Effect of Quasi-Nanometer Zirconium Carbide on the Physical Characterization of Zirconium Carbide/Polyurethane Composite Films Irradiated Under Ultraviolet Light

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ABSTRACT: We used quasi-nanometer zirconium carbide (ZrC) and a polyurethane (PU) resin under roller pressure to form a composite film and found that the tensile strength at break, elongation at break, and modulus gradually decreased with increasing ultraviolet (UV)-irradiation time for films of both PU and the PU/ZrC composite. However, this phenomenon was significantly higher for the PU film than for the ZrC/PU composite film. The construction of the PU film changed after UV irradiation, but that of the PU/ZrC composite film was almost unchanged. The degradation of PU molecules occurred in the absence of ZrC particles after irradiation with UV light but almost did not occur in the presence of ZrC particles. This was confirmed with Fourier transform infrared spectroscopy and gel permeation chromatography analyses. It was suggested that polymer radicals which formed through the photooxidation of UV irradiation and free radicals which formed through the photoreduction of nanometer ZrC/UV irradiation interacted to form a dead polymer to stop the degradation; simultaneously, the chemical bonding between polymer molecules could be re-formed from free radicals created by photooxidation and photoreduction and thus reduce the mobility of PU molecules, thereby raising the glass-transition and melting temperatures of the soft segment. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4842–4849, 2006

Key words: composites; glass transition; melting point; polyurethanes; thermogravimetric analysis (TGA)

INTRODUCTION

Mineral particles can release far-infrared rays and be used in healthy textile materials.[1] Other nanometer particles, such as nanometer titanium dioxide, have been used for their antibacterial properties, electron conductance, anionic release, and so forth.[2–4] Moreover, the addition of clay to resins such as polypropylene, nylon, and polyester resins can improve the mechanical and chemical properties of clay–resin composites.[5–12] Our previous study[13] revealed that the ether and ester groups of polyurethane (PU) could interact with zirconium carbide (ZrC) particles to improve the strength and thermal properties of composite prepared under roller pressure without the surface modification of nanometer particles.

Generally, resin or nanometer-particle/resin composite films used for decorations or other surfaces of buildings, such as floors, need stronger mechanical properties for long-term use. Exposure to ultraviolet (UV) irradiation under atmospheric conditions is unavoidable, and the degradation of resin molecules is inevitable. This degradation is known as a photooxidation reaction.[14,15] Scott and Gilead[14] pointed out that photooxidation can occur during the processing and use of materials. This photooxidation creates various forms of free radicals, but one of the final products is generally carboxylic acid. The carbonyl index is used to determine the degree of photooxidation under irradiation.[16] Abu-Zeid et al.[17] revealed that the PU polymer can be easily degraded under UV irradiation even with a low dosage. Govorčin Bajsić and Rek[18] attributed the degradation of PU under UV irradiation to two steps: the degradation of the hard segment and the degradation of the soft segment. On the other hand, nanometer particles can suffer photoreduction after absorbing UV light. Our interest is the effect of photoreduction on the physical and thermal properties of composite films, which is caused by nanometer ZrC particles under the irradiation of UV light.

In this study, we compounded quasi-nanometer ZrC with PU under a roller pressure of approximately 1.0 kg/cm^2 at room temperature and then formed films to research some mechanical properties with Fourier transform infrared (FTIR), differential

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scanning calorimetry (DSC), thermogravimetric analysis (TGA), and X-ray (wide-angle diffraction) analyses. Information about the effect of UV irradiation in the atmosphere on the physical properties of ZrC/PU composite films is lacking. Here we are interested in how quasi-nanometer ZrC affects the mechanical and thermal properties of PU in composites after UV irradiation, and we have tried to confirm the effect of nanometer ZrC on the physical properties of ZrC/PU composite films with the aforementioned methods. A pristine PU film was also investigated for comparison.

EXPERIMENTAL

Materials

Quasi-nanometer-grade ZrC ($\sim$ 500 nm) was obtained from Desunnano Co., Ltd. (Taipei, Taiwan). PU (30% solid) was obtained from Lidye Chemical Co., Ltd. (Taipei, Taiwan).

Methods

Preparation of the composite films

Quasi-nanometer-grade ZrC (3.0 w/w) was mixed with PU and squeezed between rollers repeatedly under a pressure of about 1.0 kg/cm^2 for 1 h to ensure that the surfaces of the nanometer particles were wetted with the solvent and were in contact with PU molecules. Then, the mixed solutions were coated on glass to a thickness of 0.6 mm, dried at 90°C for 4 h, and dipped in cold water for 8 h to form the films.[13]

Thermal properties

TGA was performed with a DuPont TGA-2050 (TA Instrument Inc., New Castle, DE). All samples were tested at a heating rate of 10°C/min under flowing nitrogen at a flow rate of 100 mL/min. The samples (10–15 mg) were placed on a platinum plate for each experiment.

The thermal properties of the pristine PU and ZrC/PU composites were also determined with a differential scanning calorimeter (DSC Q 10, TA Instruments). All scans were carried out at a heating rate of 10°C/min under flowing nitrogen at a flow rate of 50 mL/min. The instrument was calibrated with pure indium. Samples weighing about 5 mg were placed in standard aluminum sample pans for each DSC experiment.

Wide-angle X-ray diffraction (WAXD)

WAXD was determined with an X-ray powder diffractometer (MXP18, MAC Science, Yokohama, Japan)

equipped with Ni-filtered Cu Kα radiation and operated at 40 kV and 30 mA. Each film, 3.0 mm thick, was kept stationary and scanned in the reflection mode from 2 to 30° at a scanning rate of 2°/min.

FTIR spectroscopy

FTIR spectroscopy measurements of the films were recorded on a Spectrum One FTIR spectrophotometer (PerkinElmer Co. Ltd., Shelton, CT); 12 scans with a spectral resolution of 1 cm^{-1} were collected during each spectroscopic measurement. IR spectra of the specimens were taken from film samples with a thickness of 0.6 mm. The films used in this study were thin enough to obey the Beer–Lambert law.

Dynamic mechanical analysis (DMA)

The dynamic mechanical properties of the PU and PU/ZrC composite films before and after UV irradiation were determined with a PerkinElmer DMA 7e dynamic mechanical analyzer. The samples were molded into a bar with a cross section of 3.05 mm × 3.05 mm and scanned under flowing nitrogen at a flow rate of 25 mL/min and at a heating rate of 3°C/min from −50 to 50°C with a frequency of 10 Hz.

Gel permeation chromatography (GPC)

A PU/ZrC composite film weighing 0.5 g was dissolved in 10 mL of tetrahydrofuran and then filtered with a filter having a pore size of about 5–10 μm to prevent the clogging of the gel column by particles of ZrC. A pristine PU film was also dissolved and filtered for comparison. The values of the number-average molecular weight (M_n) were measured with GPC (Lab Alliance Series III, PerkinElmer) with 0.02-mL polymer solutions under 40°C. A PLgel column was used in this study.

RESULTS AND DISCUSSION

Table I shows the data for the tensile strength at break, elongation at break, and modulus of the PU/ZrC composite and PU films before and after UV irradiation for various periods. The tensile strength at break and modulus for the pristine PU/ZrC composite film are higher than those for the pristine PU film. Some investigations have showed similar tendencies for clay–polypropylene, clay–nylon, and clay–polyester composites.[6,9,10] Our previous study[13] pointed out that the physical properties (especially the tensile strength) of nanometer-particle/resin composite films are higher than those of a resin film. On the other hand, the elongation at break for the pristine PU film is higher than that for the pristine PU/ZrC composite film. This result is similar to that

TABLE I
Various Mechanical Properties of the PU and PU/ZrC Composite Films

Film	Irradiation time (h)	Tensile strength at break (MPa)	Elongation at break (%)	Modulus (MPa)	M_n^a
PU	0	19.35	520.95	17.48	713
	1	16.77	515.52	16.40	
	3	13.15	507.45	14.56	
	7	8.41	495.42	11.36	609
PU/ZrC	0	20.76	499.11	19.58	
	1	19.01	495.05	19.01	
	3	17.22	488.33	18.22	
	7	14.06	478.47	17.00	696

The films were prepared under roller pressure and examined before and after UV irradiation for various times.
[a] Obtained from filtered solutions of the samples.

of our previous study.[13] Additionally, the tensile strength at break, elongation at break, and modulus gradually decrease with increasing UV irradiation time for both films. This phenomenon can be attributed to photooxidation[15] under UV irradiation, under which the polymer molecules are degraded and the mechanical properties are thus lowered. However, the degree of corruption for the strength and modulus of the PU film is significantly higher than that of the ZrC/PU composite film. This phenomenon motivated us to investigate the differences in the thermal and other properties of ZrC/PU composite and PU films after UV irradiation and to determine possible reasons causing those differences.

First, the TGA patterns for the PU and PU/ZrC composite films before and after 7 h of UV irradiation are shown in Figure 1(a–d) separately. The char yield for the PU/ZrC composite film is obviously higher than that for the PU film, and the value is not changed by the irradiation of UV light. The higher char yield for the PU/ZrC composite film is clearly caused by the decomposition of ZrC particles at such temperatures. Figure 1 shows the char yield temperatures and the temperatures of 20% weight loss. They are listed in Table II. The lower char yield temperature and higher temperature of 20% weight loss for the PU/ZrC composite film, compared with those for the PU film, can be attributed to the interaction between the PU molecules and ZrC particles.[13] One interesting phenomenon that can be seen in the TGA figures is that the pattern for the pristine PU/ZrC composite film is similar to that for the PU/ZrC composite film after 7 h of irradiation; however, the pattern for the pristine PU film is obviously different from that for the PU film after 7 h of irradiation (ca. 300–400°C). Obviously, UV irradiation changes the composition of the PU film but almost does not change that of the PU/ZrC composite film.

To confirm the difference in the decomposition temperatures between the two films after UV irradia-

tion, the derivation of the weight versus the temperature of heating for the pristine PU film and pristine PU/ZrC composite film before and after 7 h of UV irradiation is shown in Figure 2(a–d) separately. From this figure, we obtained the data for the first decomposition temperature and second decomposition temperature, which are listed in Table II. These data show that the first decomposition temperature and second decomposition temperature for the pristine PU film are higher than those for the pristine PU/ZrC composite film. The easier decomposition
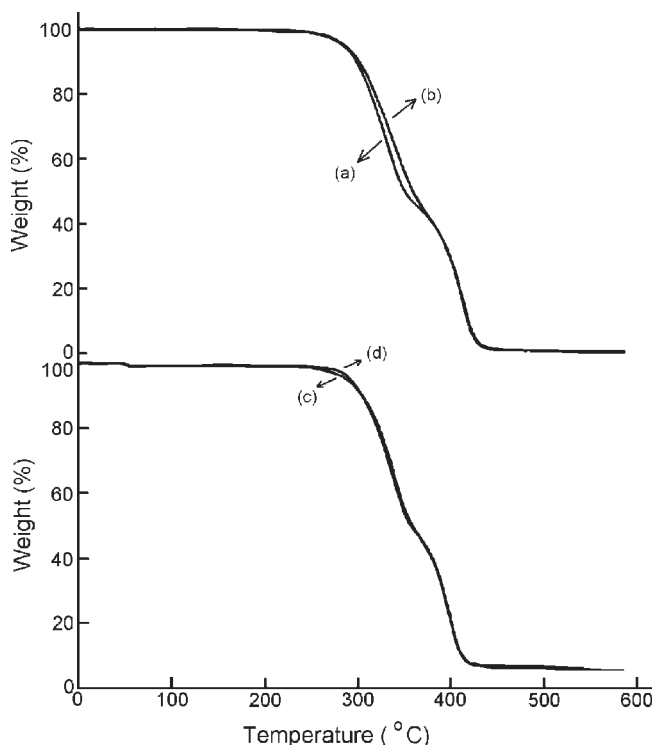

Figure 1 Patterns of TGA obtained from (a) the pristine PU film, (b) the PU film after 7 h of UV irradiation, (c) the pristine PU/ZrC film, and (d) the PU/ZrC composite film after 7 h of UV irradiation.

Film	Irradiation time (h)	Char-yield temperature (°C)[a]	$T_d^{0.2}$ (°C)[b]	First decomposition temperature (°C)[c]	Second decomposition temperature (°C)[c]
PU	0	440.7	315.1	273.8	370.9
	7	440.7	318.6	279.1	376.7
PU/ZrC	0	427.3	323.4	269.8	365.4
	7	427.3	323.0	269.8	367.4

[a] Temperature at which char was beginning to form.
[b] Temperature of 20% weight loss.
[c] Obtained from Figure 7.

for the PU/ZrC composite film is caused by the interaction between the PU molecules and ZrC particles.[13] Additionally, the first decomposition temperature and second decomposition temperature for the PU film after 7 h of UV irradiation are higher than those for the pristine PU film, but the peak for the PU film after 7 h of UV irradiation in Figure 2(b) is broader than that for the pristine PU film in the first stage of decomposition. This result reveals the more complicated structure of PU polymer molecules (lower purity of the PU polymer) after UV irradiation. However, the first decomposition temperature

and second decomposition temperature for the PU/ZrC composite film after 7 h of UV irradiation are similar to those for the pristine PU/ZrC composite film, and the peak for the PU/ZrC composite film after 7 h of UV irradiation in Figure 2(d) is similar to that for the pristine PU/ZrC composite film in the first and second stages of decomposition. These results clearly reveal that the structure of the PU polymer for the pristine PU film is different from that for the PU film after 7 h of UV irradiation; however, that for the pristine PU/ZrC composite film is similar to that for the PU/ZrC composite film after 7 h of UV irradiation. This difference is probably due to the free radicals of the PU polymer chain caused by photooxidation under UV irradiation or the reaction products formed from these free radicals in the absence of ZrC particles.

To confirm the difference in the chemical structures of the pristine PU film and PU film after UV irradiation or of the pristine PU/ZrC composite film and PU/ZrC composite film after UV irradiation, the FTIR spectra of the pristine PU film, PU film after 7 h of UV irradiation, pristine PU/ZrC composite film, and PU/ZrC composite film after 7 h of UV irradiation are shown in Figures 3(a,b) and 4(a,b) separately. The interesting and important absorbing bands are the ester group at about 1237 cm^{-1} and the ether group at about 1165 and 1036 cm^{-1}. The PU film after UV irradiation has higher intensity and a broader width for these three absorption bands than the pristine PU film [Fig. 3(a,b)]. However, the PU/ZrC composite film after UV irradiation has a similar intensity for these three absorption bands in comparison with the pristine PU/ZrC composite film [Fig. 4(a,b)]. The higher intensity and broader width of the absorption bands at about 1237, 1165, and 1036 cm^{-1} are believed to be due to the formation of carboxylic acid and alcohol groups, which have the same absorption bands near those of ester and ether groups.[19] Those of the ester and carboxylic acid or the ether and alcohol groups overlap, and this increases the intensity and broadens the width of those absorption bands. These results clearly reveal that PU molecules can be degraded
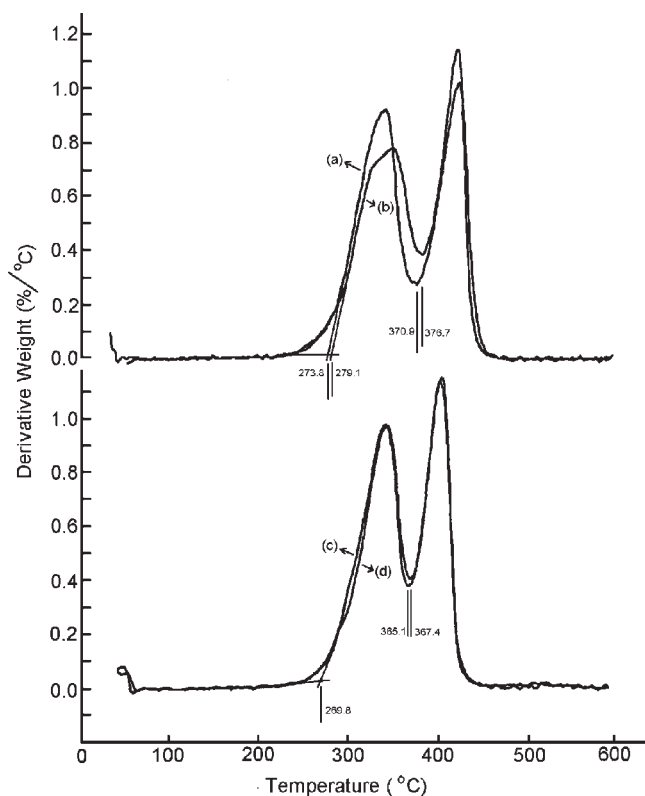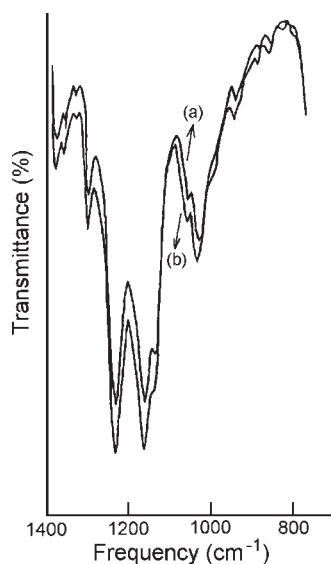

Figure 2 Patterns of the derivation of the weight versus the temperature of heating obtained from TGA for (a) the pristine PU film, (b) the PU film after 7 h of UV irradiation, (c) the pristine PU/ZrC composite film, and (d) the PU/ZrC composite film after 7 h of UV irradiation.

Figure 3 FTIR spectra obtained from (a) the pristine PU film and (b) the PU film after 7 h of UV irradiation.

under the UV irradiation of a PU film; however, the presence of quasi-nanometer ZrC can inhibit this degradation reaction.

If the degradation of ether and ester groups under UV irradiation exists in the amorphous region, the glass-transition temperature (T_g) of the PU polymer must change (decline). The DSC thermograms of the pristine PU film, PU film after 7 h of irradiation, pristine PU/ZrC composite film, and PU/ZrC composite film after 7 h of UV irradiation were examined and are shown in Figure 5(a–d) separately.
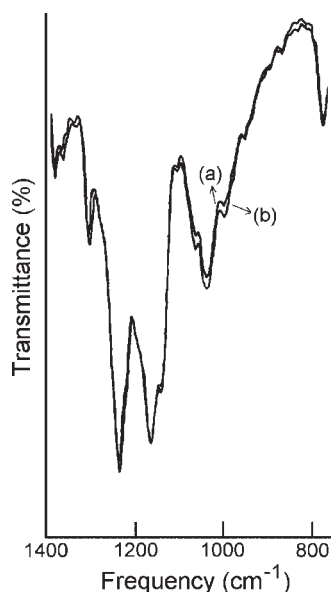

Figure 4 FTIR spectra of (a) the pristine PU/ZrC composite film and (b) the PU/ZrC composite film after 7 h of UV irradiation.
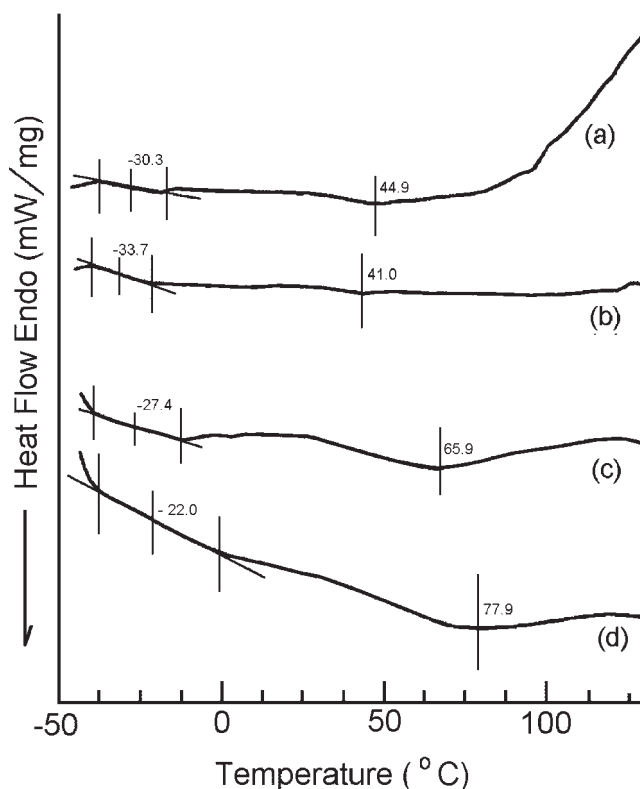
Figure 5 DSC thermograms (from −50 to 125) obtained from (a) the pristine PU film, (b) the PU film after 7 h of UV irradiation, (c) the PU/ZrC composite film, and (d) the PU/ZrC composite film after 7 h of UV irradiation.

From this figure, the T_g values of the soft segment and melting temperature (T_m) values of the soft segment have been obtained. As revealed by a previous study,[13] T_g for the pristine PU/ZrC composite film is higher than that for the pristine PU film because of the interaction between the PU molecules and ZrC particles. On the other hand, T_g for the PU film after UV irradiation is lower than that for the pristine PU film, but that for the PU/ZrC composite film after UV irradiation is higher than that for the pristine PU/ZrC composite film. The former is surely caused by the degradation of PU molecules in the amorphous region, as mentioned previously. However, the latter may be caused by the other mechanism in the presence of ZrC particles under UV irradiation.

The values of M_n obtained from the filtered solutions of the pristine PU film, PU film after 7 h of UV irradiation, and PU/ZrC composite film after 7 h of UV irradiation are listed in Table I. These values are lower because the higher molecular weight materials and ZrC particles were filtered to prevent the clogging of the gel column. With the lower value of M_n for the PU film after UV irradiation, the degradation of the PU polymer under UV irradiation can be proven. At the same time, the slight decrease in the molecular weight for the PU/ZrC composite film after
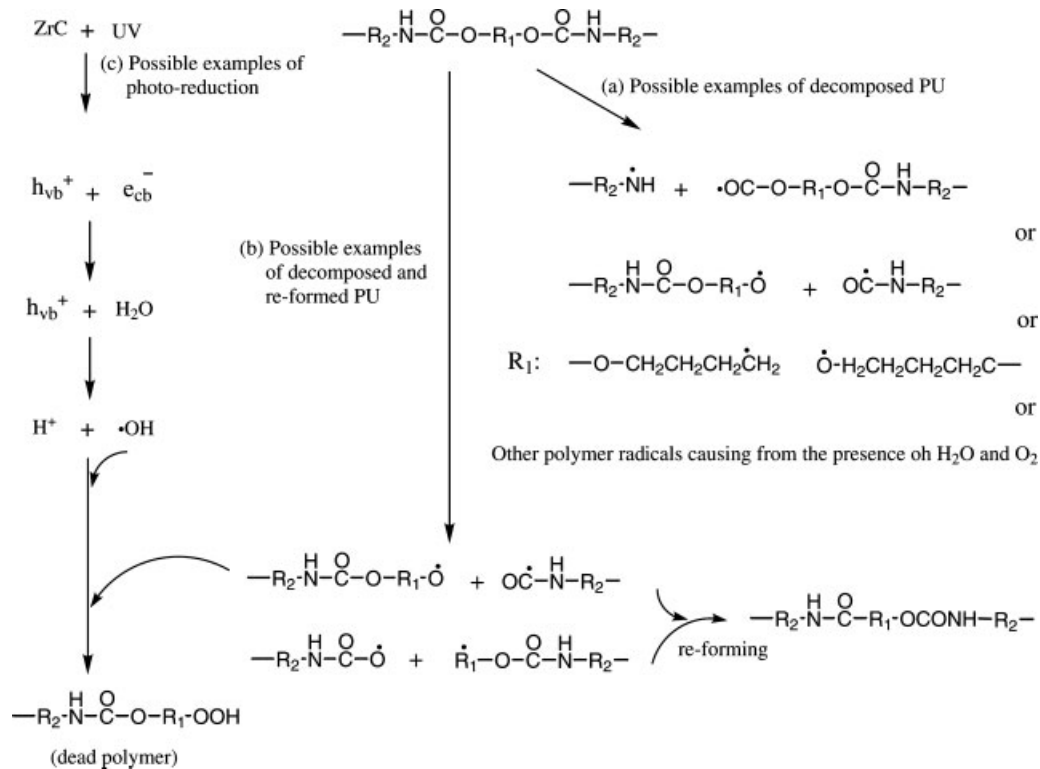
Scheme 1 Some possible photochemical reactions of PU under UV irradiation: (a) PU film, (b) PU/ZrC, and (c) ZrC.

UV irradiation reveals that the degradation is lower in the presence of ZrC particles.

Figure 5 also shows that the endothermic peak of the soft segment around T_g for the PU film after UV irradiation [Fig. 5(b)] is narrower and lower than that for the pristine PU film [Fig. 5(a)]; however, that for the PU/ZrC composite film after UV irradiation [Fig. 5(d)] is broader and higher than that for the pristine PU/ZrC composite film [Fig. 5(c)]. These phenomena reveal that the temperature range needed to convert the phase state for the PU film after UV irradiation is narrower than that for the pristine PU film; that for the PU/ZrC composite film after UV irradiation is broader than that for the pristine PU/ZrC composite film. The narrower temperature range of the phase transition and lower T_g value of the PU film after UV irradiation are surely caused by the degradation of the PU polymer in the amorphous region. However, the degradation of the polymer molecules cannot explain the higher value of T_g for the PU/ZrC composite film after UV irradiation [Fig. 5(d)]. Another possible mechanism for the PU/ZrC composite film under UV irradiation is the termination of decomposition. That is, the free radical created from the photoreduction[20,21] of ZrC under UV light might react with the radical of the PU polymer created from photooxidation[15] under UV light; therefore, the PU polymer radical becomes a dead polymer and terminates the degradation reaction. Meanwhile, those polymer radicals created by photooxidation and

photoreduction may re-form the chemical bonding between the polymer chains and thus reduce the mobility of PU molecules. On the other hand, the absorption of UV light by ZrC nanometer particles could also reduce the degradation of PU polymers.

On the basis of these experimental results, the photochemical degradation and re-formation of the PU polymer irradiated with UV in the presence or absence of ZrC particles are suggested in Scheme 1. For
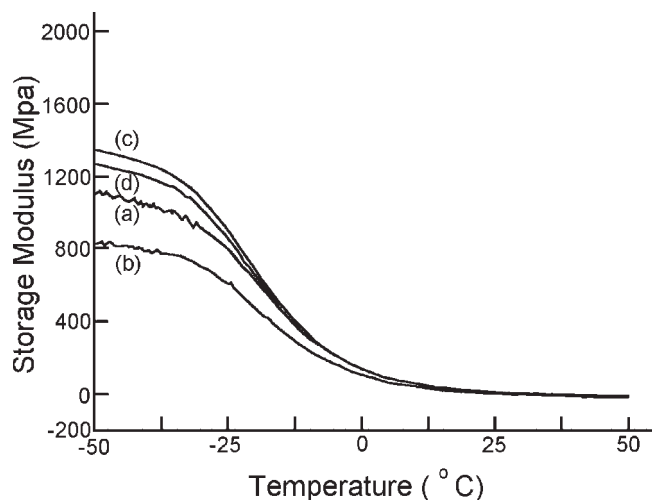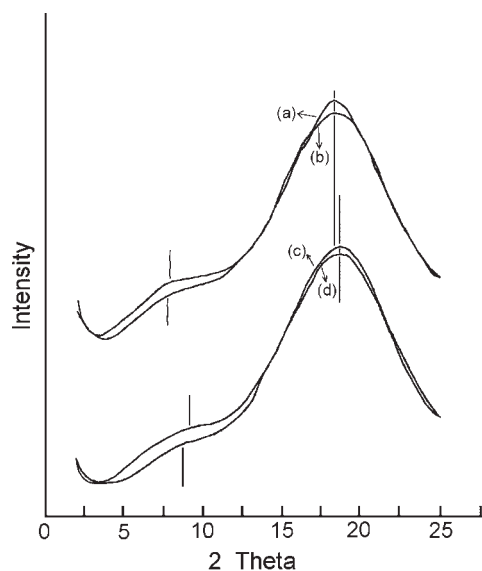

Figure 6 DMA patterns (from −50 to 50) obtained from (a) the pristine PU film, (b) the PU film after 7 h of UV irradiation, (c) the PU/ZrC composite film, and (d) the PU/ZrC composite film after 7 h of UV irradiation.

the PU film, some polymer chains are broken, so the T_g value and physical properties are significantly lowered after UV irradiation. For the PU/ZrC film, partial polymer radicals caused by PU/ZrC might be reformed to reduce the mobility of the PU molecules. Therefore, the T_g value is increased. However, the partial degradation of PU molecules makes the reduction of the physical properties of the PU/ZrC film not so significant. The higher T_g value for the PU/ZrC film versus that for the PU film indicates the higher intermolecular force and the shorter intermolecular distance between the PU polymer molecules, which might create a chance for re-forming between the polymer radicals, as shown in Scheme 1. Scheme 1 also shows the chemical reaction between the free radical created from the photoreduction of ZrC under UV light and the radical of the PU polymer created from photooxidation under UV light.

Figure 6(a–d) separately shows DMA patterns for the pristine PU film, PU film after 7 h of UV irradiation, pristine PU/ZrC composite film, and PU/ZrC composite film after 7 h of UV irradiation. The higher storage modulus means more energy is needed to move a molecular segment in the amorphous region, which has a higher value of T_g. The pristine PU/ZrC composite film has a higher storage modulus than the pristine PU film. This is due to the interaction between the PU polymer molecules and ZrC particles.[13] In addition, the storage modulus for the PU film after UV irradiation is significantly lower than that for the pristine PU film, and that for the PU/ZrC composite film after UV irradiation is only slightly lower than that for the pristine PU/ZrC composite film. These results agree with those for M_n listed in Table I and the values of T_g shown in Figure 5 for the PU film, but they do not agree with the values of T_g for the PU/ZrC composite film. The PU/ZrC composite film after UV irradiation has a lower storage modulus and M_n but has a higher value of T_g. Again, we can certainly suggest that chemical bonding re-forming among polymer molecules after UV irradiation can reduce the mobility of PU molecules and the value of T_g for the PU/ZrC composite film after UV irradiation.

Figure 5 also reveals that T_m of the soft segment for the pristine PU/ZrC composite film is higher than that for the pristine PU film. This can be attributed to the interaction between the PU polymer molecules and ZrC particles.[13] In addition, the table and figure show that T_m for the pristine PU film is higher than that for the PU film after UV irradiation, and that for the PU/ZrC composite film after UV irradiation is higher than that for the pristine PU film. Those results may be due to the changes in the crystalline structure. Figure 7(a–c) separately shows WAXD patterns for the pristine PU film, PU film after UV irradiation, pristine PU/ZrC composite film, and PU/ZrC composite film after UV irradiation. The main 2θ angles at

Figure 7 WAXD patterns obtained from (a) the pristine PU film, (b) the PU film after 7 h of UV irradiation, (c) the PU/ZrC composite film, and (d) the PU/ZrC composite film after 7 h of UV irradiation.

about 8–9° for the film of pristine PU are smaller than those for the pristine PU/ZrC composite film. This is caused by the interaction between the PU polymer molecules and ZrC particles.[13] The 2θ angle for the PU film after UV irradiation is slightly smaller than that for the pristine PU film; however, that for the PU/ZrC composite film after UV irradiation is significantly larger than that for the pristine PU/ZrC composite film. With the Bragg equation, we can determine that the interlay distance in the crystalline region of the soft segment of the pristine PU film after UV irradiation is slightly smaller than that of the pristine PU film, but that of PU/ZrC after UV irradiation is significantly smaller than that of the pristine Zr/PU composite film, and so T_m is higher (Fig. 5). The re-forming of the molecular chain in the crystalline region of the soft segment is probably caused by the radical reaction among PU molecules mentioned in the previous section.

These figures also show that the other main 2θ angle at about 18–19° for the film of pristine PU is slightly smaller than that for the pristine PU/ZrC composite film. This is caused by the interaction between the PU polymer molecules and ZrC particles.[13] On the other hand, the intensity of the X-ray diffraction slightly decreases and the diffraction peak is somewhat broader for both films after UV irradiation. This phenomenon could be due to a defect in the crystalline region caused by the irradiation of UV light.

CONCLUSIONS

Films of PU alone and the PU/ZrC composite prepared in the presence of roller pressure were irradi-

ated with UV light under the atmosphere. The tensile strength at break, elongation at break, and modulus gradually decreased with increasing UV irradiation time for both films; however, the reduction of the strength and modulus for the PU film was significantly higher than that for the ZrC/PU composite film with the same irradiation time. The results of TGA patterns showed that UV irradiation changed the composition of the molecules of the PU film but almost did not change that of the PU/ZrC composite film. UV irradiation made the structure of the PU polymer molecules more complicated. IR spectra showed the degradation of PU molecules irradiated with UV light, but this phenomenon was significantly inhibited in the presence of nanometer ZrC. This was confirmed by data obtained from GPC analyses. We suggest that the degradation of polymer radicals caused by the photooxidation of UV light might be partially stopped by the free radicals caused by the photoreduction of ZrC/UV light. At the same time, the chemical bonding between the polymer molecules is re-formed from free radicals created by photooxidation and photoreduction, and this could reduce the mobility of PU molecules and thus raise the values of T_g and T_m of the soft segment.

References

1. Jung, Y. K. U.S. Pat. 6,108,581 (2000).
2. Kim, Y. G. Eur. Pat. EP 1,390,083 (2002).
3. Cho, J. E.; Kim, E. Y. Eur. Pat. EP 1,355,866 (2003).
4. Toru, T. Jpn. Pat. JP 2003112381 (2003).
5. Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kuracshi, T.; Kamigaito, O. J Mater Res 1993, 5, 1179.
6. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Kuracshi, T.; Kamigaito, O. J Appl Polym Sci 1993, 49, 1259.
7. Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kuracshi, T.; Kamigaito, O. J Mater Res 1993, 8, 1179.
8. Ogata, N.; Kawakage, S.; Ogihara, T. J Appl Polym Sci 1997, 66, 573.
9. Laval, T. U.S. Pat. 5,876,812 (1999).
10. Ke, Y. C.; Long, C. F.; Qi, Z. N. J Appl Polym Sci 1999, 71, 1139.
11. Vaia, R. A.; Jandt, K. D.; Kramer, E. J.; Giannelis, E. P. Macromolecules 1995, 28, 8080.
12. Gonsalves, K. E.; Chen, X. H. Polym Mater Sci Eng 1995, 73, 285.
13. Suen, M. C.; Chen, C. C. J Appl Polym Sci 2006, 100, 191.
14. Scott, G.; Gilead, D. Degradable Polymers: Principles and Applications; Chapman & Hall: New York, 1995.
15. Grassie, N.; Scott, G. Degradation and Stabilization of Polymers; Cambridge University Press: Cambridge, England, 1985; Chapter 4.
16. Davis, A.; Sims, D. Weathering of Polymers; Applied Science: New York, 1983; Chapter 6.
17. Abu-Zeid, M. E.; Nofal, L. A.; Tahseen, L. A.; Abdul-Rasoul, F. A.; Ledwith, A. J Appl Polym Sci 1984, 29, 2443.
18. Govorčin Bajsić, E.; Rek, V. J Appl Polym Sci 2001, 79, 864.
19. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. Infrared Spectrometric Identification of Organic Compounds, 3rd ed.; Wiley: New York, 1974; p 136.
20. Wang, Z.; Liu, Y.; Zhang, Z. Handbook of Nanophase and Nanostructured Materials: Characterization; Kluwer Academic/Plenum: New York, 2002; p 997.
21. Li, Y. In Organic Photochemistry; Ramamurthy, V.; Schanze, K. S., Eds.; Marcel Dekker: New York, 1997; Chapter 8.