osawa plots at various conversions for the original samples. Similar results were also obtained for samples soaked in water for 120 h. Both methods exhibited very good linear relationships. The decomposition activation energies at different conversions were calculated. Those values are listed in Table III and also plotted in Figure 7. The values by both methods were in the same magnitude. However, it is worthy to note herein that the activation energy values for unaged samples were not a constant throughout the whole degradation process, as supposed in many works. It increased with increasing conversion. The detailed mecha-

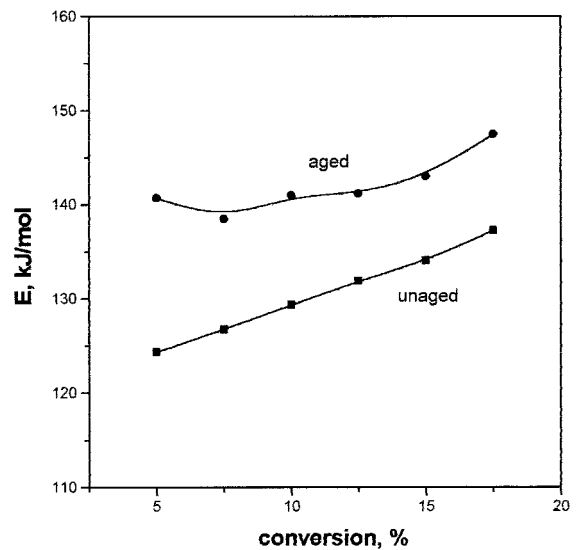


Figure 7 The activation energy change as a function of conversion for both systems.

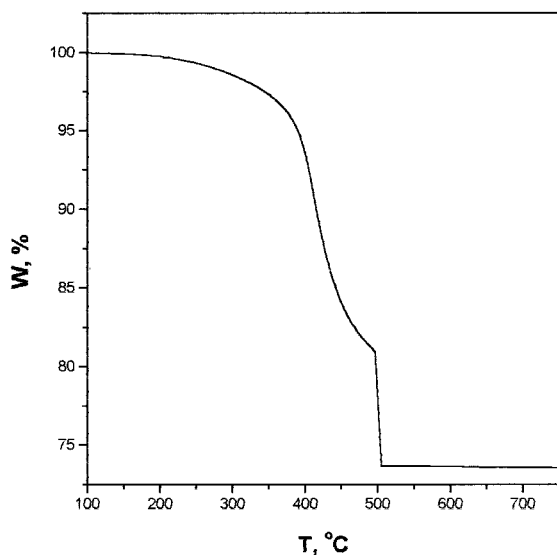


Figure 8 TG thermograms of epoxy molding compounds at 10°C/min in oxygen.

nisms are still not clear. Perhaps it was related to the fact that the samples did not reach the completed curing under isothermal conditions.

The degradation behavior of epoxy molding compound materials in oxygen were also observed. As shown in Figure 8 and Table IV, we found that the decomposition process of the materials in oxygen comprised two steps. A comparison of the results with those obtained under a nitrogen atmosphere made it clear that the first step had the same mechanism as the degradation in nitrogen. The values of T_{onset} and T_{max} and the shape of the curves were almost the same in both cases. The thermal degradation process was nearly completed according to the weight loss in the first step, which was little lower than that under nitrogen. Therefore, we concluded that the decomposition of materials contained thermal degradation and thermal oxidation; in other

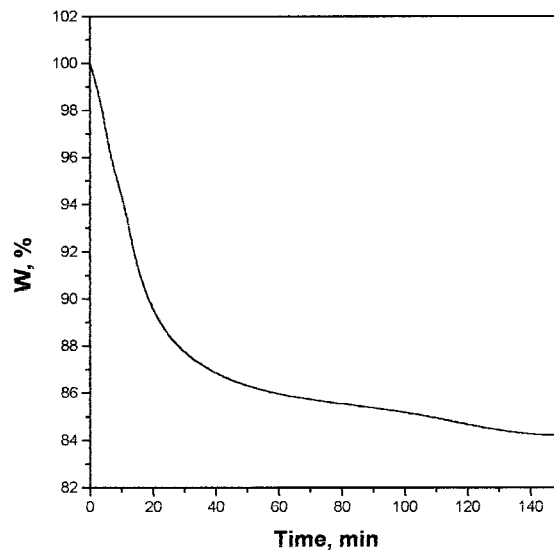


Figure 9 The weight loss as a function of time for epoxy molding compounds at 380°C in oxygen.

words, they were thermally decomposed first, then an oxidation reaction rapidly occurred. Proof of this was obtained by isothermal TGA at different temperatures. As shown in Figure 9, the thermal oxidation reaction occurred only at higher temperatures. Only a thermal degradation process (the first step) was observed for low experimental temperatures ($\leq 400^\circ\text{C}$). This was in good agreement with the result from the dynamic experiments. The activation energy values for both steps are also given in Table IV. The values calculated in the first step were approximately equal to those obtained in nitrogen. This supported the conclusions suggested above.

CONCLUSIONS

The physical properties of epoxy molding compounds can be affected by moisture. Although the

Table IV Data from TGA Experiments for Unaged Samples in O_2

Heating Rate (K/min)	T_{onset} ($^\circ\text{C}$)		T_{max} ($^\circ\text{C}$)		Residual (%)		Activation Energy, (kJ/mol)	
	Step 1	Step 2	Step 1	Step 2	Step 1	Step 2	Step 1	Step 2
5	378.9	470.8	391.4	477.9	82.07	74.25		
10	389.5	496.1	409.8	502.2	80.98	73.58		
20	412.8	515.3	432.3	525.4	81.00	73.94	123.9	156.3
50	437.6	539.1	465.1	545.7	80.04	74.01		

absorbed water plasticizes the materials, it acts predominantly as a crazing agent, continuously decreasing the mechanical strength with the time in water. The uptake of moisture and the decrease of the glass-transition temperature were equilibrated after several days. The thermal degradation behavior of the materials did not seem to be greatly influenced by the moisture absorption. The TGA results under an oxygen atmosphere showed that the decomposition of the samples was composed of two independent steps: thermal degradation and oxidation at a high temperature.

REFERENCES

- Garrett, D. W. In Proceedings of the Conference on a Broader Meaning to Thermosets, SPE-1997, Chicago; 1997; p 63.
- Barrie, J. A. In Diffusion in Polymers; Crank, J., Park, G. D., Eds.; Academic: London, 1968.
- Van Krevelen, D. W. Properties of Polymers; Elsevier: Amsterdam, 1976.
- More, E.; Bellenger, V.; Verdu, J. *Polymer* 1985, 26, 1719.
- Burton, B. L. In Proceedings of the 18th International SAMPE Technical Conference, October 7-9, 1986; p. 124.
- McQueen, R. C.; Granata, R. D. *J Polym Sci Polym Phys Ed* 1993, 31, 972.
- Duda, J. L.; Zielinski, J. M. In Diffusion in Polymers; Negoi, P., Ed.; Marcel Dekker: New York, 1996.
- Veith, W. R. Diffusion in and through Polymers; Oxford University Press: New York, 1991.
- Apicella, A.; Nicolais, L. *Adv Polym Sci* 1985, 72, 70.
- Morgan, R. J.; Mones, E. T.; Steele, W. J. *Polymer* 1982, 20, 315.
- Apicella, A.; Nicolais, L. *Ind Eng Chem PRD* 1984, 23, 288.
- Chi-Hung, G.; Springer, S. *J Compos Mater* 1976, 10, 2.
- Apicella, A.; Nicolais, L.; Cataldis, C. *Adv Polym Sci* 1984, 66, 103.
- Ellis, T. S.; Karasz, F. E.; Brinke, G. *J Appl Polym Sci* 1983, 28, 23.
- Ellis, T. S.; Karasz, F. E.; Brinke, G. *Macromolecules* 1983, 16, 244.
- Lu, M. G.; Shim, M. J.; Kim, S. W. *J Appl Polym Sci* 2000, 75, 1514.
- Lu, M. G.; Shim, M. J.; Kim, S. W. *Polym Eng Sci* 1999, 39, 274.
- Carfagna, C.; Apicella, A. *J Appl Polym Sci* 1983, 28, 2881.
- Shim, M. J.; Kim, S. W. *Polym J* 1998, 30, 73.
- Li, X. G.; Huang, M. R.; Bai, H. *Angew Makromol Chem* 1998, 256, 9.
- Osawa, T. *Polymer* 1971, 12, 150.
- Kissinger, H. E. *Anal Chem* 1957, 29, 1702.