Celite-Mediated Linking of Polyurethane Block Copolymers and the Impact on the Shape Memory Effect

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ABSTRACT: Celite, a porous inorganic material with enormous surface area and hydroxyl groups on the surface, was used as a cross-linker of polyurethane (PU) copolymer chains to improve its shape memory and mechanical properties. PU copolymers with different Celite contents were prepared and characterized by IR, DSC, and universal testing machine . The glass transition temperature of PU copolymers was maintained around 20°C independent of Celite content. The shape memory and mechanical properties were dependent on when Celite was added during the polymerization reaction. The reaction in which Celite was added at the middle stage of polymerization showed the best shape memory and mechanical properties. The best shape recovery of PU was found at 0.3 wt % Celite and increased to 97% even after the third cycle. Likewise, the shape retention also maintained a remarkable 86% after three cycles. The reasons underlining the high shape recovery and shape retention by adopting Celite as a cross-linker are discussed in this article. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 3568–3575, 2010

Key words: shape recovery; shape retention; celite; urethane; cross-linking

INTRODUCTION

A shape memory polymer (SMP) that can recover the original shape after distortion above the phase transition temperature has been researched by us and others in an effort to determine a polymer with higher strength and multifunctions.[1–7] A surprising increase in mechanical properties while maintaining high shape recovery after repetitive distortion was achieved by introducing a cross-linker in the polymer chains.[8] Likewise, the sandwich type composite made out of SMP demonstrated an excellent ability to control vibrations.[9] Celite, a natural product from earth, is primarily composed of silica and alumina, and has been used as a water filter and as an additive in agricultural chemicals, paint, cosmetics, plastic, and paper.[10,11] The reaction between inorganic powder and organic chemical is very slow and the yield is also low due to the large differences in hydrophilicity of each component and the heterogeneous reaction mixture. Inorganic particles have been used as fillers for polymers to reduce the amount of polymer used and to endow the polymer with special functions such as abrasion and heat resistance, thermal and electrical conductivity, enhanced mechanical properties, and lightness. Recently, organic–inorganic hybrid nanocomposites have been extensively researched.[2–21] The fact that the structure of Celite has innumerable pores (as seen in Fig. 1) and a large surface area in addition to surface hydroxyl groups suggests its potential use as a cross-linker if the reaction rate between the Celite surface and the polymer chain can be increased. Aggregation of inorganic particles in the polymer matrix may occur if the density of the particle is quite different from that of the polymer, which is a key point in selecting the inorganic particle. Although higher mechanical strength and uniform dispersion of inorganic particles in polymer matrix is expected if the polymer-inorganic composite is prepared by *in situ* method, the blending of polymer matrix and inorganic particles (*ex situ* method) has been frequently attempted because of the low reactivity between polymer and inorganic particle and the difficulty in compatiblization. Among the many SMPs we have researched, either polyester or polyurethane (PU) type, all cross-linkers were organic such as glycerol, sorbitol, and pentaerythritol.[22] A inorganic cross-linker such as Celite should be tested
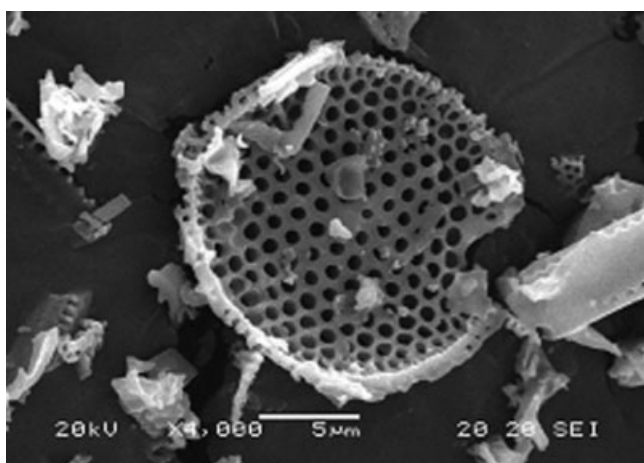
Figure 1 SEM image of Celite surface.

to demonstrate the properties such as heat and abrasion resistance not attainable by organic cross-linkers and to widen the application of SMP. In this investigation, only Celite content was varied at a fixed hard and soft segment content, because the best composition of shape memory PU was obtained from the previous experiments. Here the distribution of heterogeneous Celite and the function as a cross-linker in the PU matrix, as judged from the analytical results of IR, DSC, XRD, and universal testing machine (UTM), are studied. The reasons for the high shape recovery and mechanical properties are also discussed from the structural points of Celite.

EXPERIMENTAL

Materials

Poly(tetramethylene glycol) (PTMG, M_w = 2000 g/mol) and 4,4′-methylene bis (phenylisocyanate) (MDI, M_w=250.26 g/mol) were purchased from Aldrich Chemical. Celite powder was purchased from Korea Celite Co., and the mean particle size of Celite, measured by a Malvern Microplus particle size analyzer, was 5.91 μm with an unimodal distribution. The Celite powder was used for the synthesis without any treatment. 1,4-Butanediol (BD, Duksan Chemical) was stored over a 4 Å molecular sieve to remove moisture. The above reagents were dried under vacuum (0.1 torr) for 5 h before use.

Synthesis

PU bulk polymerization was carried out in a flat-bottomed four-neck flask. The composition of the reaction mixture is shown in Table I, in which 25 mol % excess of MDI equivalent to the sum of PTMG and BD is used to make room for coupling with the Celite surface. The molar ratio of PTMG and BD is one to three, which was found from previous studies to be

TABLE I
Composition of PU Copolymers

Sample code	MDI (mole)	PTMG (mole)	BD (mole)	Celite (wt %)[a]
PU-1	0.071	0.014	0.043	0.1
PU-2	0.071	0.014	0.043	0.2
PU-3	0.071	0.014	0.043	0.3
PU-4	0.071	0.014	0.043	0.4
PU-5	0.071	0.014	0.043	0.5

[a] wt % over total weight of all the reactants.

the optimum ratio (data not shown). The mixture of MDI and PTMG, according to the molar ratio in Table I, reacted at 70°C for 2 hrs under nitrogen purge, and the reaction continued for another hour after the addition of Celite in 20 mL dry dimethylformamide (DMF). Celite could be added at the initial stage or the final stage of the reaction to see if any improvement was made in the ability of Celite to couple with polymer chains. The polymerization proceeded for an hour for chain-extension following the addition of BD in 20 mL DMF under the same conditions. After the reaction was completed, the sticky PU mixture was dried to remove the residual DMF in an oven for a week to obtain a flexible polymer product. The PU structure is shown in Figure 2.

FTIR and thermal analysis

A thin film was prepared by dissolving PU in chloroform, allowing the chloroform to evaporate slowly and analyzed by a FTIR spectrophotometer (Bruker IFS 88) under the conditions of 4 cm^{-1} resolution and 25 scans. The melting temperature (T_m) of soft
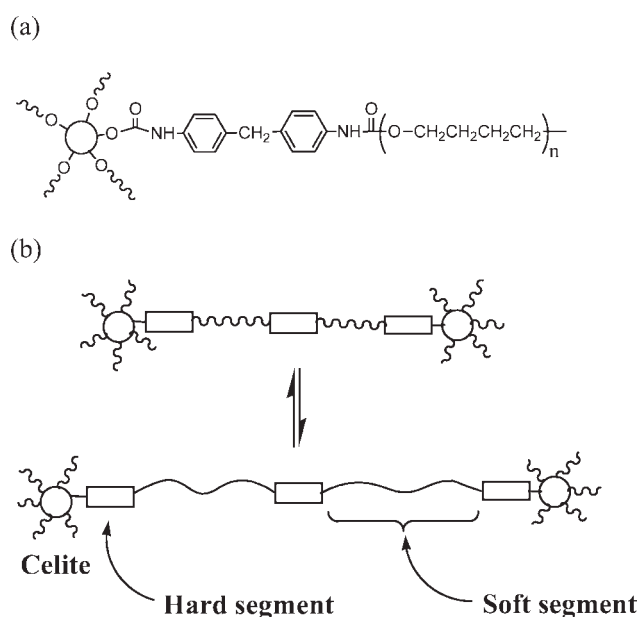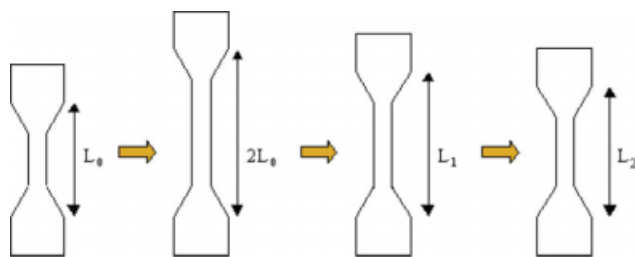

Figure 2 Schematic drawings of (a) PU on Celite surface and (b) PU chain-extension and shrinkage.

Figure 3 Shape retention and recovery test, where L_0 = initial specimen length, $2L_0$ = length of L_0 strained 100% at above T_m, L_1 = deformed length at below T_m after load removal, and L_2 = final specimen length at above T_m. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

segment in the copolymer was measured from three cyclic heating and cooling scans by a differential scanning calorimeter (Perkin–Elmer Diamond 6) by first heating the specimen to 200°C at 10°C/min, after which the temperature was maintained for 1 min, and then cooled to –30°C at −10°C/min. T_m was determined from the second heating scan.

Tensile and shape memory tests

The specimen for tensile mechanical and shape memory test was prepared by a mini-max molder (Bautek model BA-915), according to ASTM D638, in which molding temperature was adjusted to 180–210°C depending on the composition of the hard and soft segments, and the thickness was set to 3 mm. Tensile properties were analyzed by a (UTM, Lloyd LR 50K) equipped with temperature-controlled chamber using a dumbbell-type specimen prepared according to ASTM D-638 (Fig. 3). The experimental conditions were gauge length = 25 mm, crosshead speed = 10 mm/min, and load cell = 2.5 kN. Shape memory tests were carried out with the following procedures: L_1 for shape retention was the length after stretching the specimen of original length L_o twice at T_m+20°C for 5 min, and letting it shrink at T_m−20°C for 30 min; L_2 for shape recovery was measured after incubating the specimen at T_m+20°C for 10 min and cooling at T_m−20°C. Measurements were repeated three times, and shape retention and shape recovery could be calculated from L_1 and L_2 by the following equations:

$$\text{Shape retention (\%)} = (L_1 - L_0)/L_0 \times 100$$

$$\text{Shape recovery (\%)} = (2L_0 - L_2)/L_0 \times 100$$

RESULTS AND DISCUSSION

Synthesis

The PU copolymer is composed of MDI, PTMG, and BD, in which MDI and BD sections are considered

as a hard segment and the PTMG section forms a soft segment. MDI and PTMG reacted first to make an oligomer and BD extended the oligomer chains to make a lengthy PU chain. When a tensile force was exerted on PU, soft segment stretched to absorb the external stress, and the PU was restored to the original shape by the interaction similar to hydrogen bonding and dipole-dipole interaction between hard segments.[1–7] Celite was chosen as a cross-linker between PU chains because of its large surface area compared to other inorganic materials due to the highly porous structure (Fig. 1) and the availability of free hydroxyl groups on surface to be used for coupling with the organic functional groups. In addition, the density of Celite was similar enough for mixing with the reaction mixture, which was an important consideration, as aggregation of Celite may occur if the density of Celite was quite different from the reaction mixture. Because the reactivity of the heterogeneous Celite particle with an organic functional group was very low, the reactive isocyanate group of MDI was used to expedite the polymer coupling on Celite surface. In addition, the progress of polymerization depended on when Celite was added during polymerization. Three different Celite addition stages (initial, middle, and the final stage of polymerization) were tested, and the copolymer products were compared for their shape memory and mechanical properties. For convenience, each copolymer made at the different Celite addition stage was designated as the I-series for the one from the Celite addition in the initial stage, the M-series for the one from the Celite addition in the middle stage, and the F-series for the one from the Celite addition in the final stage of polymerization.

SEM analysis

In Figure 4 the scanning electron microscopy cross-section views of the Celite PU are compared. SEM images of I-series and F-series exhibit the aggregation of Celite particles, while the M-series has a relatively broad distribution of Celite particles. Therefore, Celite particles are likely to aggregate if the addition of Celite is made in the beginning or the end of polymerization. The progress of polymerization was carefully monitored to compare the SEM image and the precipitation of reaction mixture during polymerization. In the case of the I-series, a solid aggregate formed from MDI and Celite was observed as the reaction proceeded instead of a homogeneous reaction mixture. In the case of F-series, Celite particle did not react at all with the formed polymer chains, as only the chain terminus had the reactive functional group and the long and heavy polymer chain lost the mobility to quickly react with Celite. Therefore, Celite should be added
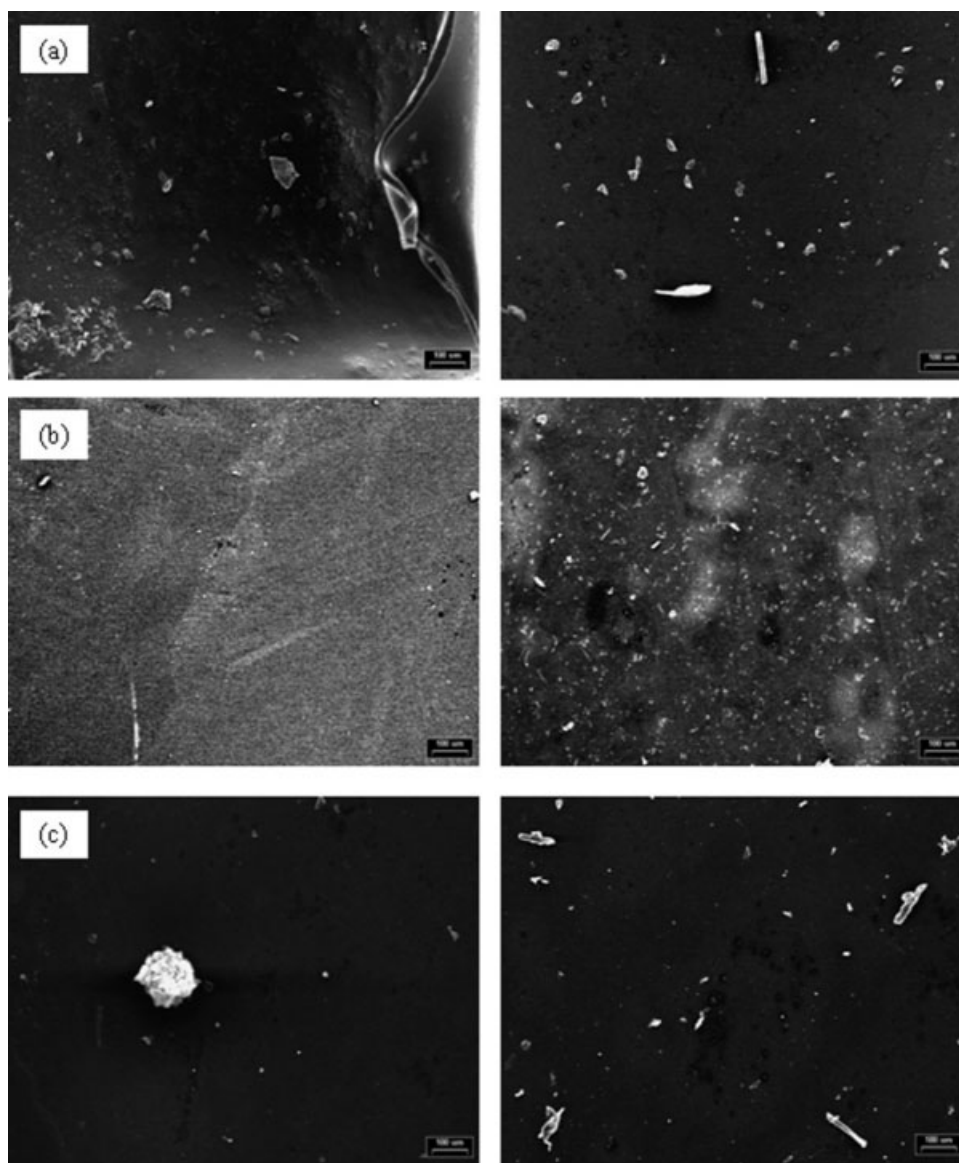
Figure 4 Cross-cut view of PU by SEM: (a) I-series, (b) M-series, and (c) F-series.

after an oligomer of MDI and PTMG have formed, but before polymerization is complete. Because Celite is not homogeneous with other components of the reaction mixture, the simple addition of Celite may ruin the polymerization as shown in the SEM result and the time for Celite addition should be carefully controlled.

IR and thermal analysis

Polymerization went to completion as judged from the complete disappearance of the NCO peak at 2420 cm^{-1} in the FTIR spectrum of PU in Figure 5. When the two IR spectra of M-0 (M-series without Celite) and M-3 (M-series with 0.3 wt % Celite) were compared, the characteristic absorption peak at 1714 cm^{-1} corresponding to the carbonyl group stretching mode was not changed, which supported the fact

that the carbonyl group of PU chain was not affected by the Celite linking. As the PU was composed of a glassy hard segment with T_g higher than room temperature and a rubbery soft segment with T_g below 0°C, thermodynamic incompatibility of these two segments led to phase-separated microstructures. The melting temperature (T_m) of soft segment was detected from the DSC thermogram in Figure 6. As the Celite content increased, the endothermic peak around 20°C and the enthalpy of transition did not change, which suggested that the soft segment of PU was not affected by Celite cross-linking.

Mechanical property

Maximum stress did not change much over the Celite content, which meant that it was not necessary to increase Celite content (Fig. 7) to get better
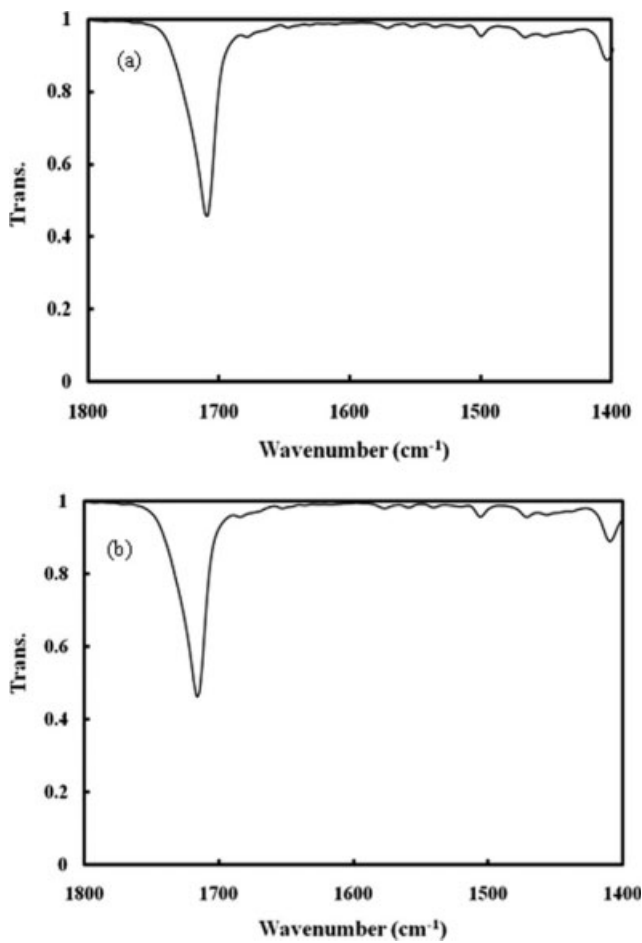
the secluded or aggregated Celite particles do not improve the mechanical properties as shown in either the I- or F-series. The highest elongation at break was obtained from M-4, and both M- and F-series showed a superior strain result than I-series. When PUs with a same Celite content are compared, the elongation at breaks of M-4 (1220 %) and F-4 (1120 %) exhibit about twice that of I-4 (610 %). As for I-series, the connection of Celite through MDI induced the aggregation of Celite and prohibited the strain of PU chains instead of cross-linking. The highest modulus (42 MPa) was observed from M-5, and the modulus of M-series was generally higher than those of I-series and F-series. Modulus of

Figure 5 Infrared spectra of (a) M-0 and (b) M-3.

mechanical properties. M-series showed a superior maximum stress compared to I- and F-series. For example, the maximum stress of M-2 (M-series with 0.2 wt % Celite) was 46 MPa that was quite contrasting with 21 MPa of F-2 (F-series with 0.2 wt % Celite) and 13 MPa of I-2. The distribution of Celite in the PU matrix plays an important role because
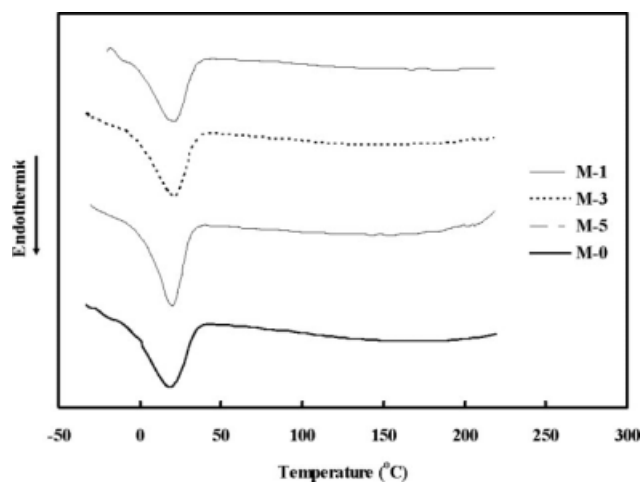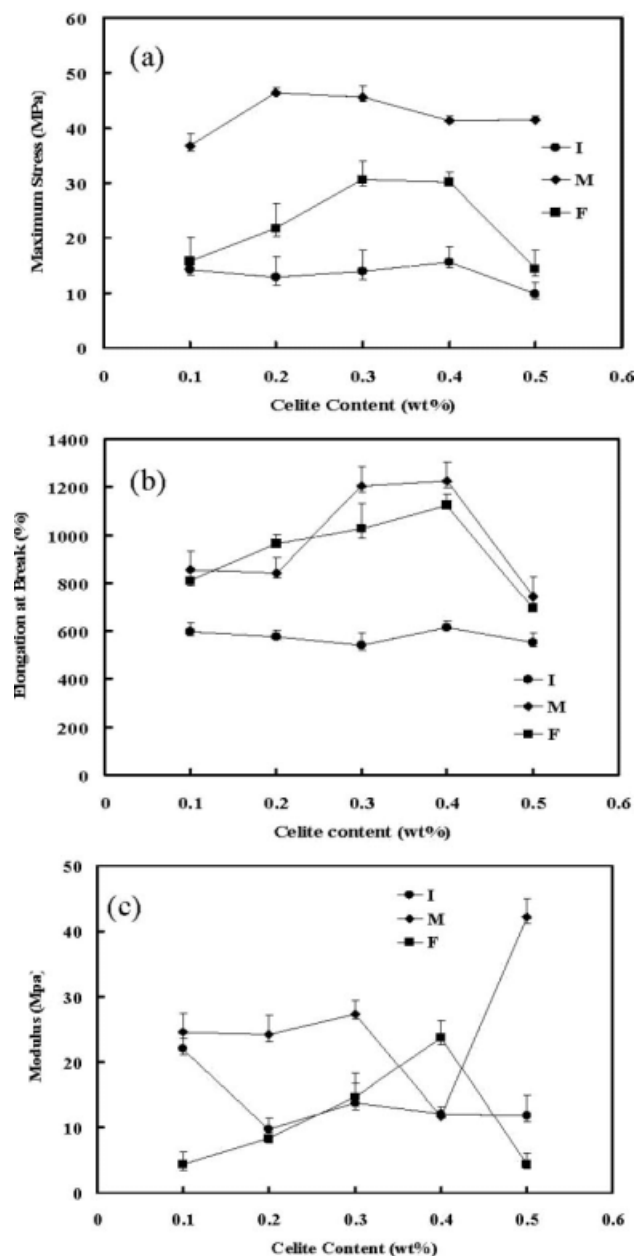

**Figure 6** DSC thermogram of M-series.

Figure 7 Comparison of (a) maximum stress, (b) strain at break, and (c) tensile modulus of I, M, and F-series.

I-series decreased as the Celite content increased, and the modulus of F-series showed the maximum at 0.4 wt %. The decrease of modulus of I-series is due to escalating aggregation as the Celite content increases. Although the modulus of F-series is higher than that of I-series, the lower modulus of F-series compared to M-series make it clear that Celite addition at the final stage of polymerization does not induce cross-linking of PU chains. Considering the above mechanical test results, the addition of Celite at the middle stage of polymerization is advantageous concerning decreased aggregation and higher cross-linking ratio.

Shape memory property

Shape memory results after each cyclic test were compared in Figures 8–11. Thermodynamic incompatibility between hard and soft segments induced the phase-separation and enabled the distinct role of each segment in the shape memory process as mentioned in the synthesis section. The shape retention was not affected after each cyclic test, but the shape recovery decreased because the repeated extension-shrinkage cycles slowly damaged hard segment attraction, an important factor for shape recovery. Three-dimensional cyclic shape memory test curves are shown in Figures 8 and 9. Three test cycles are exhibited in the Figures and the shape memory property depends on how well the strain value returns to the original one after each cycle. In Figure 8, M-2 looks excellent in following the original trajectory, and M-4 is very poor in shape memory property and mechanical strength. In Figure 9, I-series are generally inferior to M-series in overall shape memory property and mechanical strength. I-4 shows the best shape memory property. The exact shape recovery and shape retention are shown in Table II.

In Figures 10 and 11, shape recovery and shape retention of M-series and I-series were compared, and F-series was not tested because it did not meet the minimum requirement of 200% strain for the shape memory test. Shape recovery of M-2 and M-3 achieved an amazing 97% and did not fall below 95% even after the third cycle. Although many different types of SMPs have been tested by us, only two cross-linked SMPs exhibit the shape recovery higher than 95%. The M-series are different from the previous ones in that an inorganic cross-linker is used instead of the conventional organic cross-linker. The low reactivity of inorganic particle with an organic functional group limited its usage despite of the potential advantages such as high thermal stability, resistance to abrasion, better mechanical properties, and the possible development of organic-inorganic hybrid material. Shape recovery of I-series,
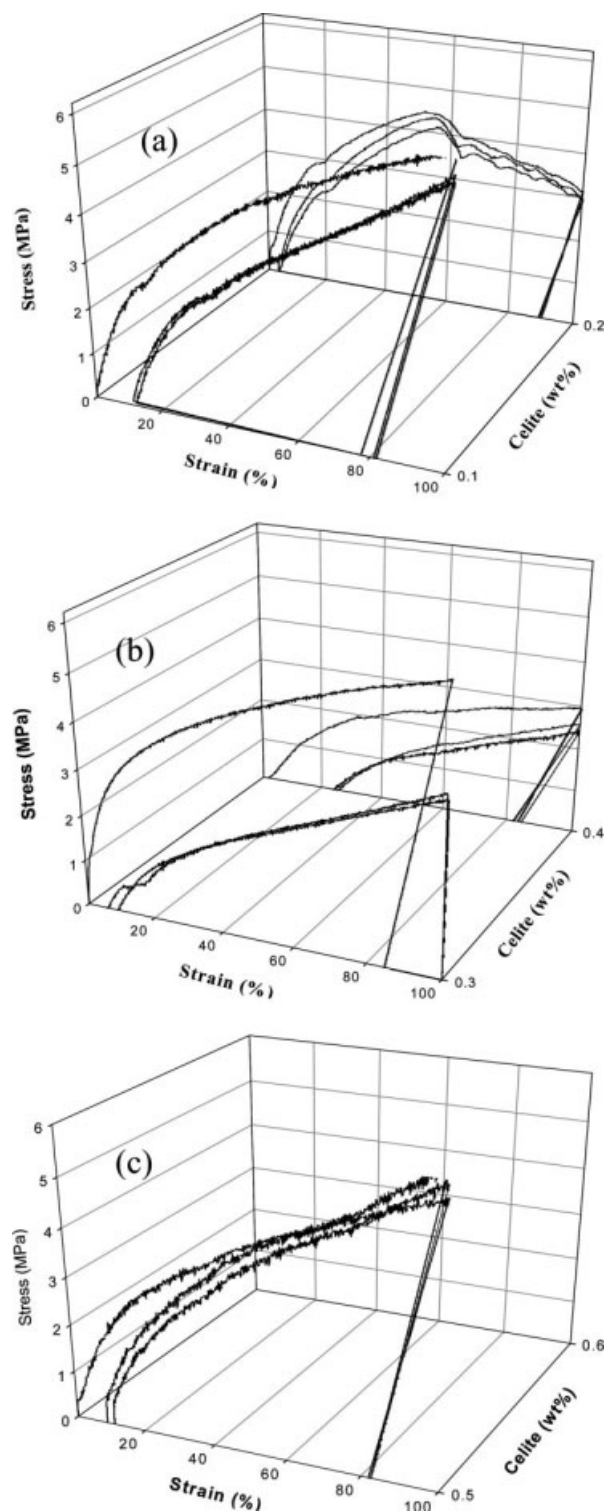
Figure 8 Cyclic shape memory test of (a) M-1 and M-2, (b) M-3 and M-4, and (c) M-5.

generally staying in the 80% range, is inferior to M-series for all of Celite contents, and became worse after the third cycle. One exception of I-series is the I-5 that shows 97% shape recovery in the first cycle, but it eventually drops to 85% after the third cycle. Shape retention of most M-series is in the low 80%
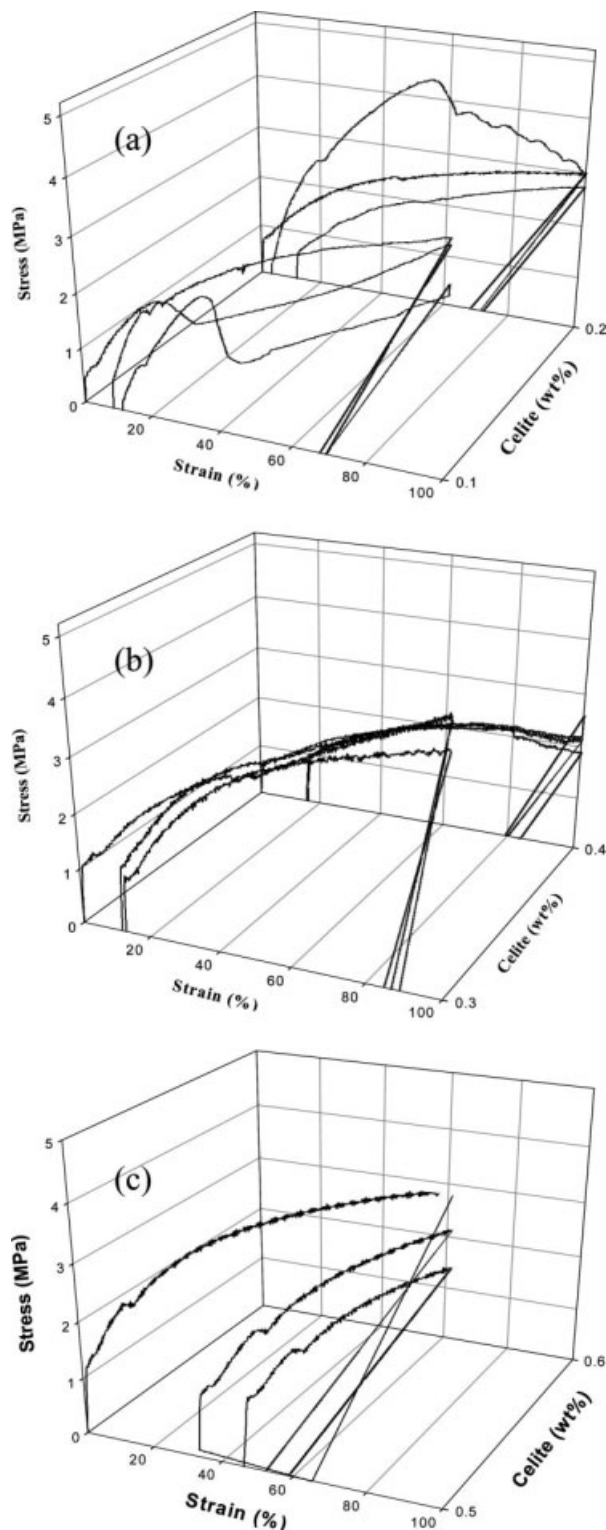
Figure 9 Cyclic shape memory test of (a) I-1 and I-2, (b) I-3 and I-4, and (c) I-5.

TABLE II
Shape Retention and Shape Recovery of PU

Sample code	Ret-1[a]	Ret-2	Ret-3	Rec-1[b]	Rec-2	Rec-3
I-1	79	67	69	89	88	87
I-2	68	71	72	84	85	82
I-3	85	87	89	97	88	85
I-4	84	80	79	92	89	89
I-5	65	52	59	67	55	57
M-1	77	82	81	88	89	88
M-2	90	89	89	97	97	96
M-3	83	84	86	95	97	97
M-4	83	82	84	80	82	80
M-5	82	83	82	89	91	91

[a] Shape retention (%) of the first cyclic test.
[b] Shape recovery (%) of the first cyclic test.

both shape recovery and shape retention. Considering both shape recovery and shape retention, M-2 demonstrated the best shape memory property among the candidate PUs. Overall, the addition step and the amount of Celite play an important role in deciding shape memory and mechanical properties.

Figure 10 Cyclic shape recovery profile of (a) M-series and (b) I-series.

range, and only the shape retention of M-2 has been close to 90% for the entire 3 cycles. The shape retention of I-series is even lower than that of M-series, which proves that M-series is superior to I-series in
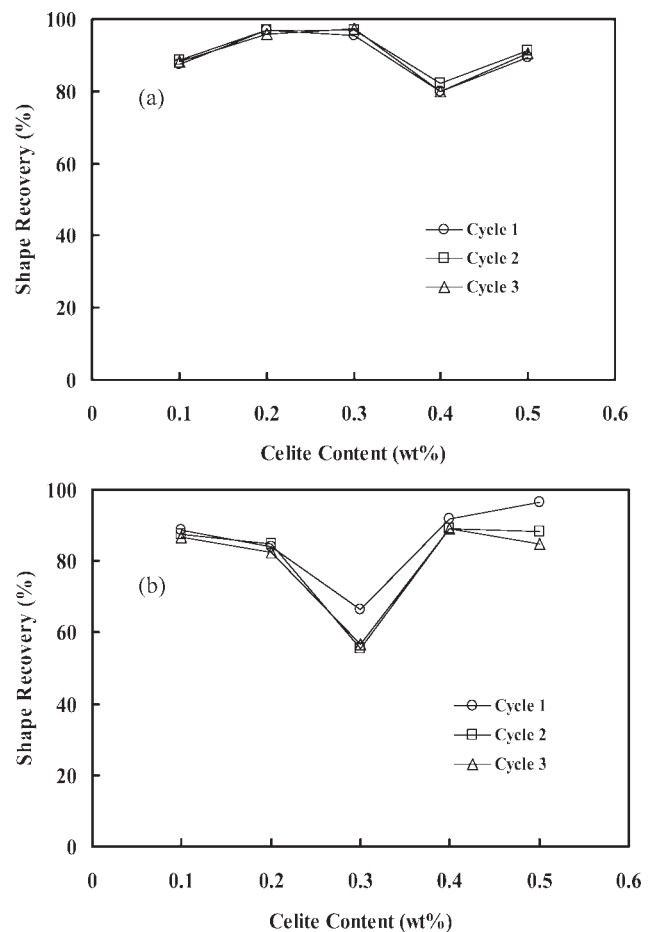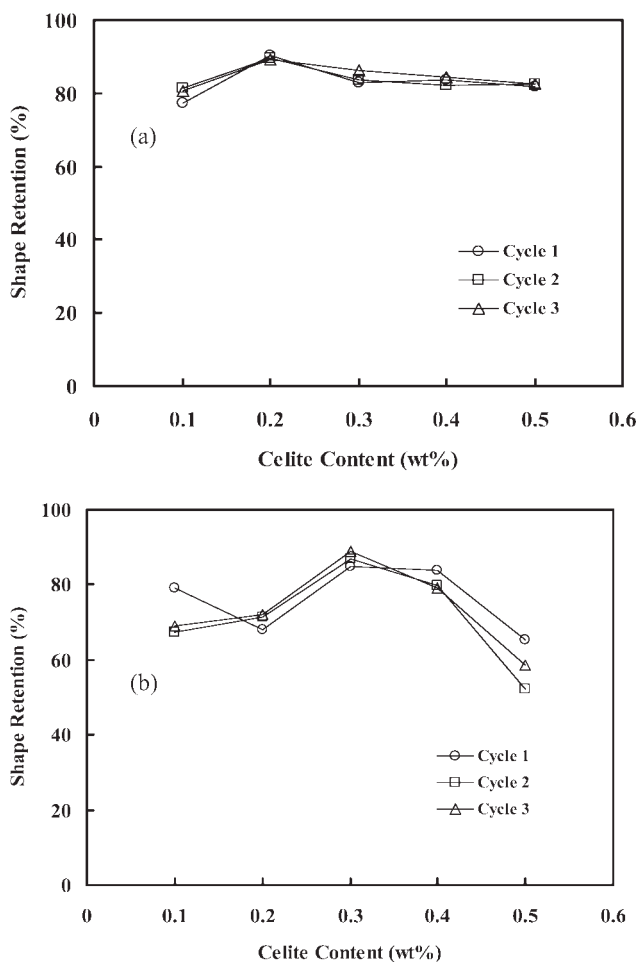
Figure 11 Cyclic shape retention profile of (a) M-series and (b) I-series.

CONCLUSION

Celite, a porous inorganic particle, was used as a cross-linker of PU copolymers. The addition step of Celite during polymerization was very important in determining the shape memory and mechanical properties. The addition of Celite at the middle stage of polymerization was found to be the best way for achieving high shape memory and mechanical properties. Control of Celite content was also important

and the optimum Celite content was 0.2%. The organic-inorganic hybrid PU is different from the previous blended one in that a covalent bonding between inorganic particle and PU chain is made and an improvement in shape memory and mechanical properties is realized.

References

1. Liang, C.; Rogers, C. A.; Malafew, E. J Intell Mat Struct 1997, 8, 380.
2. Yoo, S. R.; Lee, H. S.; Seo, S. W. Polymer (Korea) 1997, 21, 467.
3. Takahashi, T.; Hayashi, N.; Hayashi, S. J Appl Polym Sci 1996, 60, 1061.
4. Tobushi, H.; Hara, H.; Yamada, E.; Hayashi, S. Smart Mat Struct 1996, 5, 483.
5. Spathis, G.; Niaounakis, M.; Kontou, E.; Apekis, L.; Pissis, P.; Christodoulides, C. J Appl Polym Sci 1994, 54, 831.
6. Chun, B. C.; Cho, T. K.; Chung, Y. C. J Appl Polym Sci 2007, 103, 1435.
7. Safranski, D. L.; Gall, K. Polymer 2008, 49, 4446.
8. Buckley, C. P.; Priscariu, C.; Caraculau, A. Polymer 2007, 48, 1388.
9. Chun, B. C.; Cha, S. H.; Park, C.; Chung, Y. C.; Park, M. J.; Cho, J. W. J Appl Polym Sci 2003, 90, 3141.
10. Hodge, P.; Sherrington, D. C. Polymer-Supported Reactions in Organic Synthesis; Wiley: New York, 1980.
11. Polshettiwar, V.; Kaushik, M. P. Cat Comm 2004, 5, 515.
12. Kickelbick, G. Prog Polym Sci 2003, 28, 83.
13. Schmidt, G.; Malwitz, M. M. Curr Opin Col Inter Sci 2003, 8, 103.
14. Lee, S. S.; Ma, Y. T.; Rhee, H. W. Kim J Polym 2005, 46, 2201.
15. Yang, B.; Huang, W. M.; Li, C.; Cho, J. H. Eur Polym J 2005, 41, 1123.
16. Jordan, J.; Jacob, K. I.; Tannenbaum, R. Mat Sci Eng A 2005, 1, 393.
17. Avella, M.; Bondioli, F.; Cannillo, V.; Pace, E. D.; Errico, M. E.; Ferrari, A. M.; Focher, B.; Malinconico, M. Comp Sci Tech 2006, 66, 886.
18. Yokayama, R.; Suzuki, S.; Shirai, K.; Yamauchi, T.; Tsubokawa, N.; Tsuchimochi, M. Eur Polym J 2006, 42, 3221.
19. Guo, Z.; Kim, T. Y.; Lei, K.; Pereira, T.; Sugar, J. G.; Hahn, H. T. Comp Sci Tech 2008, 68, 164.
20. Gunes, I. S.; Cao, F.; Jana, S. C. Polymer 2008, 49, 2223.
21. Ki, H. S.; Yeum, J. H.; Choe, S.; Kim, J. H.; Cheong, I. W. Comp Sci Tech, to appear.
22. Cho, T. K.; Chong, M. H.; Chun, B. C.; Kim, H. R.; Chung, Y. C. Fib Polym 2007, 8, 7.