

Polyamide 6/Silica Nanocomposites Prepared by *In Situ* Polymerization

FENG YANG, YUCHUN OU, ZHONGZHEN YU

State Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

Received 3 June 1997; accepted 2 November 1997

ABSTRACT: A polyamide 6 (PA 6)/silica nanocomposite was obtained through a novel method, *in situ* polymerization, by first suspending silica particles in ϵ -caproamide under stirring and then polymerizing this mixture at high temperature under a nitrogen atmosphere. The silicas were premodified with aminobutyric acid prior to the polymerization. The effects of the addition of unmodified and modified silicas on the dispersion, interfacial adhesion, isothermal crystallization, and mechanical properties of PA 6 nanocomposites were investigated by using scanning electron microscopy, dynamic mechanical analysis, differential scanning calorimetry, and mechanical tests, respectively. The results show that the silicas dispersed homogeneously in the PA 6 matrix. The addition of silicas increases the glass transition temperature and crystallization rate of PA 6. The mechanical properties such as impact strength, tensile strength, and elongation at break of the PA 6/modified silica nanocomposites showed a tendency to increase and decrease with increase of the silica content and have maximum values at 5% silica content, whereas those of the PA 6/unmodified silica system decreased gradually. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 355–361, 1998

Key words: *in situ* polymerization; nanocomposites; mechanical properties; polyamide 6; silica

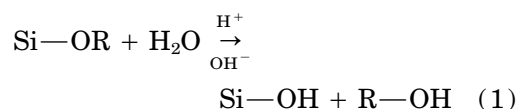
INTRODUCTION

Particle-filled polymer composites have attracted strong interest for a long time because of their widespread applications in the automobile, household, and electrical industries.¹ The employment of inorganic particle-filled composites not only can improve the physical properties of the materials such as the mechanical properties, thermal resistance, and chemical reagent resistance,^{2,3} but also can provide high-performance materials at a lower cost.¹ Recently, according to the development of the nanotechnology, there has been a growing interest in the field of nanocomposites due to their special properties: Not only can they provide

the properties of traditional composites, but also they exhibit unique optical, electric, and magnetic properties.^{4–11}

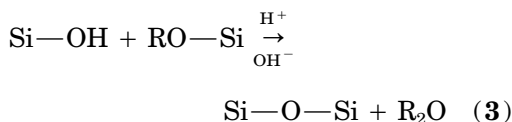
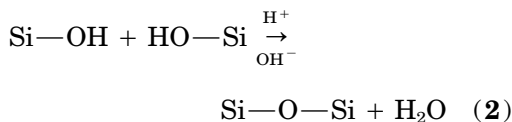
At present, organic/inorganic nanocomposites are prepared mainly via three methods:

- (I) Sol-gel processing,^{12–18} which includes two approaches: hydrolysis of the metal alkoxides and then polycondensation of the hydrolyzed intermediates. Most of the interest in this method is concentrated on metal organic alkoxides, especially silicon oxide (silica) since they can form an oxide network in organic matrices. The hydrolysis approach can be described as formulation (1):



Correspondence to: Y. Ou.

According to the difference of final products, there are two reaction types of polycondensation, which are shown as formulations (2) and (3):



The sol-gel process provides a method for the preparation of inorganic metal oxides under mild conditions starting from organic metal alkoxides. This permits structural variation without compositional alteration. However, the formation of a crosslinking network of organic metal oxides makes it difficult to process, and it is a disadvantage that circumscribed the application of this method.

- (II) *In situ* intercalative polymerization, which is a good method for the preparation of polymer/clay mineral hybrid or nanocomposites,^{19–22} such as the PA 6/montmorillonite hybrid.²² Usuki et al.^{22–24} reported that ω -amino acid can intercalate between the *n*-montmorillonite layer and so the montmorillonite can be swollen. Many other experiments reported on the syntheses of polymers in the interlayer space of clay.^{25–27} The thickness of montmorillonite in the resulting composite ranged from 1 to 3 nm while the diameter of them is approximately 100 nm. It is an effective method to prepare a polymer/clay composite which can provide high-performance materials at a relative low cost, but this method only adapts to clay minerals, which is also a significant disadvantage for its application.
- (III) *In situ* polymerization,^{28–31} which is a method where nanometer scale inorganic fillers or reinforcements are dispersed in the monomer first; then, this mixture is polymerized using a technique similar to bulk polymerization. It is obvious that the most important factors that affect the properties of composites are the dispersion and the adhesion at the polymer and

filler interfaces.^{28,32,33} Inorganic particles may disperse homogeneously in the polymer matrices when they are premodified by a coupling agent. Furthermore, the resulting materials obtained by this method also can be easily processed since they have good flowing properties.

In this article, we employed *in situ* polymerization to prepare PA 6/silica nanocomposites. The interfacial interaction between PA 6 and silica was investigated to explain the relationship of the structure and properties of this composite. Other properties such as crystallization behavior and mechanical properties were also characterized to show the efficiency of this method.

EXPERIMENTAL

Materials

ϵ -Caproamide and aminocaproic acid were used to prepare PA 6. The inorganic filler used was silica (AEROSIL, R972).

Preparation of Composites

The surface of the silica was premodified by aminobutyric acid first; then, the modified silica was dried in oven for the preparation of PA 6/silica nanocomposites. The preparation of PA 6/silica nanocomposites included two processes: The modified silicas were dispersed in ϵ -caproamide at 90°C first, and aminocaproic acid as the initiator was added at the same time; then, this mixture was polymerized at high temperature under a nitrogen atmosphere. The PA 6/unmodified silica composite can also be prepared by this method.

Measurements

The dynamic mechanical loss ($\tan \delta$) and glass transition temperature (T_g) of the samples were tested by a Perkin-Elmer DMA-7 tester. The mode of force loading was three-point bending. The testing frequency, heating rate, and temperature scanning range were 1 Hz, 10°C/min, and -50–200°C, respectively. The surface of the sample was covered with aluminum foil and then a dielectric analysis tester was used to measure the dielectric dissipation and dielectric constant of the sample at room temperature. The testing fre-

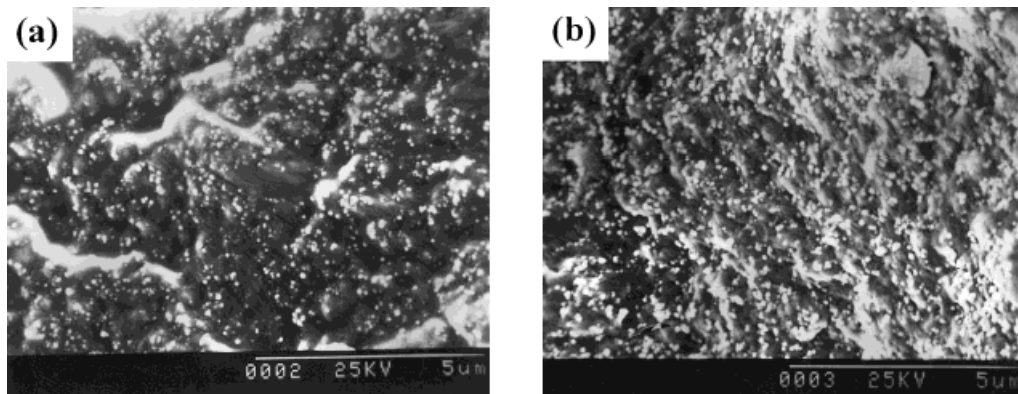


Figure 1 SEM micrographs of (a) PA 6/10% unmodified silica nanocomposite and (b) PA 6/10% modified silica nanocomposite.

quency range was 500–9000 Hz. Isothermal and nonisothermal crystallization behaviors of the sample were measured by a Perkin–Elmer DSC-7 tester in the scanning range of 60–250°C and the scanning rate of 10°C/min. Scanning electron micrographs were obtained with a Hitachi S-530 scanning electronic microscope. Tension testing was examined by a CS-183 mechanical tester with the tension rate at 5 rpm.

RESULTS AND DISCUSSION

SEM Observation

To investigate the dispersion quality of silica particles, the morphology of PA 6/silica composites were studied and the results are shown in Figure 1. It is evident that the modified silicas have a more homogeneous dispersion in the PA 6 matrix compared with the unmodified silicas. It can also be seen from Figure 1 that the sizes of both the modified and unmodified silica particles are mostly in the range of 50–110 nm except the aggregated silicas, suggesting that *in situ* polymerization is a good method for preparing inorganic/organic nanocomposites.

Interfacial Interaction

Dynamic mechanical analysis (DMA) is an efficient method to investigate the interfacial interaction of a composite. Figure 2 shows the DMA results of the resulting composites prepared through *in situ* polymerization. The T_g of the PA 6/silica nanocomposites shifts to a high temperature whether the silicas were premodified or not, while the shift of the PA 6/modified silica nano-

composite is more significant than that of the PA 6/unmodified silica system, indicating that the interfacial interaction between silica and PA 6 can be improved by premodifying the silica surface. It also can be seen that the premodification of the silicas reduces the areas of the dynamic loss peak of PA 6 nanocomposites in comparison with the PA 6/unmodified silica system, which means that good adhesion between the modified silica particles and the nylon 6 matrix can limit the motion of the PA 6 molecular chain.

Furthermore, to obtain more information about the interfacial interaction of the PA 6/silica nanocomposite, dynamic dielectric tests were performed. As shown in Figure 3, the addition of the unmodified silica improves the dielectric constant of PA 6, while the modification of silica reduces slightly the dielectric constant of the PA 6 nanocomposite. Based on the theory of interfacial po-

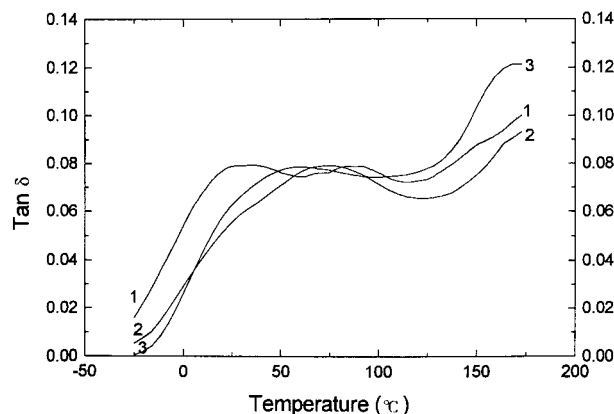


Figure 2 Dynamic mechanical spectra of (1) PA 6, (2) PA 6/modified silica nanocomposite, and (3) PA 6/unmodified silica nanocomposite.

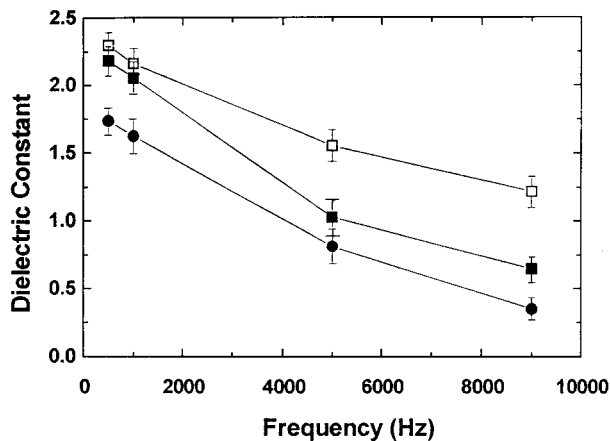


Figure 3 Dielectric constant versus frequency of (●) PA 6, (■) PA 6/10% modified silica nanocomposite, and (□) PA 6/10% unmodified silica nanocomposite.

larization, the existence of faults in the interface between the silica particles and the PA 6 matrix such as lattice vacancy and electron vacancy can lead to the variation of the dissipation of positive and negative electric charges. When the sample was exposed to an electric field, positive and negative electric charges move to the cathode and anode, respectively, and as a result, these electric charges accumulate at the faults in the interface of the composite and formed an electric dipole moment, resulting in the polarization of space electric charges. Due to the good interfacial adhesion and dispersion quality of the PA 6 nanocomposite containing the modified silicas, its faults mentioned above are much fewer than those in the composite containing the unmodified silicas, and this may be the principal reason why the dielectric constant of the PA 6 nanocomposite decreases when the silica surface was modified.

Crystallization Behavior of PA 6/Silica Nanocomposite

It is generally known that the crystallization of crystalline polymers can be divided into two processes: nucleation and crystal growth. The most successful description of the crystallizing rate of a polymer is of the kinetics equations of Avrami published in 1939,^{34,35} which have been amended many times^{36,37} in the following years and gained worldwide acceptance. The equations are listed in the following:

$$f(\alpha) = n(1 - \alpha)[- \ln(1 - \alpha)]^{(n-1/n)} \quad (1)$$

$$\partial\alpha/\partial t = K^{1/n}(T)f(\alpha) \quad (2)$$

$$\ln K(T) = \ln K_0 - E_a/RT \quad (3)$$

$$\ln(\partial\alpha/\partial t) = \frac{1}{n} \ln K(T) + \ln n + \ln(1 - \alpha) + \frac{n-1}{n} \ln[- \ln(1 - \alpha)] \quad (4)$$

$$\ln(\partial\alpha/\partial t) - \ln(1 - \alpha) = \frac{1}{n} \ln K(T) + \ln n + \frac{n-1}{n} \ln[- \ln(1 - \alpha)] \quad (5)$$

In eqs. (1) and (2), $\partial\alpha/\partial t$, $K(T)$, and n represent the crystallizing rate, the constant of crystallizing rate, and the Avrami index, respectively. K is a function of temperature which obeys the theory of Arrhenius shown in eq. (3), in which E_a is the crystallizing activation energy. Equation (4) is derived from eqs. (1) and (2), and eq. (5) is the transformation of eq. (4), in which $K(T)$ and n are independent of time. If we let $\ln[- \ln(1 - \alpha)]$ be the abscissa and $\ln(\partial\alpha/\partial t) - \ln(1 - \alpha)$ be the ordinate, we get n and $\ln K(T)$. Furthermore, according to eq. (3), E_a can also be obtained, and the results are listed in Table I.

Based on the Avrami theory, n depends on the geometry of the crystal growth and on the type of nucleation. Athermal nucleation and spherulitic growth lead to an Avrami exponent of 3, whereas thermal nucleation and spherulitic growth, to a value of 4. According to the experimental data listed in Table I, it can be seen that the n of pure PA 6 is approximately 4, while those of PA 6 in the other two composites are nearly 3. The decrease of n is due to that the silicas in the PA 6 nanocomposites act as heterogeneous nucleation sites, followed by three-dimensional spherulitic growth. Moreover, the data of E_a indicate that the addition of silica particles enhances the crystallization of PA 6.

According to eq. (6),²⁵ the half-time of crystallization can be calculated. Figure 4 gives the plots of half-time versus temperature of PA 6 and its composites. The unmodified silicas indeed increase the crystallization rate of PA 6. On the other hand, the modification of the silica surface causes a slight decrease in the crystallization rate of the crystallization of PA 6. There are two effects of the silicas on the crystallization of PA 6: First, the silicas serving as nucleation sites accelerate the process of PA 6 crystallization; on the other

Table I Data of Isothermal Crystallization Kinetics Parameters by DSC

Sample	T ($^{\circ}\text{C}$)	n	$1/t_{1/2}$ (S^{-1})	E_a (kJ/mol)
PA 6	195	4.23	3.306×10^{-2}	1064.129
	194	4.00	2.087×10^{-2}	
	193	4.19	1.083×10^{-2}	
	192	4.20	2.776×10^{-3}	
PA 6/10%SiO ₂ (modified)	195	3.15	4.858×10^{-2}	518.98
	194	2.18	4.251×10^{-2}	
	193	2.05	2.776×10^{-2}	
	192	2.66	2.93×10^{-3}	
PA 6/10%SiO ₂ (unmodified)	195	2.91	5.223×10^{-2}	448.956
	194	2.93	4.569×10^{-2}	
	193	2.88	3.770×10^{-2}	
	192	2.59	5.945×10^{-3}	

hand, the good adhesion between PA 6 and the modified silicas impedes the motion of the PA 6 molecular chains, hampering the crystallization of the PA 6 matrix. The latter effect is much smaller compared with the former in our experiment, so the addition of the modified silicas also improves the crystallization rate of the PA 6 matrix:

$$t_{1/2} = (\ln 2/K)^{1/n} \quad (6)$$

Mechanical Properties of Nylon 6/Silica Nanocomposite

Figure 5 shows the mechanical properties of PA 6 nanocomposites filled with unmodified or modified silicas. It can be seen that the tensile

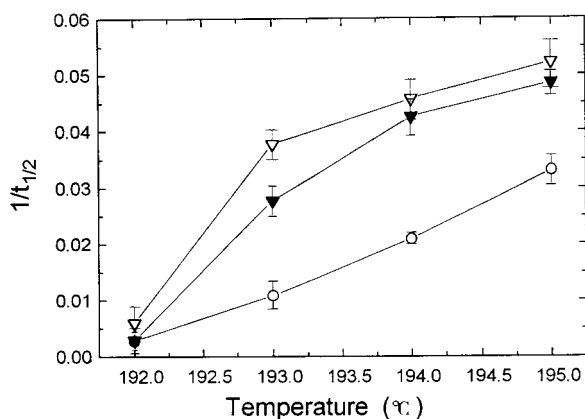


Figure 4 Reciprocal of half-time of crystallization ($1/t_{1/2}$) versus temperature for (\circ) PA 6, (\blacktriangledown) PA 6/10% modified silica nanocomposite, and (\triangledown) PA 6/10% unmodified silica nanocomposite.

strength, elongation at break, and impact strength of the PA 6/modified silica nanocomposites increase remarkably with the content of the filler and possess maximum values at 5 wt % filler content, whereas those of the PA 6/unmodified silica system decrease gradually with increasing filler content. According to the analysis above, the composites containing the modified silicas have good dispersion and interfacial adhesion, so when under tensile stress, the force is transferred to silica particles through the interphase and the silica particles become the receptor of the tensile force. When the tensile stress added on the composites is beyond a critical value, the damage to the composite results from the destruction of the interphase between PA 6 and the silicas. Due to the difference in the interfacial adhesion, the modified and unmodified silicas show different effects on the toughness of PA 6. The unique mechanical behavior of a silica-modified nanocomposite is mainly because of the agglomeration of silica particles beyond the silica contents of 5 wt % as we described in another article.³⁸ The deterioration of the toughness of unmodified composites appears to be related mainly to the bad interfacial adhesion between unmodified silica and nylon 6, which led to many defects and flaws in the areas of the interphase and, consequently, made the damage to the composites easier. In addition, the addition of silicas improved the modulus of the resulting composites whether the silicas were modified or not.

CONCLUSION

In situ polymerization is a good method for the preparation of inorganic/organic nanocomposites

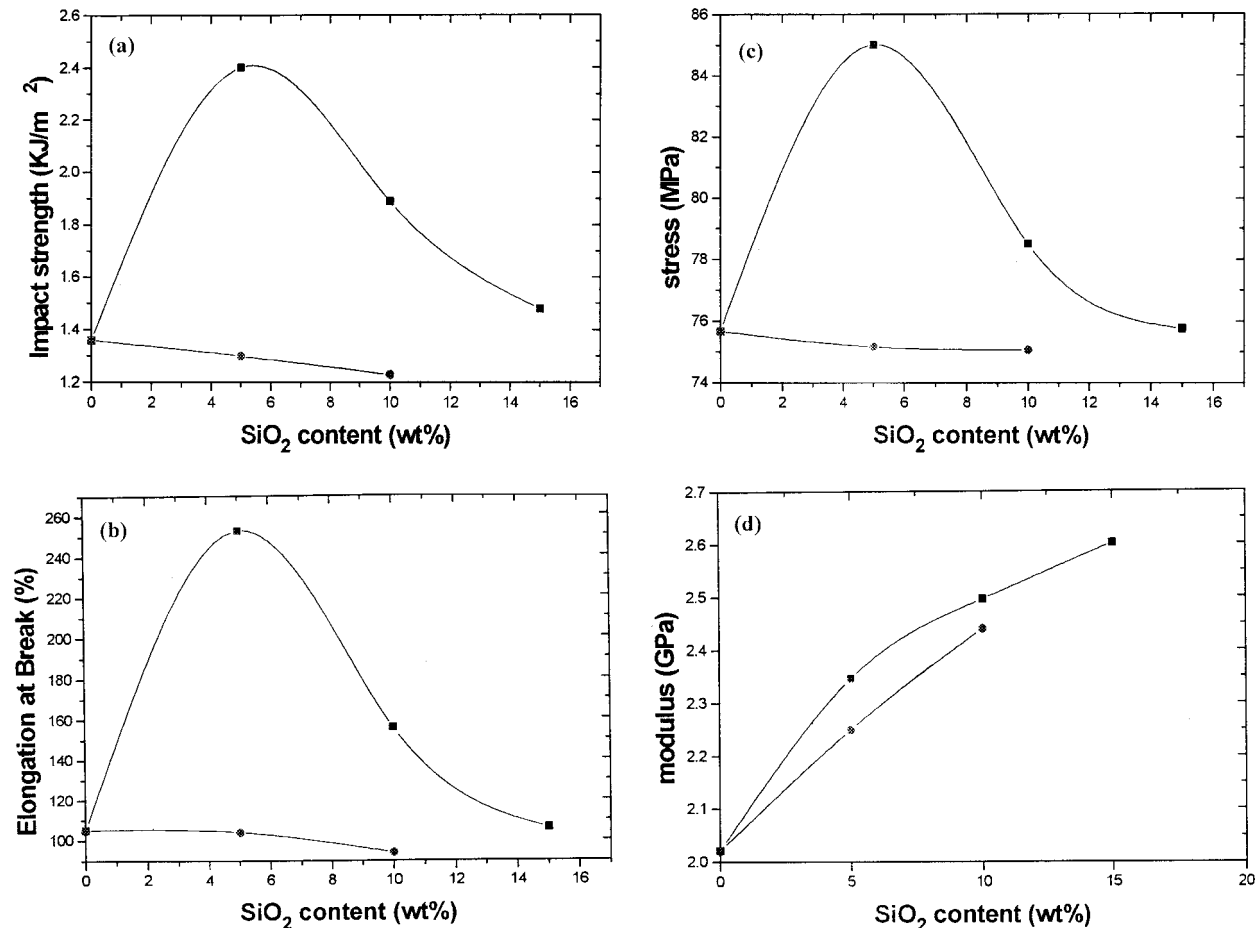


Figure 5 (a) Impact strength, (b) elongation at break, (c) tensile strength, and (d) modulus versus silica content for (●) unmodified and (■) modified silica-filled PA 6 nanocomposites.

which can avoid the agglomeration of inorganic particles in polymer matrices and improve the interfacial interaction between an inorganic component and the polymeric matrix. SEM observation shows that the modified silicas disperse more homogeneously in the PA 6 matrix in comparison with the unmodified silicas. According to the DMA results, the addition of silicas, particularly the modified one, significantly increases the glass transition temperature of PA 6. Isothermal crystallization behaviors indicate that the silicas increase the crystallization rate of PA 6. The impact strength, tensile strength, and elongation at break of the PA 6/modified silica nanocomposites show a tendency to increase and decrease with increase of the silica content and have maximum values at 5 wt % silica content, while those of the PA 6/unmodified silica system decrease gradually.

REFERENCES

1. M. I. Kohan, Ed., *Nylon Plastics*, Wiley, New York, 1973.
2. Y. Ou, Z. Yu, and Y. Feng, *Chin. J. Polym. Sci.*, **11**, 31 (1993).
3. L. E. Nielsen, *Mechanical Properties of Polymers and Composites*, Marcel Dekker, New York, 1974.
4. G. Philipp, H. Schmidt, *J. Non-Cryst. Solids*, **63**, 283 (1984).
5. A. Morikawa, Y. Iyoku, M. Kakimoto, and Y. Imai, *Polym. J.*, **24**, 107 (1992).
6. B. M. Novak, M. W. Ellsworth, and C. Verrier, *Polym. Mater. Sci. Eng.*, **70**, 266 (1993).
7. H. Schmidt and H. Wolter, *N. Non-Cryst. Solids*, **121**, 428 (1990).
8. M. Popall, H. Meyer, H. Schmidt, and J. Schulz, *Mater. Res. Soc. Symp. Proc.*, **180**, 995 (1990).
9. R. H. Glaser and G. L. Wilkes, *Polym. Bull.*, **19**, 51 (1989).

10. E. J. A. Pope and J. D. Mackenzie, *MRS Bull.*, **12**, 29 (1987).
11. E. J. A. Pope, A. Asami, and J. D. Mackenzie, *J. Mater. Res.*, **4**, 1018 (1989).
12. E. L. Warrick and O. L. Pierce, *Rubb. Chem. Technol.*, **52**, 437 (1973).
13. G. L. Wilkes, H. A. Huang, and R. H. Glaser, in *Silicon Based Polymer Science. A Comprehensive Resource*, J. M. Ziegler and F. G. Feazon, Eds., *Advances in Chemistry Series 224*, American Chemical Society, Washington, DC, 1990, pp. 207–236.
14. J. E. Mark, *J. Appl. Polym. Sci. Appl. Polym. Symp.*, **50**, 273 (1992).
15. G. S. Sur and J. E. Mark, *Eur. Polym. J.*, **21**, 1051 (1985).
16. H. H. Huang, B. Orler, and G. L. Wilkes, *Polym. Bull.*, **14**, 557 (1985).
17. M. W. Ellsworth and B. M. Novak, *J. Am. Chem. Soc.*, **113**, 2756 (1991).
18. C. J. T. Landry, B. K. Coltrain, J. A. Wesson, N. Zumbulyadis, and J. L. Lippert, *Polymer*, **33**, 1496 (1992).
19. C. R. Smith, *J. Am. Chem. Soc.*, **56**, 1561 (1934).
20. A. Akelah, N. Salahuddin, A. Hiltner, E. Baer, and A. Moet, *NanoStruct. Mater.*, **4**, 965 (1994).
21. A. Blumstein, *J. Polym. Sci. A*, **3**, 2653 (1965).
22. A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, and O. Kamigaito, *J. Mater. Res.*, **8**, 1179 (1993).
23. A. Usuki, M. Kawasumi, Y. Kojima, A. Okada, T. Kurauchi, and O. Kamigaito, *J. Mater. Res.*, **8**, 1174 (1993).
24. Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi, and O. Kamigaito, *J. Mater. Res.*, **8**, 1185 (1993).
25. H. Z. Friendlander and C. R. Frick, *J. Polym. Sci. B*, **2**, 475 (1964).
26. D. H. Solomon, *J. Appl. Polym. Sci.*, **12**, 1253 (1968).
27. O. L. Glaveti and L. S. Polak, *Neftekhim.* **3**, 905 (1963).
28. G. Kiss, *Polym. Eng. Sci.*, **27**, 410 (1987).
29. Y. Ou, F. Yang, and J. Chen, *J. Appl. Polym. Sci.*, **64**, 2317 (1997).
30. Y. Ou and F. Yang, *Polym. Eng. Sci.*, to appear.
31. Y. Ou and Y. Feng, *Polym. Int.*, submitted.
32. J. L. Thomason, in *Interfaces in Polymer, Ceramic, and Metal Matrix Composites*, H. Ishida, Ed., Elsevier, New York, 1988.
33. H. Ishida, *Polym. Compos.*, **5**, 101 (1984).
34. M. Avrami, *J. Chem. Phys.*, **7**, 1103 (1939).
35. M. Avrami, *J. Chem. Phys.*, **8**, 212 (1940).
36. J. Tomka, *Eur. Polym. J.*, **4**, 237 (1968).
37. J. H. Flynn, *J. Therm. Anal.*, **37**, 293 (1991).
38. Y. Ou, F. Yang, and Z. Yu, *J. Polym. Sci. B Polym. Phys.*, to appear.