

# NOTES

## Thermal Crosslinking of Chlorinated Polydimethylsiloxane–Poly(vinyl Chloride) Blends

### INTRODUCTION

Crosslinking is a useful and important technology in the polymer industry to improve properties of polymers, for instance, heat deformation resistance, chemical resistance, stress cracking resistance, and so on. In silicone rubber technology, high-temperature peroxide crosslinking, platinum-catalyzed hydrosilylation, and moisture-sensitive hydrolysis curing are well known for silicone vulcanization.<sup>1</sup>

Silicone polymers usually have poor miscibility with other polymers. Therefore, phase separation readily occurs, and the silicone polymers are mainly accumulated on surfaces because of their low surface energy, when silicone polymers are blended with other types of polymers.

In order to avoid surface migration of the silicone components due to phase separation, introduction of chemical bonds between two or more polymers is preferable to fix their dispersion states just after dynamic mixing. Crosslinking is a useful method to chemically fix two or more polymers. For the combination of silicone polymers with poly(vinyl chloride) (PVC), chlorine-containing silicone polymers are convenient to form chemical bonds, rather than other types of silicone polymers.

As was reported previously, chlorinated polydimethylsiloxanes (C-PDMS) were readily crosslinked by multifunctional thiols and amines that induced their nucleophilic substitution reactions on the chloromethyl group.<sup>2</sup> Also, PVC itself is well known to crosslink with triazine thiol-metal oxide systems, as studied intensively by Nakamura and Mori.<sup>3–11</sup> Therefore, this method will become a promising process for crosslinking of polymer blends including chlorine-containing polymers, as some studies described crosslinking between two kinds of polymers.<sup>12–16</sup>

In this work thermal crosslinking of immiscible C-PDMS–PVC blends has been studied by the use of 6-dibutylamino-1,3,5-triazine-2,4-dithiol (DB) as a crosslinking agent. The possibility of cocrosslinking (Scheme 1) and the properties of their crosslinked blends were also studied.

### EXPERIMENTAL

#### Materials

A chlorinated polydimethylsiloxane (C-PDMS) was prepared by peroxide-catalyzed chlorination as described elsewhere.<sup>17</sup> (ClCH<sub>2</sub> content 5.2 mol %,  $M_n = 46,000$ ,  $M_w = 550,000$ .)

A commercial poly(vinyl chloride) (PVC) was used as received (Shin-Etsu Chemical Industry, TK-800, degree of polymerization,  $P = 800$ ). Dioctyltinmercaptide, magnesia (Ishidzu Pharmaceutical Co.), silica (Aerosil 200), and 6-dibutylamino-1,3,5-triazine-2,4-dithiol (DB, Snkyo Kasei Co.) as a stabilizer, an acid acceptor, a filler, and a crosslinking agent, respectively, were obtained commercially.

#### Compounding and Crosslinking

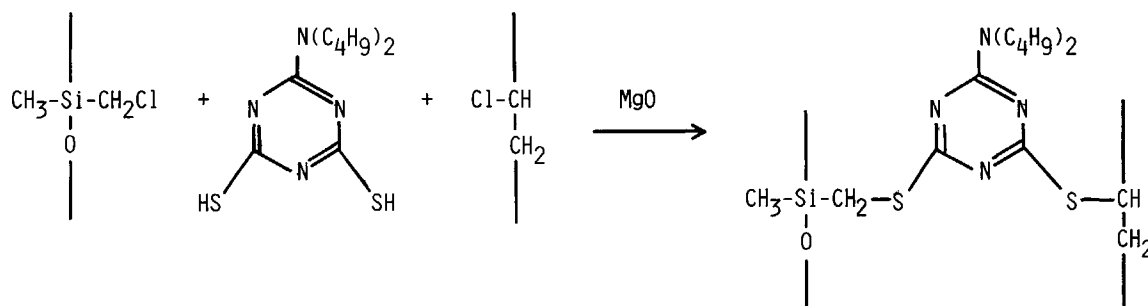
The compounding formulas without and with a plasticizer are shown in Tables I and II, respectively.

These materials were first mixed in beakers and then blended on a laboratory mill with rolls of 160 mm width and 75 mm diameter at the conditions described in Tables I and II. The blended materials thus obtained were compression molded at 160 or 170°C under 5–6 MPa to prepare cured sheets, which were tested and analyzed.

#### Measurements and Analyses

Tensile properties were measured using a Shimadzu Autograph DSS-5000 at 23°C and 50% RH with a crosshead speed of 5 mm/min. The compression-molded sheets of 2 mm in thickness were stamped using a die modified from JIS into dumbbell forms having 5 mm width and 20 mm chuck distance. Three measurement data were averaged.

A JEOL T-300 was used for scanning electron microscopic analysis. Gold was vacuum deposited on the tensile fracture surfaces. Dynamic mechanical analysis (DMA) in tensile mode was carried out at 10 Hz using a Iwamoto viscoelastic spectrometer, VES-S, with a heating rate of 2°C/min. Differential scanning calorimetry (DSC) of the



**Scheme 1** Cocrosslinking of C-PDMS-PVC blends.

crosslinked blends was performed by a Rigaku thermal analyzer, DSC 8230, with a thermal station TAS-100 at a heating rate of 10°C/min in a nitrogen stream.

Degree of crosslinking for the cured blends were estimated by solvent extraction. The cured blends were first extracted with *n*-hexane for 24 h to estimate gel contents of C-PDMS component. Then, it was succeeded by extraction with tetrahydrofuran (THF) to estimate gel contents of PVC component.

## RESULTS AND DISCUSSION

Tables I and II show compounding formulas and curing conditions for C-PDMS-PVC blends in the absence and the presence of dioctylphthalate as a plasticizer, respectively. Mixing temperatures of a laboratory mill were adjusted depending on viscosity of the mixtures and increased with PVC content. The curing of the compounded blends were performed with a hot press set at 160 or 170°C.

**Table I** Compounding Formulas and Crosslinking Conditions for C-PDMS-PVC Blends in the Absence of Plasticizer

	Run No. <sup>a</sup>						
	311-1	311-2	311-3	310-2	311-4	311-5	311-6
C-PDMS (%)	100	80	60	50	40	20	0
PVC (%)	0	20	40	50	60	80	100
Mixing temp. (°C) <sup>b</sup>	rt	rt	rt	rt	80	140	165
Curing temp. (°C)	170	170	160	170	170	170	170
Curing time (min)	30	30	60	30	30	30	30

<sup>a</sup> Polymers 100%; stabilizer (dioctyltinmercaptide) 3%; MgO 5%; DB 4%; Silica 5%.

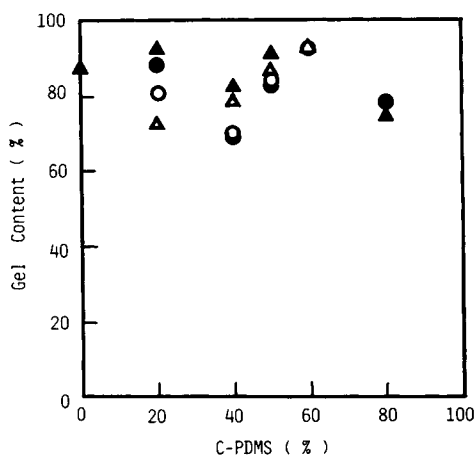
<sup>b</sup> rt, room temperature.

**Table II** Compounding Formulas and Crosslinking Conditions for C-PDMS-PVC Blends in the Presence of a Plasticizer

	Run No. <sup>a</sup>					
	316-1	316-2	316-3	316-4	316-5	316-6
C-PDMS (%)	100	80	60	40	20	0
PVC (%)	0	20	40	60	80	100
Mixing temp. (°C) <sup>b</sup>	rt	rt	rt	rt	100	140
Curing temp. (°C)	170	170	170	170	170	170
Curing time (min)	30	30	30	30	30	30

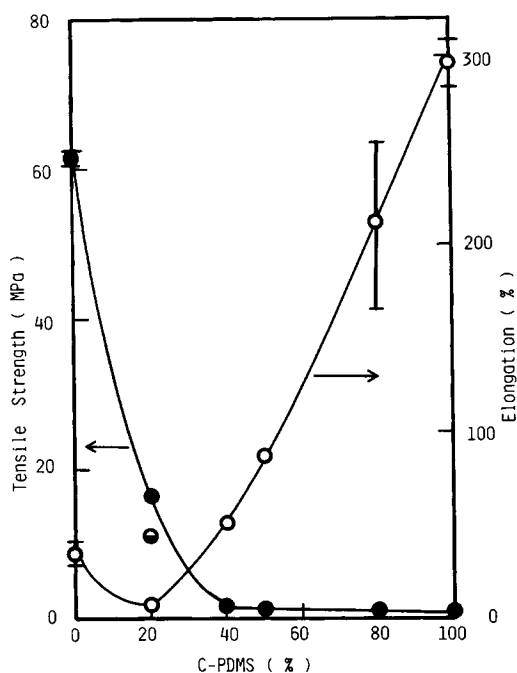
<sup>a</sup> Polymers 100%; stabilizer (dioctyltinmercaptide) 3%; MgO 5%; plasticizer (dioctylphthalate) 40%; DB 4%; silica 5%.

<sup>b</sup> rt, room temperature.

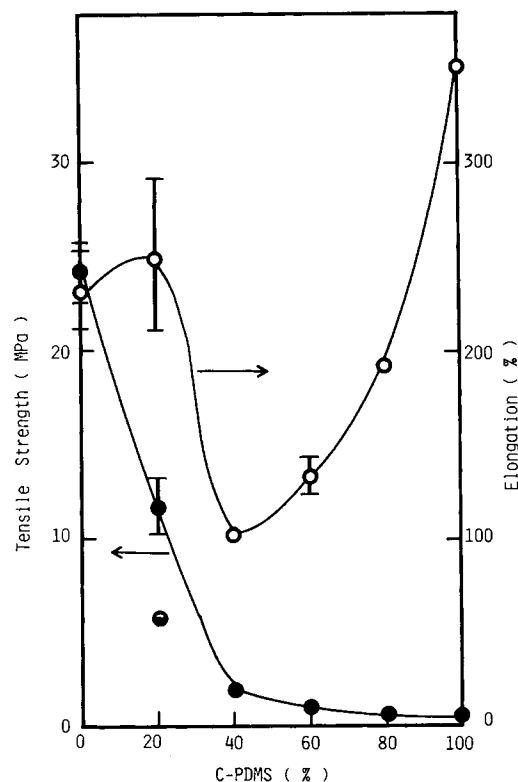


**Figure 1** Gel contents of cured C-PDMS-PVC blends extracted with *n*-hexane and tetrahydrofuran. Curing temperature: at 160°C, (○) C-PDMS, (△) PVC; at 170°C, (●) C-PDMS, (▲) PVC.

The cured blends were colored light brown, due to slight thermal degradation of PVC, although lower temperature for curing (160°C and 60 min) was employed to avoid this coloration.



**Figure 2** Tensile properties of cured C-PDMS-PVC blends without plasticizer. Polymers 100%; stabilizer (dioctyltinmercaptide) 3%; MgO 5%; DB 4%; Silica 5%. Curing: 170°C, 30 min: (●) tensile strength, (○) elongation, (◐) tensile strength in the absence of DB.



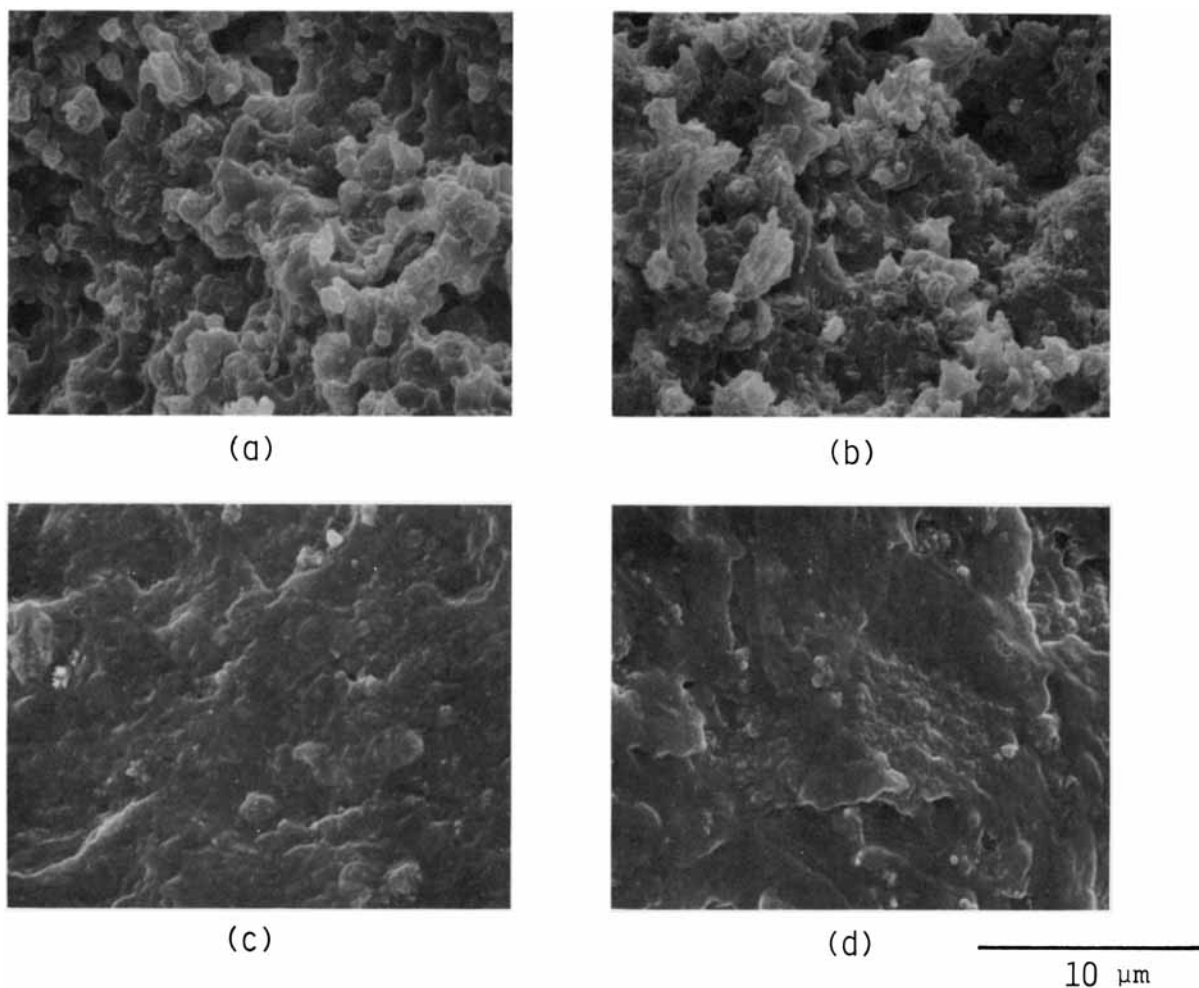
**Figure 3** Tensile properties of cured and plasticized C-PDMS-PVC blends. Polymers 100%; stabilizer (dioctyltinmercaptide) 3%; plasticizer (dioctylphthalate) 40%; MgO 5%; DB 4%; silica 5%. Curing: 170°C, 30 min: (●) tensile strength, (○) elongation, (◐) tensile strength in the absence of DB.

As shown in Figure 1, gel contents of C-PDMS and PVC in the blends were estimated to be more than almost 70%. Infrared analysis suggested that *n*-hexane-soluble fractions consisted of C-PDMS, but THF-soluble fractions included both C-PDMS and PVC. Therefore, even the loosely crosslinked C-PDMS appeared to be extracted with a good solvent, THF, and to become a contaminant for the soluble PVC. However, the crosslinked PVC essentially amounts to more than 70% in the compounded PVC.

Thus, the triazine thiolate ion evidently exhibits high nucleophilicity toward not only the primary chlorides in C-PDMS but also the secondary chlorides in PVC,<sup>3,4</sup> leading to their crosslinking.

Tensile properties (i.e., tensile strength and elongation) of the cured blends without and with a plasticizer are shown in Figures 2 and 3, respectively.

In these figures the blend specimens at C-PDMS-PVC = 20/80 prepared in the presence of DB exhibited 1.5 to 2.0 times higher tensile strength at break than those prepared in the absence of DB, indicating that the crosslinking evidently served to improve their mechanical prop-



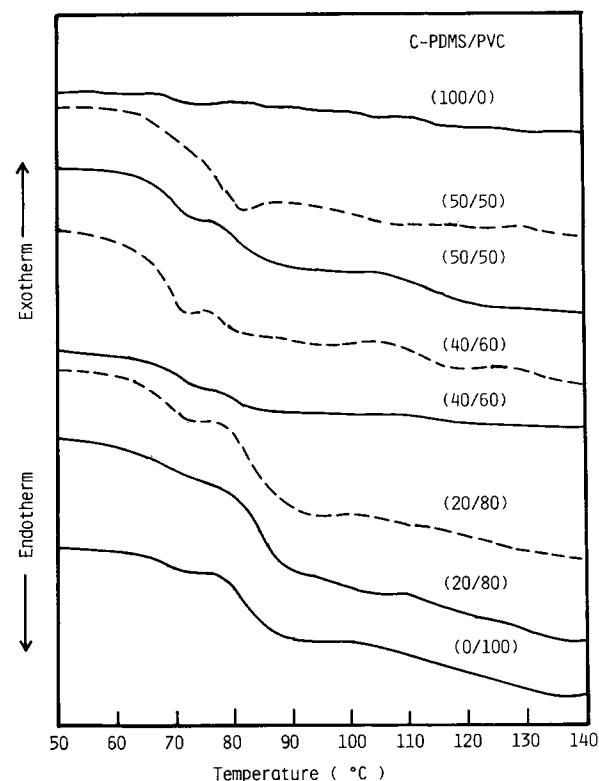
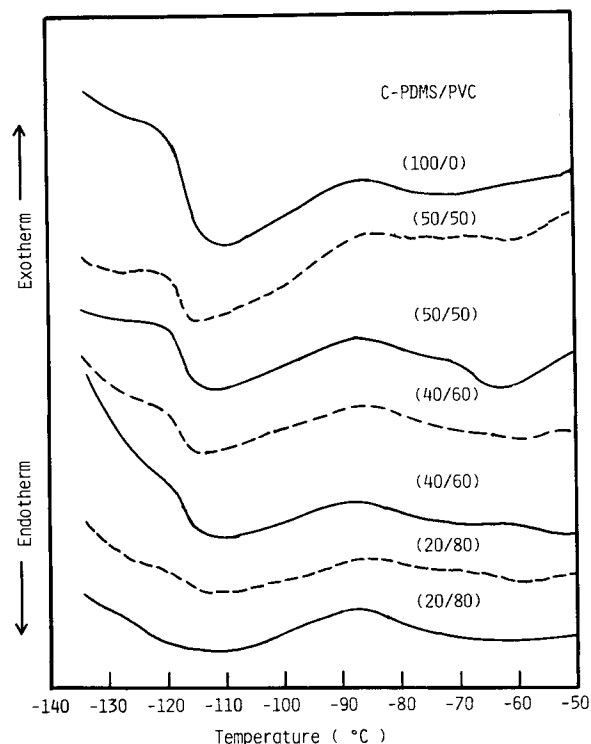
**Figure 4** Scanning electron micrographs of fractured surfaces of the cured blends. Magnification  $\times 5000$ , acceleration voltage 10 kV. (a) C-PDMS-PVC = 20/80 blend without DB; (b) C-PDMS-PVC = 20/80 blend with DB (run No. 311-5); (c) C-PDMS-PVC = 50/50 blend with DB (run No. 310-2B); (d) C-PDMS-PVC = 80/20 blend with DB (run No. 311-2).

erties. However, the tensile strength at break abruptly decreased with C-PDMS content. The tensile modulus also decreased with C-PDMS content in a similar manner as the tensile strength. Moreover, in more than 40% of C-PDMS contents, the relatively low tensile strength corresponded inversely to their high elongation for both cured blends.

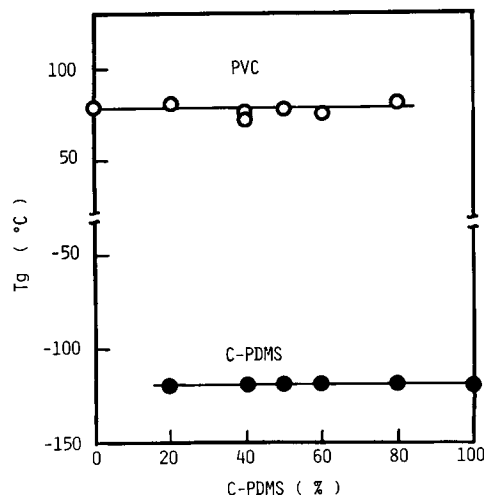
These blends essentially consist of immiscible, phase-separated systems. The phase structure of the cured blends plays an important role in controlling mechanical properties. Therefore, morphological study was performed with a scanning electron microscope. Figures 4(a), 4(b), 4(c), and 4(d) show scanning electron micrographs of the fracture surfaces in the uncrosslinked and the crosslinked blends with compositions of C-PDMS-PVC = 20/80, 50/50, and 80/20.

The morphological comparison between the fracture surfaces of the uncrosslinked and the crosslinked blends, as shown in Figures 4(a) and 4(b), indicates slight agglomeration in the latter blends but no significant difference between them. This is probably because the fracture occurred mainly in the C-PDMS phases, but the morphological difference was very small in the 20/80 blends. Relatively smooth surface morphology was observed in the crosslinked 50/50 and 80/20 blends suggesting that the fracture propagates through the C-PDMS matrices with poor tensile strength and loose crosslinking, as shown in Figures 4(c) and 4(d). The fillers, magnesia and silica, are covered with C-PDMS components of low surface energy.

A possibility of the presence of partially miscible phases in the cured blends was studied by means of differential



**Figure 5** DSC thermograms of cured C-PDMS-PVC blends. Curing temperature: (—) 170°C; (---) 160°C. (a) Low-temperature region; (b) high-temperature region.



**Figure 6** Glass transition temperatures ( $T_g$ 's) of cured C-PDMS-PVC blends estimated from DSC analysis.

scanning calorimetry (DSC). The DSC thermograms of cured blends are illustrated in Figures 5(a) and 5(b).

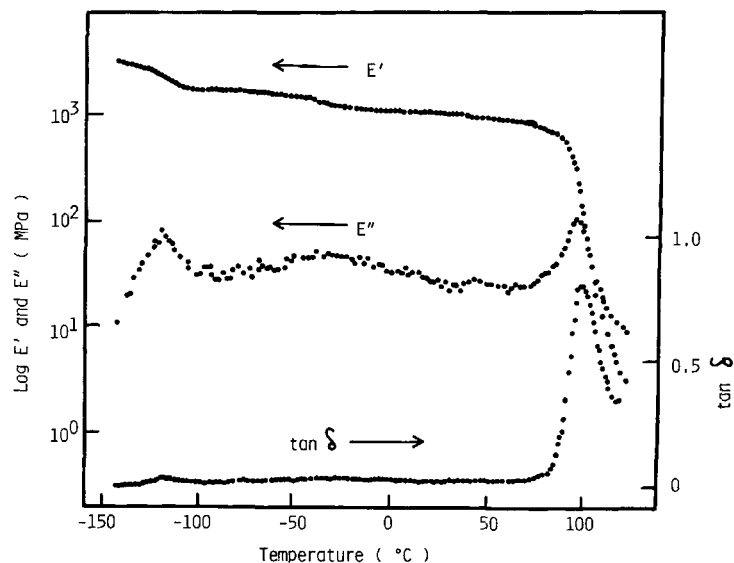
The presence of two distinct glass transitions ( $T_g$ 's) around  $-120$  and  $80^\circ\text{C}$  due to C-PDMS and PVC components, respectively, was evidently confirmed. It is also noted that their components in the cured blends have the  $T_g$ 's similar to those of their original components without any significant variation, as can be seen from Figure 6. This phenomenon supports the absence of any partial miscibility between two components.

Figure 7 shows dynamic mechanical analysis (DMA) of the cured C-PDMS-PVC blend (20/80).

The cured C-PDMS-PVC (20/80) blend has glass transitions around  $-120$  and  $100^\circ\text{C}$ , corresponding to those of C-PDMS and PVC, respectively, although the latter transition is a little higher than that obtained from the DSC analysis. These data also support the phase-separated structures for the cured C-PDMS-PVC blends. Unfortunately, the crosslinked blends with more than 40% of C-PDMS were too brittle to perform DMA measurements in tensile mode.

Thus, C-PDMS was found to crosslink with PVC in the presence of the triazinethiol, DB. However, the evidence for the crosslinking bond formation at the interface between two polymers was still ambiguous, although the blends were apparently cured. Further study will be necessary for the C-PDMS-PVC blends to obtain some informations with regard to formation of cocrosslinking bonds.

The cured C-PDMS-PVC blends are expected to exhibit specific properties inherent to silicone polymers, for example, excellent water repellency, flexibility, weatherability, and electric resistance. This crosslinking technology using C-PDMS is possible to apply to other halogen-containing polymers, such as polychloroprene and poly(epichlorohydrin), instead of PVC, endowing the functions inherent to silicone polymers.



**Figure 7** Dynamic mechanical analysis of cured C-PDMS-PVC blends. Formulation: Run no. 311-5 in Table I (C-PDMS-PVC = 20/80).

## REFERENCES

1. K. Ito (Ed.), *Silicone Handbook*, Nikkan Kogyo Simbunsha, Tokyo, 1990.
2. H. Inoue and K. Matsukawa, *J. Appl. Polym. Sci.*, to appear.
3. K. Mori and Y. Nakamura, *J. Polym. Sci. Polym. Chem. Ed.*, **16**, 2055 (1978).
4. K. Mori and Y. Nakamura, *J. Polym. Sci. Polym. Chem. Ed.*, **16**, 1981 (1978).
5. K. Mori, Y. Nakamura, and T. Hayashi, *Angew. Makromol. Chem.*, **66**, 169 (1978).
6. K. Mori, Y. Nakamura, and K. Tamura, *J. Appl. Polym. Sci.*, **22**, 2685 (1978).
7. K. Mori and Y. Nakamura, *J. Macromol. Sci. Chem.*, **A12**, 209 (1978).
8. K. Mori, Y. Nakamura, and A. Arai, *Kobunshi Ronbunshu*, **36**, 27 (1979).
9. K. Mori and Y. Nakamura, *Kobunshi Ronbunshu*, **35**, 353 (1978).
10. M. Behl and N. Duchacek, *J. Appl. Polym. Sci.*, **37**, 429 (1989).
11. T. Hjertberg, R. Dahl, and E. Sorvik, *J. Appl. Polym. Sci.*, **37**, 1239 (1989).
12. Y. Nakamura, K. Mori, Y. Yoshida, and K. Tamura, *Kobunshi Ronbunshu*, **41**, 531 (1984).
13. Y. Nakamura, K. Mori, R. Takezawa, and M. Saito, *Nippon Gomu Kyokaishi*, **52**, 584 (1979).
14. Y. Nakamura, K. Mori, and R. Takezawa, *Nippon Gomu Kyokaishi*, **52**, 240 (1979).
15. Y. Nakamura, K. Mori, and K. Wada, *Nippon Gomu Kyokaishi*, **57**, 561 (1984).
16. Y. Nakamura, K. Mori, and K. Wada, *Kobunshi Ronbunshu*, **41**, 539 (1984).
17. H. Inoue and S. Kohama, *J. Appl. Polym. Sci.*, **32**, 3853 (1986).

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Received September 20, 1991

Accepted October 30, 1991