Surface and Thermal Characteristics of Rubber-Modified Aromatic Polyamide

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ABSTRACT: Polyamide/epoxysilane (coupling agent) composites were reacted with poly(dimethylsiloxane) (PDMS), a condensation product of diethoxydimethylsilane (DEDMS), by a sol–gel process. Polyamide–PDMS nanocomposites were obtained. The existence of the condensation product of DEDMS and the reaction between the epoxy group and the polyamide were confirmed with Fourier transform infrared, attenuated total reflection, and wide-scanning X-ray photoelectron spectroscopy. Atomic force microscopy and contact-angle measurements showed that the surface properties of polyamide were greatly improved by the addition of PDMS. The pyrolysis temperature of polyamide with PDMS was approximately 400°C, and the pyrolysis temperature was similar to that of pure polyamide. Also, the char contents increased with the addition of PDMS. The glass-transition temperature of polyamide with or without PDMS was approximately 140°C according to differential scanning calorimetry. © 2004 Wiley Periodicals, Inc.
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Key words: nanocomposites; polyamides; silicones; toughness

INTRODUCTION

In the sol–gel process, an organometallic compound is hydrolyzed to form a solid; this is followed by a condensation reaction that forms a gel, and eventually a ceramic is produced.[1,2] This process is performed via hydrolysis and condensation and can be catalyzed by the addition of an acid or base catalyst. With the sol–gel process, various kinds of ceramics, such as powders, fibers, and films, can be fabricated. Also, this process has been used widely to produce organic–inorganic hybrid composites because it can produce a high-purity ceramic phase in a polymer matrix at a lower temperature.[3–10] In producing organic–inorganic hybrid composites, tetraethyl orthosilicate has been widely used. This is because it can be purified readily by distillation, and the slow hydrolysis speed makes it simple to control.[4,5,11,12] Polymers with functional groups that can react with ceramic phases are applied in sol–gel processes, and in a number of studies, researchers have already fabricated hybrid composites.[13–19] Because of their good mechanical, thermal, and electric characteristics, high-temperature polymers such as poly-amide,[20–23] and polyimide[24–30] have been employed for research into hybrid composites. However, as much research has shown, high-temperature polymers do not have enough reacting groups. This causes the separation of the macrophase, which leads to the weakening of the interfacial bonding strength. This brings about the deterioration of the total properties. This can be resolved by the direct attachment of the reacting groups to the polymers[23,24] or by the use of coupling agents.[3,16,18,20–22,26,31] In addition, the use of coupling agents can reduce the size of the particle and improve transparency. Organic–inorganic hybrid composites were named *cramers* by Wikes et al.[32] and *ormisils* and *ormocers* by Schmidt.[33] Nanosize ceramic particles in the polymer matrix are called *nanocomposites*. In this study, we formed a rubber phase, not a ceramic phase, in an aromatic polyamide (Trogamid T) matrix to produce polyamide–poly(dimethylsiloxane) (PDMS) nanocomposites by the sol–gel process of diethoxydimethylsilane (DEDMS). The bond strength between the newly produced rubber phase and polyamide matrix is enhanced by the addition of 3-glycidoxypropyltrimethoxysilane (epoxysilane) as a coupling agent. The significance of this research is the production of new nanocomposites by low-temperature curing and the expansion of the applications of the sol–gel process from the ceramic phase to the rubber phase. Our previous research has shown that they exhibit some improved ultimate properties, including toughness.[21]

EXPERIMENTAL

Materials

Poly(trimethylhexamethyleneterephthalamide) (Trogamid T) was donated by Hüls America Inc. (Somerset, NJ) and was used as polyamide. Polyamide was dried at 60°C for 24 h in a vacuum-drying oven. *N,N*-Dimethylacetamide (DMAc; 99.8%, anhydrous) and 3-glycidoxypropyltrimethoxysilane were used as the solvent and coupling agent, respectively. The catalysts were 1,4-diazabicyclo[2.2.2]octane (trimethyl diamine; 98%) and tin(II) 2-ethylhexanoate [2-ethylhexanoic acid and tin(II) salt]. Diethylamine (>99.5%) and DEDMS (a difunctional silane) were also used. All raw materials used in these experiments were purchased from Aldrich Chemicals Co. (Milwaukee, WI).

Synthesis of the polyamide coupling agent

Polyamide (20 g) and 0.2 g of 1,4-diazabicyclo[2.2.2]-octane were poured into a 500-mL triangular flask with a magnetic stirring bar. This was dried in a vacuum-drying oven at 60°C for 24 h. The mixture was then capped with a rubber septum connected to a balloon filled with nitrogen, and 200 mL of anhydrous DMAc as a solvent was injected into the flask of polyamide. Polyamide was dissolved completely upon the heating of stirrer at 50°C for 4 h. The flask was cooled to room temperature, and a coupling agent was added to it. The polyamide coupling agent was reacted with agitation in the flask at 50–60°C for 3 days.

Fabrication of the polyamide–PDMS nanocomposite films

After the addition of a selected amount of DEDMS to the polyamide/epoxysilane reactant, diethylamine was dissolved in DMAc, and water was added for hydrolysis and condensation. Afterwards, five to six drops of tin(II) 2-ethylhexanoate were added to catalyze the reaction. The compound was placed in a shaking water bath at 60°C for 12 h and cooled down to be poured into a Teflon mold. A polyamide–PDMS nanocomposite film was fabricated and kept in a vacuum-drying oven set at 80°C for 24 h. The fabricated film was stored in the vacuum-drying oven until the physical properties were measured.

Instruments

Chemical analysis was conducted with a Bruker IFS-66 Fourier transform infrared (FTIR) instrument (Bruker Instruments, Billerical, MA). The transmittance was measured in the form of a thin film. Attenuated total reflection (ATR) was used for surface analysis. Wide-scanning X-ray photoelectron spectroscopy (XPS) via a VG-Microtech ESCA-200 (Therma VG Scientific, West Sussex, UK) was also performed. The contact angles were measured with an SEO 300x (SEO Co., Ansan, Korea). Twice distilled water was used. The static contact-angle method was used to measure the contact angle of each sample. In this method, a thin film of each sample was fixed on a plate that had a uniform surface, and water was dropped at a regular rate. The morphology of the surface was observed by atomic force microscopy (AFM) with a Nanoscope-3a (Digital Instruments, Santa Barbara, CA). The thermal characteristics were investigated with a TGA 2050 (TA Instruments, New Castle, DE). The measured temperature range was 30–800°C, the heating rate was 20°C/min, and N_2 and O_2 gas was deposited at a rate of 50 mL/min. Differential scanning calorimetry (DSC; TA Instruments) was used to measure the glass-transition temperature. The measured temperature range was 30–250°C, the heating rate was 10°C/min, and N_2 gas was injected at a rate of 50 mL/min.

RESULTS AND DISCUSSION

FTIR

Scheme 1 shows the reaction of polyamide and epoxysilane. In this reaction, amide hydrogen in polyamide and the epoxy group of epoxysilane reacted to form a polyamide with a silane group. As shown in Figure 1, this silane group went through condensation by itself or simultaneously acted as a crosslinking agent with the coupling agent by condensation with PDMS. This condensation reaction was executed at a relatively low temperature (<60°C), and the condensation product was eliminated *in vacuo*. Figure 1(a) is the condensate structure of polyamide/epoxysilane, in which the silane group functioned as a crosslinking agent and polyamide was grafted onto it. Also, a small quantity of unreacted alcohols or alkoxy groups existed. Figure 1(b) shows the structure in which PDMS, the condensate of DEDMS, was added to the polyamide/epoxysilane composite. It coexisted in three forms: PDMS bonding to both ends of the condensate structure of polyamide/epoxysilane, bonding to only one end, and not bonding at all. The strong interaction between silica and polyamide by the epoxysilane coupling agent was already proved with scanning electron microscopy (SEM) photographs.[20] PDMS, having the same functional group as silica, should have a strong interaction with polyamide via the epoxysilane coupling agent. Figure 2 shows the changes in the IR spectra along with the changes in the concentration of PDMS, the condensation product of DEDMS. The Si—O—Si stretching vibration peak near 1000–1100 cm^{-1} appeared with the C—O—C stretching vibration peak, and as the content of PDMS increased, the peaks became larger. This was caused by the increased concentration of PDMS, which led to an increase in
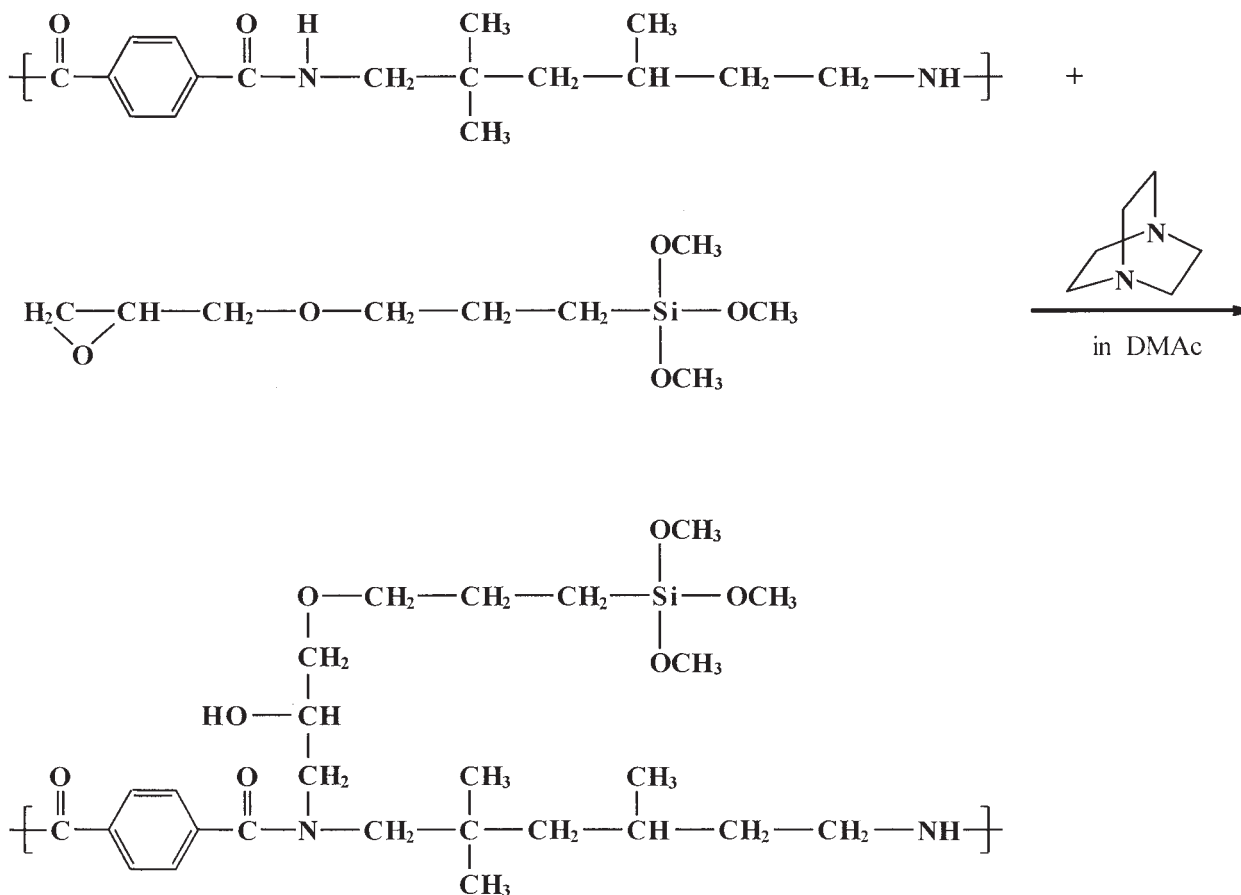
Scheme 1 Synthesis of polyamide with the epoxysilane coupling agent.

Si—O—Si. The peaks of $Si(CH_3)_n$ ($n = 1, 2, 3,$ or 4) near 1250–1280 cm^{-1} and those of $Si(CH_3)_2$ near 800–850 cm^{-1} showed that there was a noticeable difference caused by the difference in the concentration of the difunctional silane. Because the Si—CH$_3$ group only existed in PDMS, it was known that the intensity of the peaks became greater as the concentration of oligomeric PDMS increased.

The Si—OH stretching vibration peak near 950 cm^{-1} was very weak, regardless of the PDMS contents, and so the concentration of remaining silanol groups without condensation could be considered small.

ATR

In general IR spectroscopy, information is obtained from the IR absorbance when a beam is transmitted through the sample. On the other hand, ATR is based on internal total reflection. The light source passes the prism, penetrates the sample, and reflects. The surface of the sample and incident radiation interact to produce an absorbance at specific wavelengths. In the ATR method, internal reflection occurs many times, providing higher resolution. In this research, ATR

spectra were used to observe the surface properties of PDMS-added polyamide. In Figure 3, FTIR and ATR spectra for polyamide/epoxysilane (30 wt %) composites with 40 wt % PDMS, the condensation product of DEDMS, were compared. The transmission spectra could be used as the standard spectra of the sample, with uniformly distributed additives across the sample thickness. The intensities of the Si—O—Si peak near 1000–1100 cm^{-1} as well as the Si—CH$_3$ peak overlapping with the Si—O—Si peak at 800 cm^{-1} were stronger in the ATR spectra. These results suggested that a large amount of PDMS with less surface tension existed on the surface of polyamide.

XPS

Elemental analyses by wide-scanning XPS for various samples are shown in Figure 4. Figure 4(A) is the XPS spectrum of pure polyamide. The main chain of polyamide had much C and less O and N. Figure 4(B) is the XPS spectrum of the polyamide/epoxysilane (30 wt %) composite: the intensity of the C peak decreased, and a Si peak appeared that did not exist in pure polyamide. This happened because self-crosslinkings of silane groups formed new siloxane bonds (Si—O).
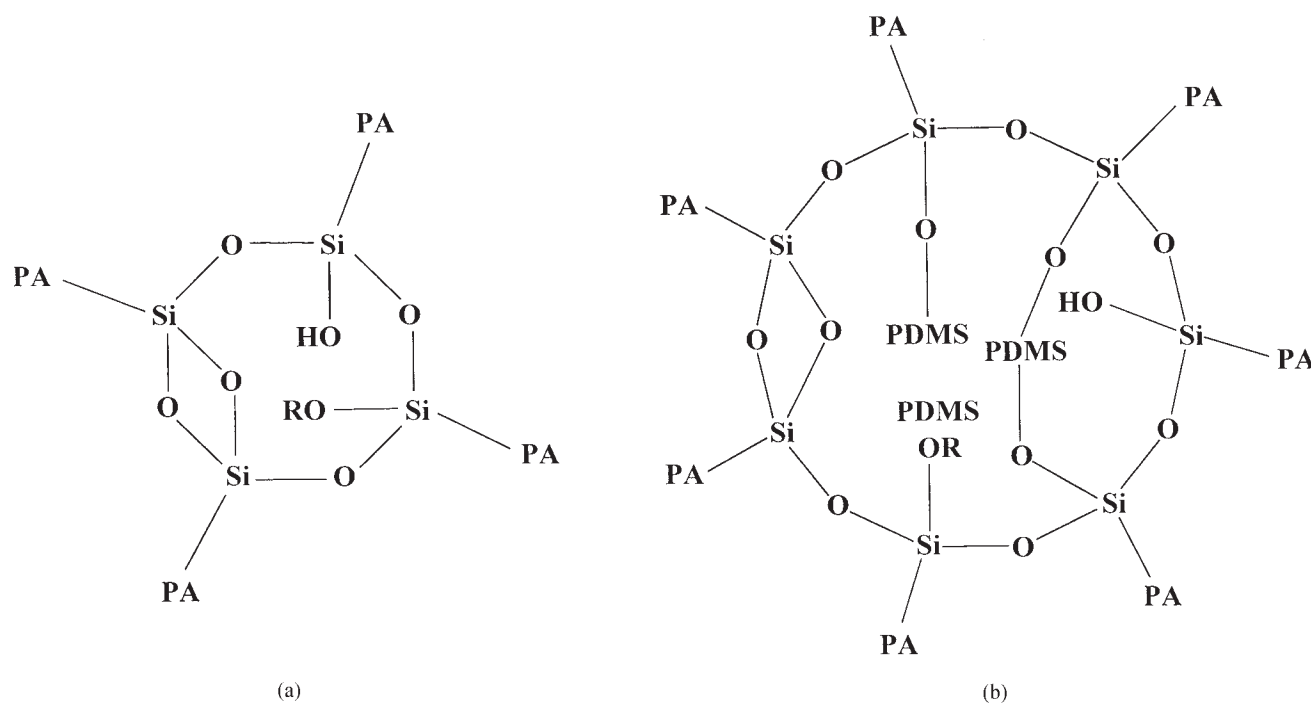
Figure 1 Condensed product of polyamide (PA)/epoxysilane: (a) PA/epoxysilane composite and (b) PA/epoxysilane composite with PDMS.
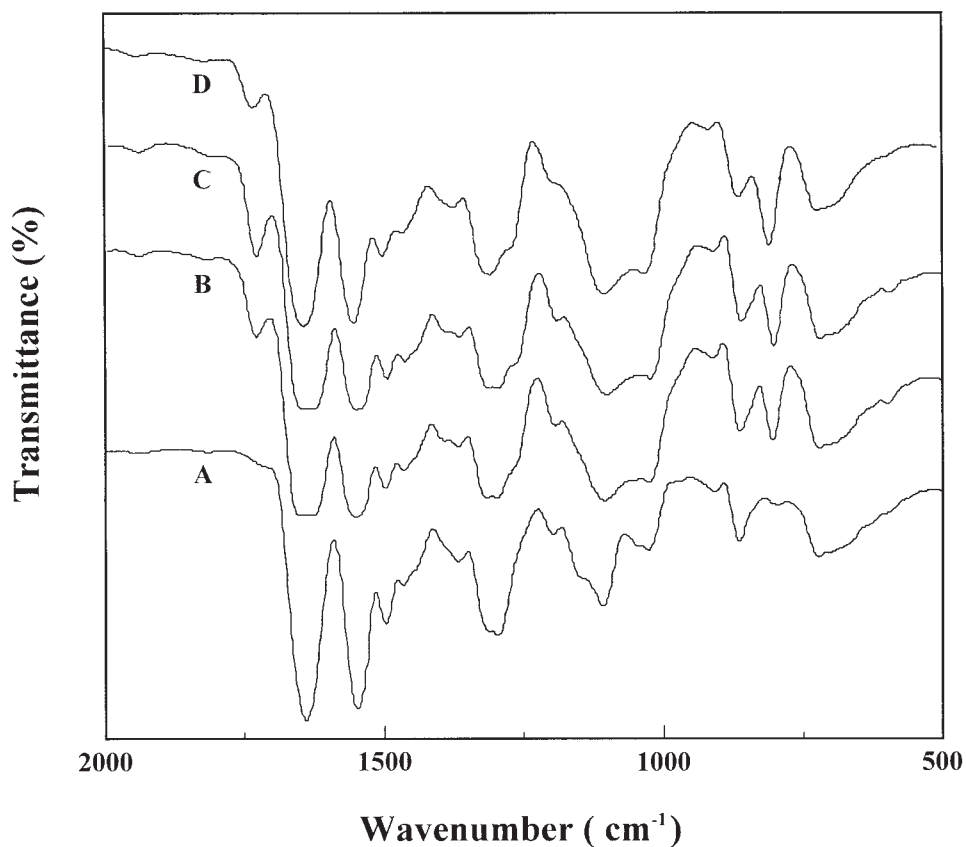
Figure 2 FTIR spectra of polyamide/epoxysilane (30 wt %) composites with various PDMS contents: (A) polyamide only, (B) 0 wt %, (C) 20 wt %, (D) 40 wt %.
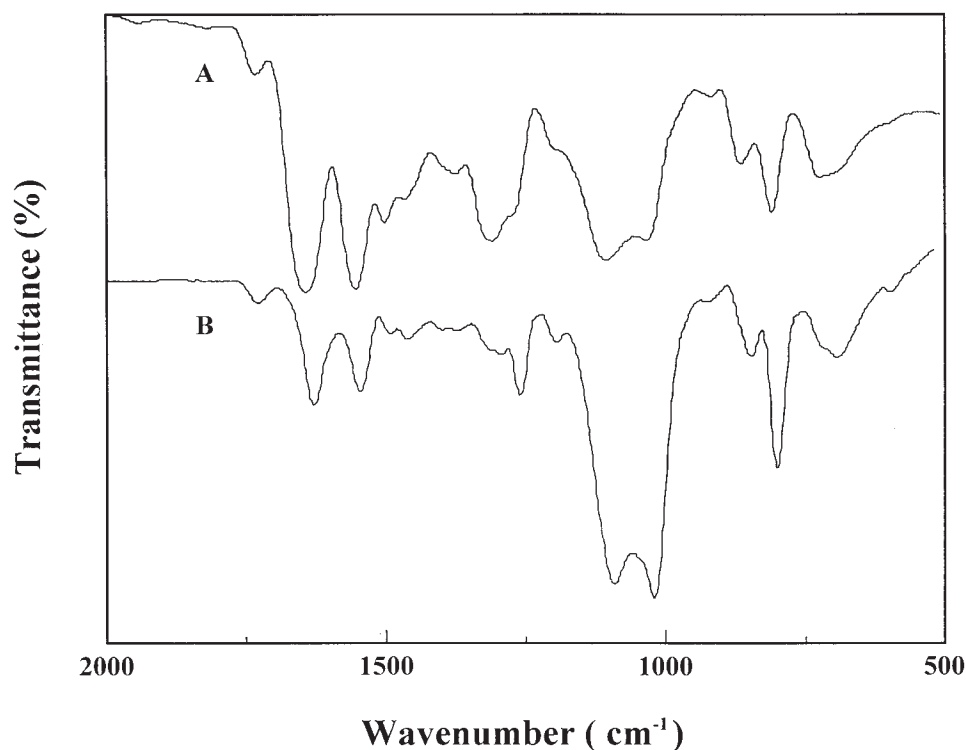
Figure 3 Comparison of (A) FTIR and (B) ATR spectra for polyamide/epoxysilane (30 wt %) composites with 40 wt % PDMS.

Figure 4(C) is the XPS spectrum of a sample composed by the addition of 30 wt % of PDMS to the sample of Figure 4(B), and it showed a similar tendency. Figure 4(B,C) showed no significant difference. This result indicated that a small number of silane groups could be dispersed on the sample surface. It was also thought that the surface characteristics could be varied.

Contact angle

The Wilhelmy plate method has been used the most generally. With more than two kinds of liquids for which the surface tension is already known, various interfacial information, including the contact angle, can be provided. However, its measurement is somewhat complicated. In this research, the simplest but relatively accurate method measuring the direct contact angle of a sample and water was applied. Figure 5 shows the contact angle for the pure polyamide, polyamide/epoxysilane composite, and polyamide/epoxysilane composite with various PDMS contents. The pure polyamide had an angle of 72°, and the samples with epoxysilane and PDMS added had contact angles of approximately 112°. Epoxysilane and composites with PDMS had contact angles 40° higher on average than that of pure polyamide. This resulted from the fact that hydrophobic siloxane was dispersed on the surface of polyamide to reflect the strong water-

resistant surface property. These surface characteristics are considered to be applicable to the semiconductor and electronics industries.

AFM

The principle of AFM is distinguished from that of SEM or transmission electron microscopy. Maintaining the repulsive force between the surface and the scanning needle, it transforms the spatial distribution of the height of the scanning needle into a surface image. From the change in the signal accompanied by the adjacent scanning of the sample surface, geographical structures can be observed on the atomic scale. The surface can be observed without a surface treatment, and surface atomic arrangement can be understood to the scale of angstroms with a relatively simple method. It is also possible to observe nonconducting materials such as polymers. This research was performed in the tapping mode to minimize possible damage to the surface of the samples. The samples were coated onto silicon wafers with low roughness. Figure 6 presents an AFM image of polyamide/epoxysilane (30 wt %) composites with 30 wt % PDMS. The size of the PDMS particles on the surface was approximately 2.5 μm. In the AFM image, clear phase separation of PDMS on the surface of the polymer could be observed, and the size of the PDMS particles was approximately 2.5 μm. Generally, particles in sil-
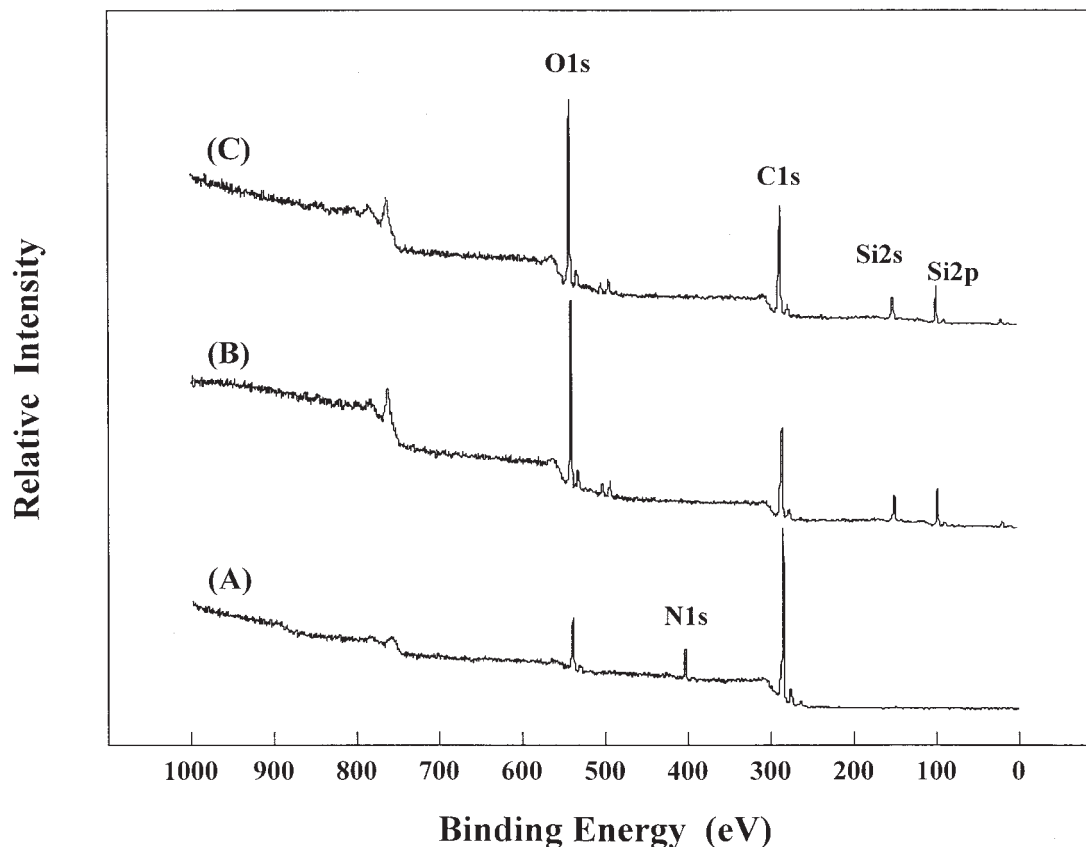
Figure 4 XPS spectra of various samples at an angle of 45°: (A) polyamide only, (B) polyamide/epoxysilane (30 wt %) composite, and (C) polyamide/epoxysilane (30 wt %) composite with 30 wt % PDMS.

ica/polymer composites made by a sol–gel process are nanoscale. We then examined the factors affecting the phase separation. On the polyamide surface, the PDMS particles, the condensation product of DEDMS, had the shape of small oil drops floating on water.

Thermogravimetric analysis (TGA)

Figure 7 presents TGA curves in a nitrogen atmosphere for polyamide/epoxysilane composites with various PDMS contents. For the pure polyamide, the weight decline progressed slowly until 220°C because of the condensation reaction that small substances drained away. A low condensation temperature could lead to incompleteness of the condensation. A weight decline occurred again above 400°C because of pyrolysis. A small amount of the residue, which consisted of stable aromatic compounds, existed up to 800°C. The char concentration was approximately 3%. Polyamide with PDMS had a similar tendency of weight decline with the pure polyamide, and the pyrolysis temperature was also about 400°C. A weight decline did not occur above 500°C. It was thought that a stable silicate ceramic formed after pyrolysis. The char concentration was higher by 10% for samples with PDMS

(10–15%) than for pure polyamide. In a nitrogen atmosphere, polyamide with PDMS had a similar pyrolysis temperature but a higher final char concentration than the pure polyamide.

DSC

The general glass-transition temperature for Trogamid T is known to be around 140°C. As shown in Figure 8, polyamide with PDMS had a glass-transition temperature around 140°C. Therefore, it had a glass-transition temperature similar to that of the pure polyamide. The results indicated phase separation between the two phases. If measurements had been performed at −180°C with liquid N_2, the glass-transition temperature of PDMS would have been measured to be −60°C.

CONCLUSIONS

The fact that epoxy groups and polyamide react fluently and that PDMS, the condensation product of DEDMS, can exist in a polyamide matrix, has been confirmed with FTIR spectra. With coupling agents, the bonding strength between the rubber phase
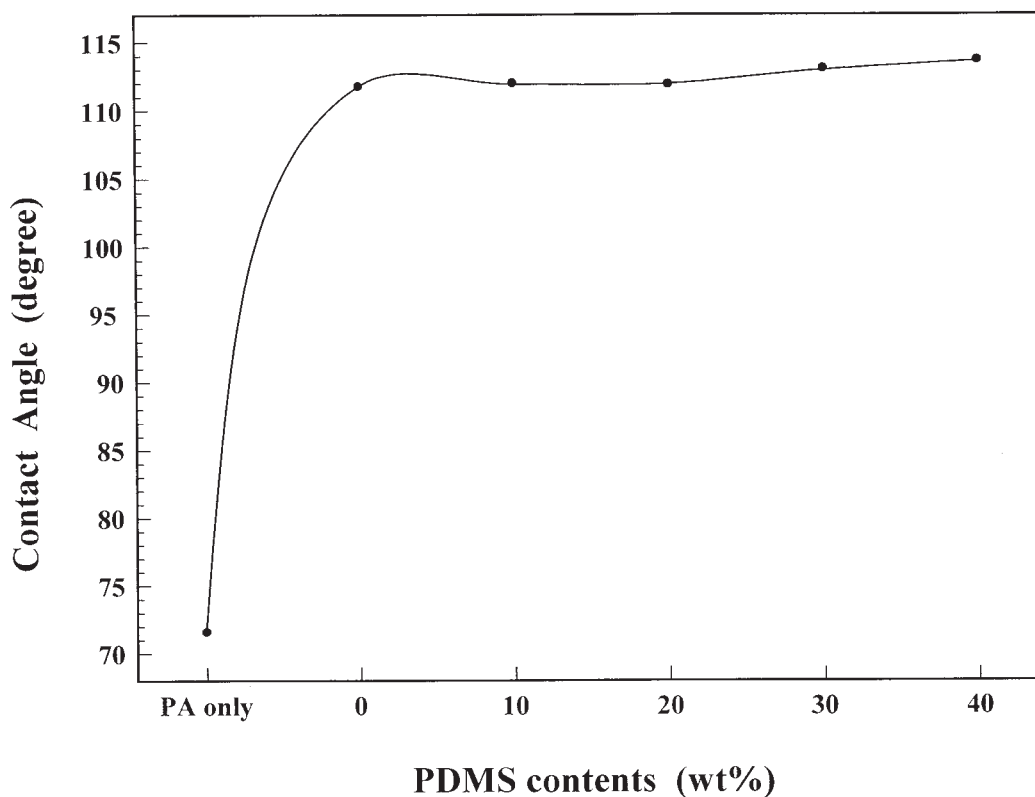
Figure 5 Contact angle for the polyamide only and polyamide/epoxysilane (30 wt %) composites with various PDMS contents.

(PDMS) fabricated by the sol–gel process and the polymer phase (polyamide) can be enhanced. It has been confirmed by ATR, contact-angle measurements, and AFM imaging that silane groups with lower surface tension are concentrated on the surface of polyamide. The pyrolysis temperature for the samples with
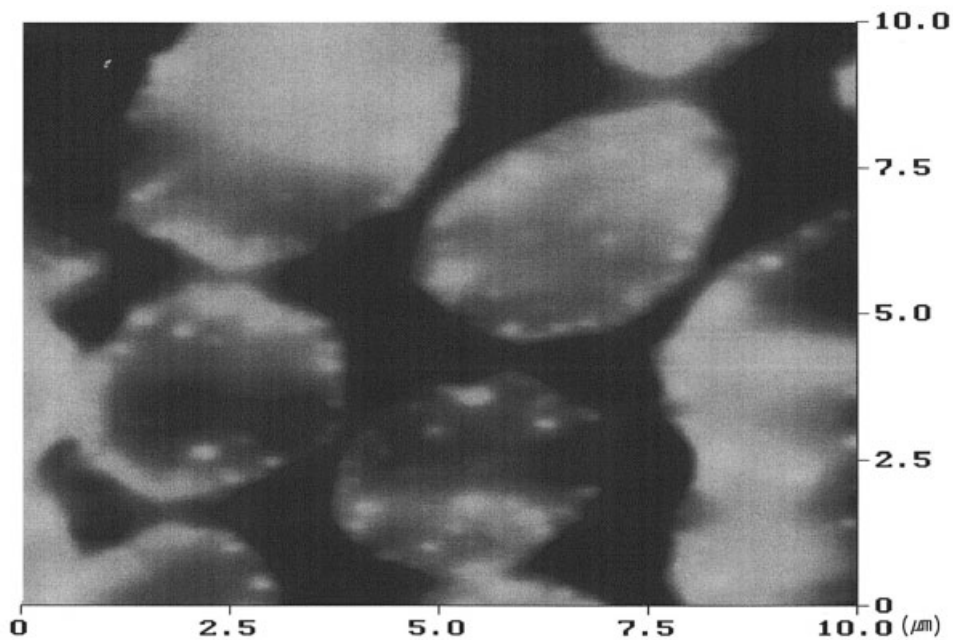
Figure 6 AFM image of polyamide/epoxysilane (30 wt %) composites with 30 wt % PDMS.
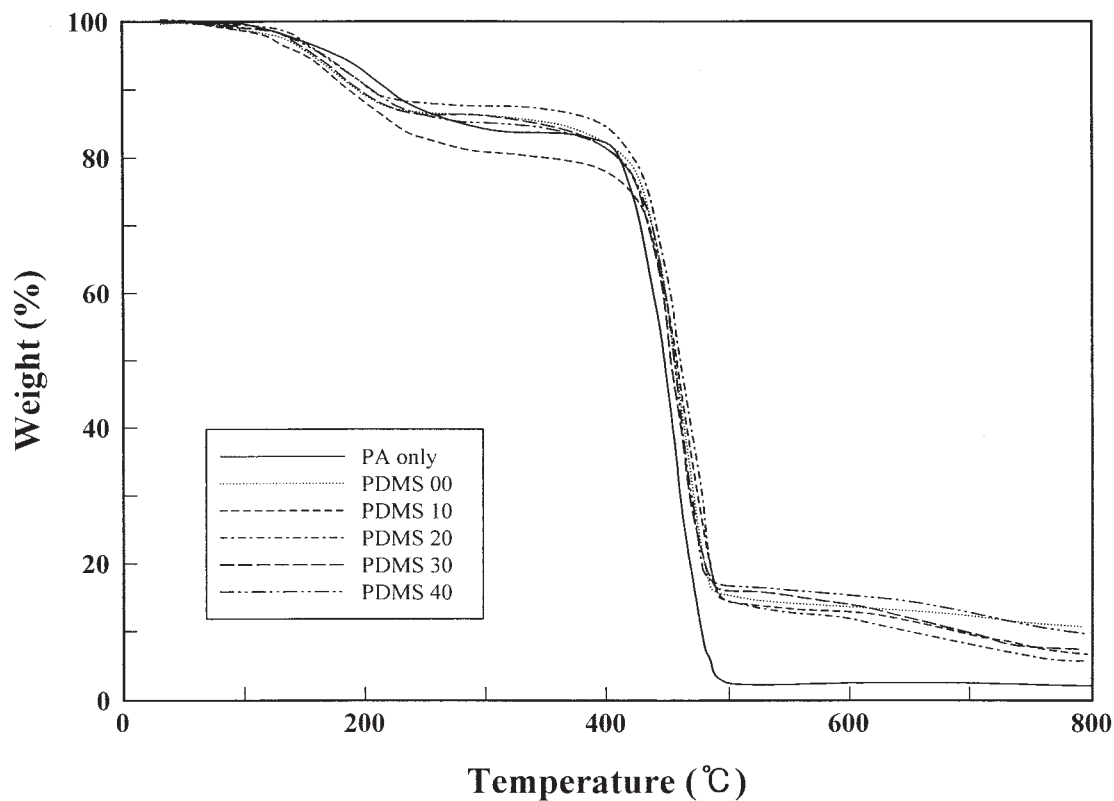
Figure 7 TGA curves under a nitrogen atmosphere for polyamide (PA)/epoxysilane (30 wt %) composites with various PDMS contents.
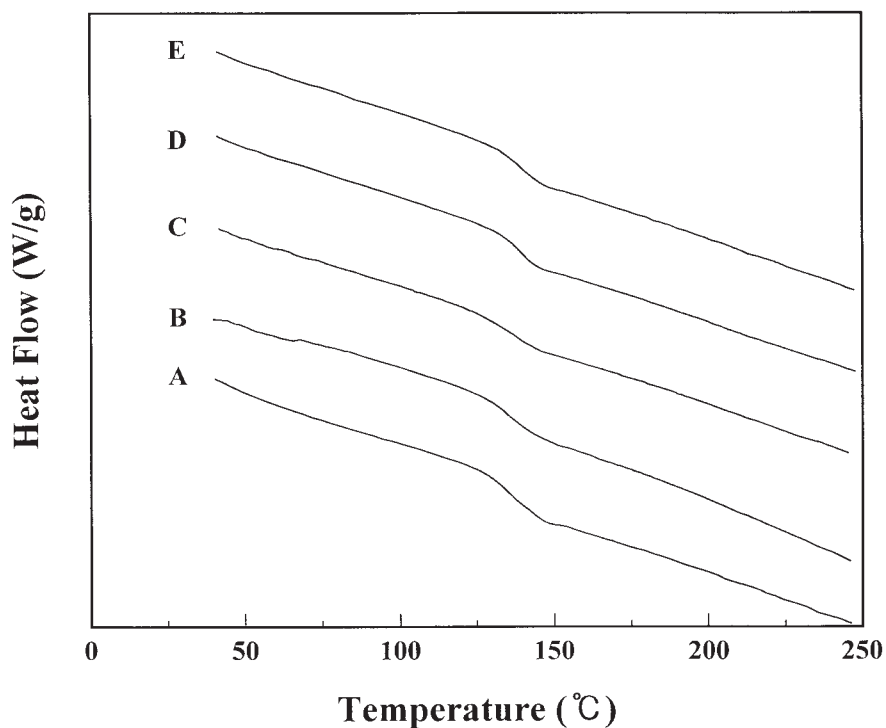
Figure 8 DSC curves for polyamide/epoxysilane (30 wt %) composites with various PDMS contents: (A) 0, (B) 10, (C) 20, (D) 30, and (E) 40 wt % PDMS.

PDMS was 400°C, similar to that of pure polyamide. The final char contents for samples with PDMS were 10% higher than that of pure polyamide. This was thought to be due to the stable silicate ceramic that formed after pyrolysis. For aromatic polyamide, the glass-transition temperature is known to be approximately 140°C, and the polyamide–PDMS nanocomposites had a similar value. New nanocomposites obtained from this research have been produced through the formation of a rubber phase in the polymer phase. The significance of this is that the application of the sol–gel process has been expanded from a ceramic phase to a rubber phase, and the fabrication can be conducted by low-temperature curing under 60°C.

References

1. Brinker, C. J.; Scherer, G. W. Sol–Gel Science; Academic: London, 1990.
2. Wright, J. D.; Sommerdijk, N. A. J. M. Sol–Gel Materials: Chemistry and Applications; Gordon & Breach: Amsterdam, 2001.
3. Ahmad, Z.; Mark, J. E. Chem Mater 2001, 13, 3320.
4. Mark, J. E. Heteroat Chem Rev 1996, 3, 307.
5. Mark, J. E. Polym Eng Sci 1996, 36, 2905.
6. Wen, J.; Wikes, G. L. Chem Mater 1996, 8, 1667.
7. Collinson, M. M. Trends Anal Chem 2002, 21, 30.
8. Zarzycki, J. J Sol-Gel Sci Technol 1997, 8, 17.
9. Chujo, Y. Curr Opin Solid State Mater Sci 1996, 1, 806.
10. Imai, Y. React Funct Polym 1996, 30, 3.
11. Mark, J. E. Curr Opin Solid State Mater Sci 1999, 4, 565.
12. Mark, J. E. J Macromol Sci Pure Appl Chem 1996, 33, 2005.
13. Landry, C. J. T.; Coltrain, B. K.; Landry, M. R.; Fitzgerald, J. J.; Long, V. K. Macromolecules 1993, 26, 3702.
14. Hsiue, G. H.; Kuo, W. J.; Huang, Y. P.; Jeng, R. J. Polymer 2000, 41, 2813.
15. Chan, C. K.; Chu, I. M. Polymer 2001, 42, 6089.
16. Premachandra, J.; Kumudinie, C.; Zhao, W.; Mark, J. E.; Dang, T. D.; Chen, J. P.; Arnold, F. E. J Sol-Gel Sci Technol 1996, 7, 163.
17. McCarthy, D. W.; Mark, J. E.; Clarson, S. J.; Schaefer, D. W. J Polym Sci Part B: Polym Phys 1998, 36, 1191.
18. Zhou, W.; Mark, J. E.; Unroe, M. R.; Arnold, F. E. J Appl Polym Sci 2001, 79, 2326.
19. Kumudinie, C.; Premachandra, J. K.; Mark, J. E.; Dang, T. D.; Unroe, M. R.; Arnold, F. E. Polymer 2001, 42, 5275.
20. Park, Y. W.; Mark, J. E. Polym-Plast Technol Eng 2000, 39, 875.
21. Park, Y. W.; Mark, J. E. Colloid Polym Sci 2000, 279, 665.
22. Ahmad, Z.; Sarwar, M. I.; Mark, J. E. J Mater Chem 1997, 7, 259.
23. Ahmad, Z.; Sarwar, M. I.; Mark, J. E. J Appl Polym Sci 1997, 63, 1345.
24. Morikawa, A.; Iyoku, Y.; Kakimoto, M. A.; Imai, Y. J Mater Chem 1992, 2, 679.
25. Cornelius, C. J.; Marand, E. Polymer 2002, 43, 2385.
26. Mascia, L.; Kioul, A. Polymer 1995, 36, 3649.
27. Morikawa, A.; Iyoku, Y.; Kakimoto, M. A.; Imai, Y. Polym J 1992, 24, 107.
28. Zhu, Z. K.; Yang, Y.; Yin, J.; Qi, Z. N. J Appl Polym Sci 1999, 73, 2977.
29. Huang, J. C.; Zhu, Z. K.; Yin, J.; Zhang, D. M.; Qian, X. F. J Appl Polym Sci 2001, 79, 794.
30. Hsiue, G. H.; Chen, J. K.; Liu, Y. L. J Appl Polym Sci 2000, 76, 1609.
31. Sarwar, M. I.; Ahmad, Z. Eur Polym J 2000, 36, 89.
32. Wikes, G. L.; Orler, B.; Huang, H. Polym Prepr 1985, 26, 300.
33. Schmidt, H. J Non-Cryst Solids 1985, 73, 681.