

Energetic Studies on Epoxy–Polyurethane Interpenetrating Polymer Networks

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ABSTRACT: A blend system prepared from epoxy resin (EP) and polyurethane (PU) was investigated in terms of glass-transition temperature (T_g), contact angle, mechanical interfacial, and mechanical properties. Deionized water and diiodomethane were chosen as the angle testing liquids. In this work, the models of Owens–Wendt and Wu, using a geometric mean, were studied to analyze the surface free energy of the EP/PU blend system. Fourier transform infrared (FTIR) spectroscopy was employed to investigate the intermolecular hydrogen bonding and functional group changes. The impact test was carried out at room and cryogenic temperatures to determine the low-temperature performance of PU. As a result, mechanical interfacial and mechanical properties give a maximum value at 40 phr of PU, and the deviation of T_g of EP/PU was the closest at 40 phr of PU. Thus it is concluded that EP and PU have the best compatibilities at this ratio. Furthermore, the specific (or polar) component of the surface free energy of the blend system was largely influenced on the addition of the PU, resulting in increasing the critical stress intensity factor (K_{IC}) and the impact strength for the excellent low-temperature performance. These results could be explained by means of improvement of hydrogen bonding between the hydroxyl group in EP and isocyanate group in PU. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 775–780, 2001

Key words: epoxy; polyurethane; surface free energy; critical stress intensity factor (K_{IC}); impact test

INTRODUCTION

Since the first synthesis by Miller in 1960, the term interpenetrating polymer networks (IPNs) has been used to describe the combination of crosslinked polymer networks in which at least one polymer is synthesized and/or crosslinked in the immediate presence of the other.^{1,2} There are two principal routes for preparing IPNs, that is, sequential and simultaneous polymerization of the two components.^{3,4} Sequential IPNs are gen-

erally prepared by swelling the first-formed network with the second monomer, which is then polymerized *in situ*. Of necessity, simultaneous IPNs result from one-shot, one-stage process.

Epoxy resins (EP) are well known for some unique properties, including outstanding adhesion to most surfaces, high mechanical strength, and chemical resistance. They have been used as adhesives, coatings, and resin matrices for advanced composites.⁵ However, it is also well known that epoxy resins are rigid and brittle in nature, and have poor crack resistance in a real application.^{6–8} To overcome these problems, a considerable amount of study has been done in the direction of toughening epoxies, with some

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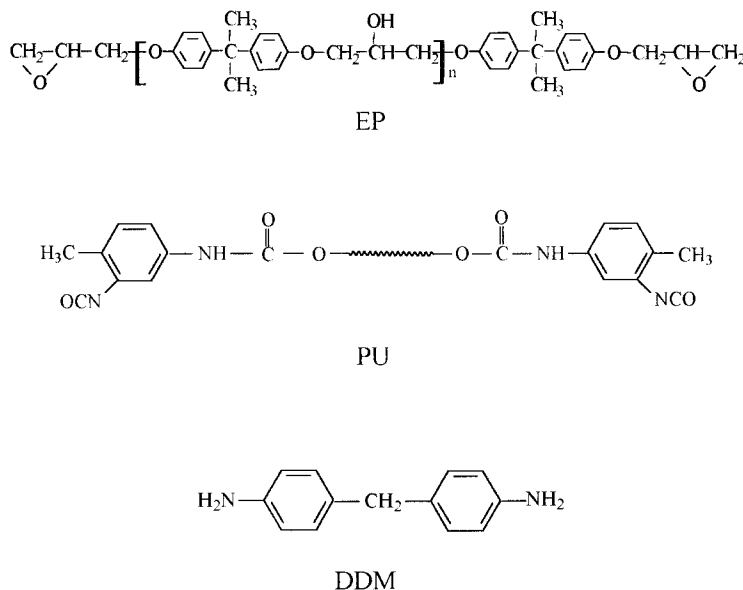


Figure 1 Chemical structures of the EP, PU, and DDM.

research focused on introducing a rubber phase into epoxy networks.^{9–12}

Polyurethane (PU) elastomers are segmented copolymers consisting of “soft”-segment domains derived from a macrodiol, and “hard”-segment domains derived from a diisocyanate and a chain extender. Generally, the two segments are incompatible, resulting in microphase separation, which is primarily responsible for their excellent mechanical properties. The hard-segment structure, weight fraction, soft-segment structure, molecular weight, polydispersity, and crosslinking in either phase influence phase separation and copolymer properties.¹³

Many important applications of polymers require that they adhere well to other substances. Adhesion is a manifestation of the attractive forces that exist between all atoms or molecules, falling into two broad categories: primary (chemical bond) and secondary (van der Waals force and hydrogen bond). Recent advances in the understanding of the surface dynamics of a solid have been made on several kinds of the intermolecular interactions at interfaces: London dispersive force, Debye inductive force, Keesom orientational force, hydrogen bonding, and energetically homogeneous and heterogeneous interactions.¹⁴

It is generally agreed in theory that attraction resulting from only physical or secondary forces including hydrogen bonding is sufficient to produce adhesive joints between polymers of strength equal to that of the polymers them-

selves, without the need for chemical or primary bonds. Because these forces decrease as the inverse sixth power of the distance between molecules, it is apparent that surfaces to be adhered must come into intimate, wetting contact.¹⁵

The aim of this work is to propose the effect of the degree of adhesion or surface free energy on mechanical interfacial and mechanical properties of the EP/PU blend system.

EXPERIMENTAL

Materials

In the system studied, the epoxy resin was the diglycidyl ether of bisphenol A (YD-128, supplied by Kukdo Chemical Co. of Korea) and the viscosity of polyurethane (NCO content 4.1%, ADIPRENE supplied by Kangshin Industrial Co. of Korea) was 18,000 cps. The epoxide equivalent weight of the EP was 185–190 g/eq and the density was 1.16 g/cm³ at 25°C. The 4,4'-diaminodiphenyl methane (DDM) was used as a curing agent for epoxy resin. The chemical structures of EP, PU, and DDM are shown in Figure 1.

Sample Preparation and Analysis

The formulations of material used in this work are listed in Table I. The epoxy resin was measured in a glass beaker and heated to melt at 50°C for 30 min. After melting of epoxy resin, the PU

Table I Composition of EP/PU/DDM System

EP	PU	DDM
100	0	20
100	10	20
100	20	20
100	40	20
100	60	20

was added into the beaker with DDM, and the reactants were homogenized by a stirrer. Samples were then degassed in a vacuum oven at 60°C. The homogeneous mixture was then poured into a mold and the cure cycle of a fully cured EP/PU blend system was 70°C for 30 min, 140°C for 2 h, and finally postcured at 200°C for 1 h.

The glass-transition temperature (T_g) was carried out at a heating rate of 10°C min⁻¹ using Du Pont DSC910 (Du Pont, Wilmington, DE). Small sample quantities were then placed in hermetically sealed aluminum pans. Thermal equilibrium of the sample and reference holder was achieved in less than 1 min, and 30 mL min⁻¹ of nitrogen gas was introduced into the DSC cell.

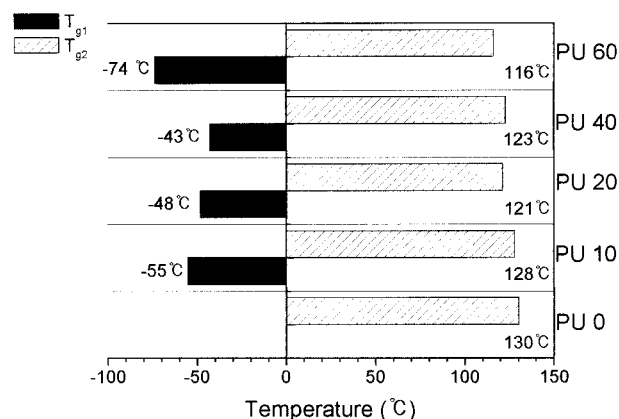
Infrared spectra of the casting samples were measured by FTIR spectroscopy (Digital FTS-80, Bio-Rad, Hercules, CA). The scans were from 400 to 4000 cm⁻¹ and required 40 s to complete.

Contact Angle Measurement

The contact angle was measured using the sessile drop method¹⁶ on a Ramé–Hart goniometer (Ramé–Hart, Mountain Lakes, NJ). About 5 μL of wetting liquids was used for each measurement at 20°C. Readings within 5 s of drop formation were taken for the critical surface tension.^{16–18} More than 10 drops were tested for each of the EP/PU blend system surfaces studied. For this work, the total surface free energies (or surface tension) and their London dispersive and specific (or polar) components for the wetting liquids are

Table II Specific (γ_L^{SP}) and London Dispersive (γ_L^L) Components of Surface Tension (γ_L) in Wetting Liquids (Subscript L) Measured at 20°C

Wetting Liquids	γ_L^{SP} (mJ/m ²)	γ_L^L (mJ/m ²)	γ_L (mJ/m ²)
Water	51	21.8	72.8
Diiodomethane	0.38	50.42	50.8

**Figure 2** Glass-transition temperature (T_g) of EP/PU IPNs.

shown in Table II. The testing liquids used were deionized water and diiodomethane.

Mechanical Properties

In polymer blend systems, the adhesion, dispersion, and morphology of component phases are greatly affected by the interfacial energies, which thereby play an important role in determining the mechanical properties of a multiphase polymer blend. In this work, the EP/PU blend system was characterized by mechanical interfacial properties, such as critical stress intensity factor (K_{IC}), and impact test. An analytical expression for K_{IC} may be characterized by single-edge notched (SEN) beam fracture toughness test according to ASTM E 399. The impact strength was tested by using the Izod method according to ASTM D 256. The impact test was carried out at room and cryogenic (77 K) temperatures to determinate the low-temperature performance of PU.

RESULTS AND DISCUSSION

Glass-Transition Temperature

Figure 2 shows the T_g with 20 phr of DDM in the EP/PU blend system. For the pure EP, T_g at room

Table III Contact Angle Determination (in Degrees) of EP/PU with Content of PU

	PU 0	PU 10	PU 20	PU 40	PU 60
Water	73	69	65	61	68
Diiodomethane	30	30	29	30	31

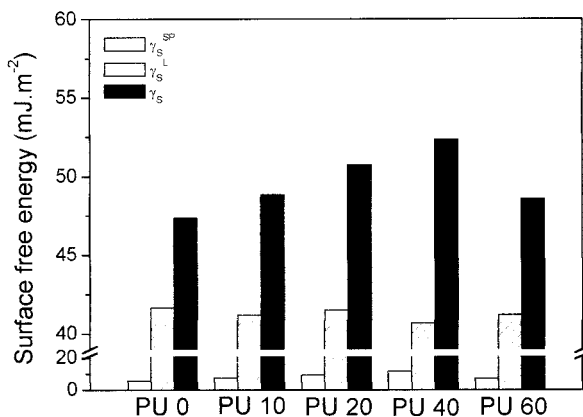


Figure 3 Surface free energies (in mJ/m^2) of EP/PU as content of PU using a two-liquid geometric method.

temperature (T_g) is about 130°C , and the range of T_{g2} of the system is about $116\text{--}128^\circ\text{C}$ in the content of PU. The deviation of T_g at cryogenic temperature (T_{g1}) is greater than that at T_{g2} , and it is seen that when the EP/PU is 100/40 phr, the deviation of T_g of the two polymers is the closest. Thus it is concluded that EP and PU have the best compatibilities at this ratio.¹⁹

Contact Angle Measurements

In the early 1960s, Fowkes²⁰ introduced the concept of surface free energy γ , which can be resolved into a London dispersive component (superscript L) and a specific (or polar, SP) component.^{20–23}

$$\gamma = \gamma^L + \gamma^{SP} \quad (1)$$

where γ is total of surface free energy, γ^L is the London attraction of van der Waals force, and γ^{SP} is the nondispersive component of other types for physical interactions.

During the equilibrium contact angle (here, abbreviated θ) measurements for a liquid drop on an ideally smooth and homogeneous solid surfaces, Owens and Wendt,¹⁵ and Wu²¹ extended the Fowkes' concept using geometric means, as follows:

$$\gamma_L(1 + \cos \theta) = 2(\gamma_L^L \gamma_S^L)^{1/2} + 2(\gamma_L^{SP} \gamma_S^{SP})^{1/2} \quad (2)$$

where subscripts L and S are the liquid and solid states, respectively.

In a more practical relationship based on two simultaneous liquids of widely different properties on solid surfaces (e.g., water and diiodomethane for largely polar and nonpolar liquids, respectively), γ_S^L and γ_S^{SP} can be solved according to eq. (2), as follows^{21,23}:

$$\begin{aligned} \gamma_S^L &= \frac{1}{4} \left[\frac{(1 + \cos \theta_1) \gamma_1 (\gamma_2^{SP})^{1/2} - (1 + \cos \theta_2) \gamma_2 (\gamma_1^{SP})^{1/2}}{(\gamma_1^L \gamma_2^{SP})^{1/2} - (\gamma_2^L \gamma_1^{SP})^{1/2}} \right]^2 \end{aligned} \quad (3)$$

$$\begin{aligned} \gamma_S^{SP} &= \frac{1}{4} \left[\frac{(1 + \cos \theta_2) \gamma_2 (\gamma_1^L)^{1/2} - (1 + \cos \theta_1) \gamma_1 (\gamma_2^L)^{1/2}}{(\gamma_1^L \gamma_2^{SP})^{1/2} - (\gamma_2^L \gamma_1^{SP})^{1/2}} \right]^2 \end{aligned} \quad (4)$$

where subscripts 1 and 2 represent water and diiodomethane, respectively.

Table III shows the contact angles obtained under water and diiodomethane on the EP/PU blend system. As a result, the contact angle of water is significantly changed by increasing the content of PU on the EP/PU blend system. This is clearly expected because the polar component of

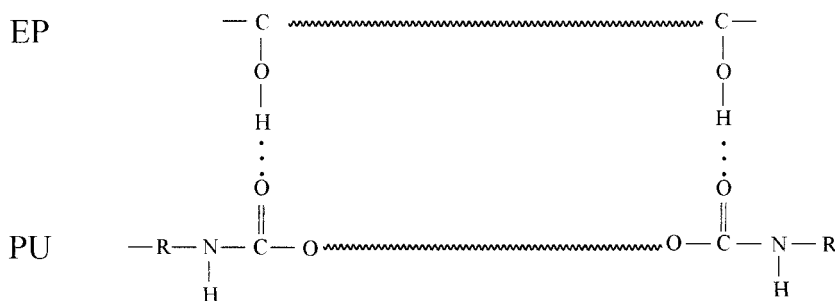


Figure 4 Intermolecular hydrogen bonding between EP and PU.

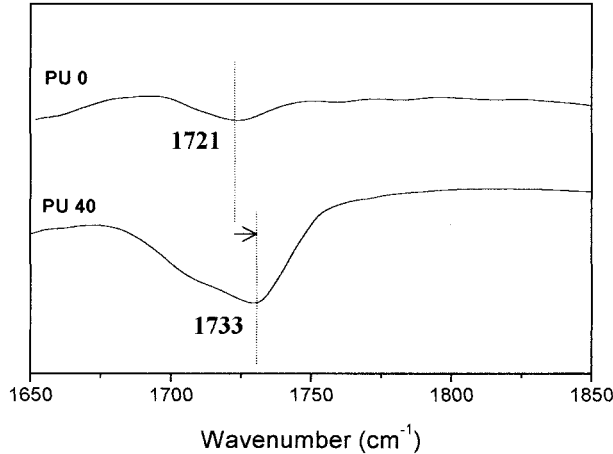


Figure 5 Shift of IR peak for the carbonyl absorption in the blend system.

the blend system is largely influenced by the addition of PU.

The results of surface free energies or surface tensions of the EP/PU blend system determined by eqs. (3) and (4) are shown in Figure 3. It is interesting to note that 40 phr of PU in the blend system gives a maximum surface free energy, which is mainly attributed to its higher specific component γ_S^{SP} . Moreover, this surface free energy increase can be attributed to the intermolecular hydrogen bonding between the hydroxyl group in EP and the isocyanate group in PU (as seen in Fig. 4), which is one of the specific component of surface free energies. This is evidenced from the shift of carbonyl absorption in the IR spectra as shown in Figure 5. The original carbonyl peak of PU 0 occurs at 1721 cm^{-1} . Upon the addition of 40 phr of PU, the carbonyl peak shifts to a higher wave number at 1733 cm^{-1} because the isocyanate group of PU can physically interact with the hydroxyl group of EP to hydrogen bonding.²³

Mechanical Properties

For the EP/PU blend system, the fracture toughness can be measured by the three-point bending test for the critical stress intensity factor (K_{IC}) according to ASTM E 399. For the single-edge notched (SEN) beam fracture toughness test, the value of K_{IC} is calculated as follows:

$$K_{IC} = \frac{PS}{BW^{3/2}} f(a/W) \quad (5)$$

and

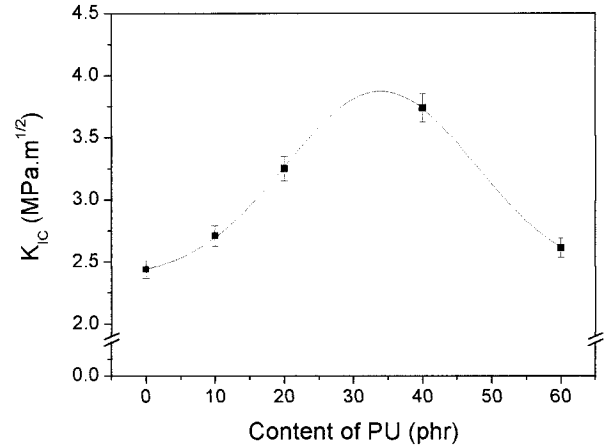


Figure 6 Evolution of K_{IC} with the content of PU.

$$f(a/W) = \frac{3(a/W)^{1/2}[1.99 - (a/W)(1 - a/W)(2.15 - 3.93a/W + 2.7a^2/W^2)]}{2(1 + 2a/W)(1 - a/W)^{3/2}} \quad (6)$$

where P is the rupture force, S is the span between the supports, and W and B are the specimen width and thickness, respectively.

Figure 6 shows the evolution of K_{IC} in flexure of the EP/PU blend system with the content of PU. This result indicates that the maximum K_{IC} value is found about $3.8\text{ MPa}\sqrt{m}$ at 40 phr of PU. As mentioned earlier, this result can be explained by means of hydrogen bonding between the hydroxyl group in EP and the isocyanate group in PU, as shown in Figures 4 and 5. However, a marginal decrease in K_{IC} is observed in this work.

Meanwhile, it is noted that impact properties are directly related to overall toughness or ductil-

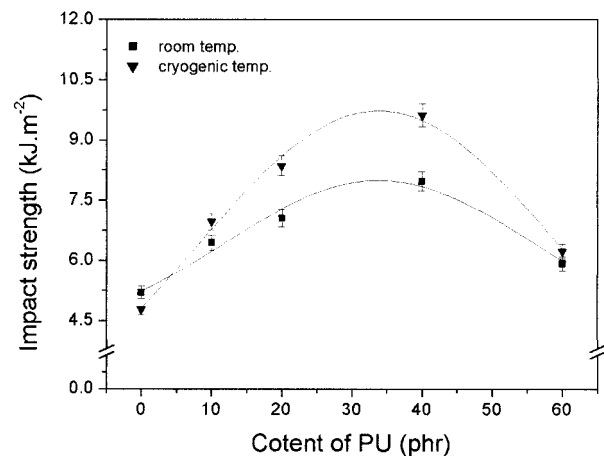


Figure 7 Impact strength measured with the content of PU at room and cryogenic (77 K) temperatures.

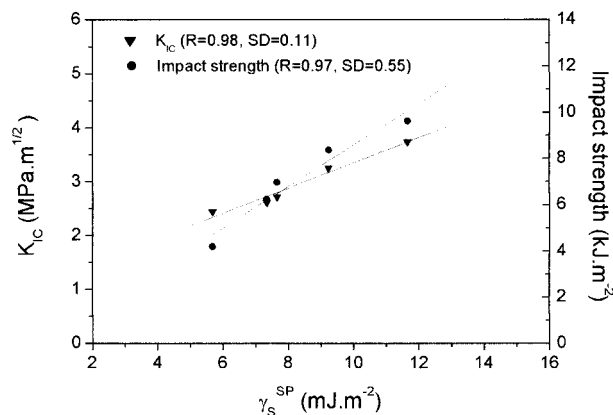


Figure 8 Dependence of the critical stress intensity factor (K_{IC}) and the impact strength measured at cryogenic temperature on γ_s^{SP} (R , coefficient of regression; SD, standard deviation).

ity of the materials, which can be defined as the ability of the blend system to absorb applied energy. In this work, the impact tests are carried out at room and cryogenic temperatures to determine the low-temperature performance of PU. As an experimental result, the addition of PU improves the toughness of the EP/PU blend system, as seen in Figure 7, from which it is clearly seen that the degree of improvement of impact strengths measured at cryogenic temperature is much higher than that of impact strengths measured at room temperature. It is concluded that PU possesses high impact strength and excellent low-temperature performance.²⁴

A good correlation between the specific component of surface free energy and both the resulting mechanical interfacial and mechanical properties is shown in Figure 8. The linearity of these various confirms, again, the validity of our theoretical analysis.

CONCLUSIONS

In this work, the EP/PU blend system based on surface free energies and mechanical interfacial or mechanical properties is studied for optimum casting of specimens. It reveals that the presence of intermolecular hydrogen bonding between the hydroxyl group in EP and the isocyanate group in PU exerts an important role in increasing good network interlocking in the IPN formation.

As the experimental results show, the addition of 40 phr of PU in the blends appears to increase the specific component of the surface free energy,

which is related to the mechanical interfacial or mechanical properties, effectively resulting in optimum toughness properties on the castings. Moreover, PU-reinforced epoxies are found to possess high impact strength at cryogenic temperatures.

REFERENCES

- Zhang, Y.; Hourston, D. J. *J Appl Polym Sci* 1998, 69, 271.
- Sperling, L. H. *Interpenetrating Polymer Networks and Related Materials*; Plenum Press: New York, 1981.
- Thomas, D. A.; Sperling, L. H. in *Polymer Blend*, Vol. 2; Paul, D. R.; Newman, S., Eds.; Academic Press: New York, 1978.
- Widmaier, J. M.; Sperling, L. H. *Br Polym J* 1986, 16, 46.
- Varik, R.; Ille, A.; Vig, A.; Czajlik, I.; Rusznak, I. *Radiat Phys Chem* 1996, 47, 457.
- May, C. A. *Epoxy Resins: Chemistry and Technology*, 2nd ed.; Marcel Dekker: New York, 1988; p. 551.
- LeMay, J. D.; Kelley, F. N. in *Structure and Ultimate Properties of Epoxy Resins*; Dusek, K., Ed.; Springer-Verlag: New York, 1986; Vol. 78, p. 115.
- Ng, H.; Manas-Zloczower, I. *Polym Eng Sci* 1993, 33, 211.
- Drakf, R.; Siebert, A. *SAMPE Q* 1975, July, 11.
- Riew, C. K.; Gillham, J. K. *Rubber-Modified Thermoset Resins*; Publisher: Washington, DC, 1984.
- Hsieh, H. S. Y. *Polym Eng Sci* 1990, 30, 493.
- Bishoop, J. A. *Int J Adhes Adhesives* 1992, 12, 178.
- Meckel, W.; Goyert, W.; Wieder, W. in *Thermoplastic Elastomers*; Legge, N. R.; Holden, G.; Schroeder, H. E., Eds.; Hanser: Munich, 1987; p. 13.
- Park, S. J. in *Interfacial Forces and Fields: Theory and Applications*; Hsu, J. P., Ed.; Marcel Dekker: New York, 1999; Chapter 5.
- Owens, D. K.; Wendt, R. C. *J Appl Polym Sci* 1969, 13, 1741.
- Adamson, A. W. *Physical Chemistry of Surfaces*, 5th ed.; Wiley: New York, 1990.
- Schwarcz, A. *J Polym Sci Part B Polym Phys* 1974, 12, 1195.
- Kim, A.; Park, S. J.; Lee, J. R. *J Colloid Interface Sci* 1998, 197, 119.
- Li, Y.; Mao, S. *J Polym Sci Part A Polym Chem* 1996, 34, 2371.
- Fowkes, F. M. *J Phys Chem* 1962, 66, 382.
- Wu, W. *Polymer Interface and Adhesion*; Marcel Dekker: New York, 1982.
- Park, S. J.; Brendlé, M. *J Colloid Interface Sci* 1997, 188, 336.
- Park, S. J.; Park, W. B.; Lee, J. R. *Polym J* 1999, 31, 28.
- Hsia, H. C.; Ma, C. C. M.; Li, M. S.; Li, Y. S.; Chen, D. S. *J Appl Polym Sci* 1994, 52, 1137.