

Study on Mechanical Properties and Intermolecular Interaction of Silicone Rubber/Polyurethane/Epoxy Blends

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ABSTRACT: The aggregation structure and mechanical properties of liquid silicone rubber, polyurethane (PU), and epoxy (EP) blends were studied. The molecular structure was evaluated by FTIR, and the intermolecular interaction of the three-phase polyblends was measured by dynamic mechanical analysis. The mechanical properties, including the tension, compression, shear, and tear performance, were measured by a material testing system. From the relationship between the intermolecular interaction and mechanical properties, we found that the aggregation structure of the

three-phase blends was influenced by the reaction between silicone and PU, silicone and EP, and PU and EP, which resulted in a change of the crosslinking density and an interpenetrating polymer network structure. Thus, the dominant three-phase mechanical properties are closely related to the aggregation structure. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 959–970, 2003

Key words: silicone; polyurethane; epoxy; intermolecular interaction; aggregation structure

INTRODUCTION

Polymer blending is the mixing of two or more polymers of different proportions to achieve a certain expected performance.^{1–3} Its advantages include simplicity, because it is conducted with existing equipment and technology^{4,5}; various predicted components; and physical and chemical properties, which facilitate the evaluation of the properties of the mixture.

Silicone rubber has been widely applied to various industrial products because of the characteristics of silicon oxide, including thermal stability, high mechanical and chemical resistance, weatherproof, ozone and radiation resistance, and so forth.^{6,7} The molecular structure of polyurethane (PU) is composed of urethane compounds (—NH—COO). Generally speaking, the block copolymer PU comprises rigid diisocyanate, short-chain diol or diamine, and yield polyol. Because it is resistant to chemicals, soft, waterproof, and weatherproof, it can be used for different purposes.⁸ Epoxy (EP), a widely applied thermosetting macromolecular material, is extensively used by industry because of its superb mechanical properties, heat and melting resistance, and dimensional stability.^{9–12}

Because silicone and PU have a flexible network structure and EP has a hard one, the aggregate structure of the mixture can be adjusted effectively through an easy processing approach. Consequently, this study makes use of PU features like flexibility and adhesion properties and EP mechanical properties and rigidity. We use silicone rubber as the main body and mix PU and EP in different proportions to explore the mechanical properties and aggregate structure of a mixed rubber consisting of silicone, PU, and EP (SPE). In addition, the relationship between the three-phase reaction and changes of the aggregate structure is investigated to serve as a design direction for shockproof and energy absorption features, as well as a performance and heat resistant material in the future.

EXPERIMENTAL

Material

The materials used are liquid silicone rubber [poly(dimethylsiloxane), product 9050] manufactured by Dow Corning, PU [toluene diisocyanate and poly(butylene adipate), product name Corol] made by Kuan Je, and EP resin (bisphenol A and epichlorohydrin, product name Araldite F) produced by Ciba-Geigy. The hardening agent is carboxylic acid anhydride (HY-905).

Mixture and production of test piece

The sample for testing was produced by evenly mixing silicone rubber, PU, and EP in accordance with the

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TABLE I
Compositions of Silicone Rubber/PU/Epoxy Blends (wt %)

Material	Code No.						
	SPE100	SPE010	SPE001	SPE730	SPE721	SPE712	SPE703
Silicone	100	—	—	70	70	70	70
PU	—	100	—	30	20	10	0
Epoxy	—	—	100	0	10	20	30

SPE-xyz, the silicone content (x), PU content (y), and epoxy content (z).

mixing proportions specified in Table I and then placing in a mold. After soaking it in a vacuum for 30–40 min, the mold was maintained at 150°C for a 20-min hardening. Upon cooling, the test piece was removed from the mold and trimmed to a proper size for testing.

Analysis of hardened structure of polyblends

FTIR testing was conducted with a Bio-Rad FTS-7. The silicone rubber, PU, and EP were mixed in the proportions specified in Table II and evenly stirred. Then the sample was applied to KBr and hardened at 150°C for 20 min. We measured the FTIR drawing at room temperature and observed the structural changes of the polyblends.

Testing of mechanical properties of SPE polyblends

The tensile stress and strain were measured with a Universal tensile tester with a tension velocity of 500 mm/min in compliance with the specifications of ASTM D412C. The tear strength was measured with a tension velocity of 500 mm/min according to ASTM D624C.

Measurement of compression stiffness and shear stiffness

A material testing system (MTS-810) was utilized to test the compression stiffness and shear stiffness of the test piece, which had a diameter of 29 ± 0.5 mm and a width of 12 ± 0.5 mm under a deformation range of 6 mm. The experimental definitions of compression

TABLE II
FTIR Compositions of Silicone Rubber/PU/Epoxy Blends (wt %)

Material	Code No.					
	SPE100	SPE010	SPE001	SPE101	SPE110	SPE011
Silicone	100	—	—	50	50	—
PU	—	100	—	—	50	50
Epoxy	—	—	100	50	—	50

SPE-xyz, silicone content (x), PU content (y), and epoxy content (z).

stiffness and shear stiffness are shown in Figure 1 and Figure 2, respectively.¹³

Measurement of dynamic mechanical properties

The polyblends were trimmed to 2 mm wide, and they had dimensions of $2 \times 10 \times 5$ mm. Dynamic mechanical analysis (DMA) was conducted on a model TA2980 analyzer with a temperature rising rate of 5°C/min within the range of -150 to 150 °C under a frequency of 1 Hz for temperature scanning. Therefore, the relationships between the storage modulus (E'), loss modulus (E''), damping ($\tan \delta$), and temperature could be measured.

RESULTS AND DISCUSSION

Analysis of hardening structure of SPE polyblends

Because polysiloxane has excellent but peculiar properties, there are many studies on the property changes of general organic macromolecules through the use of polysiloxane. According to numerous reports, the reaction to EP occurs regardless of what the end radical of polysiloxane is (amine, carboxyl, acid, or hydroxyl), resulting in changes in the properties of the molecular chains.^{14–36} The molecular structure was evaluated by

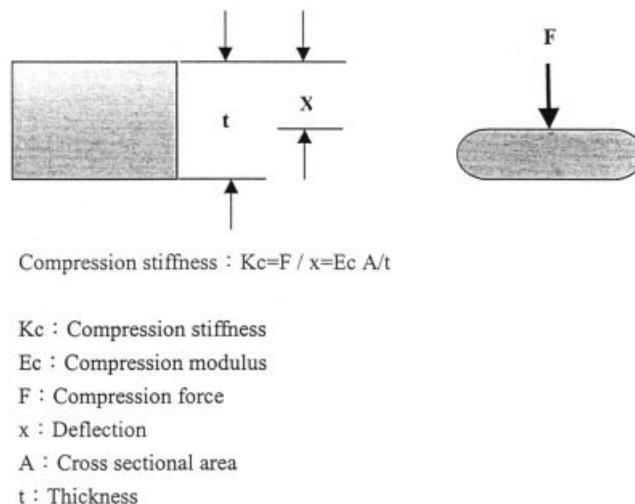


Figure 1 The rubber block in compression.

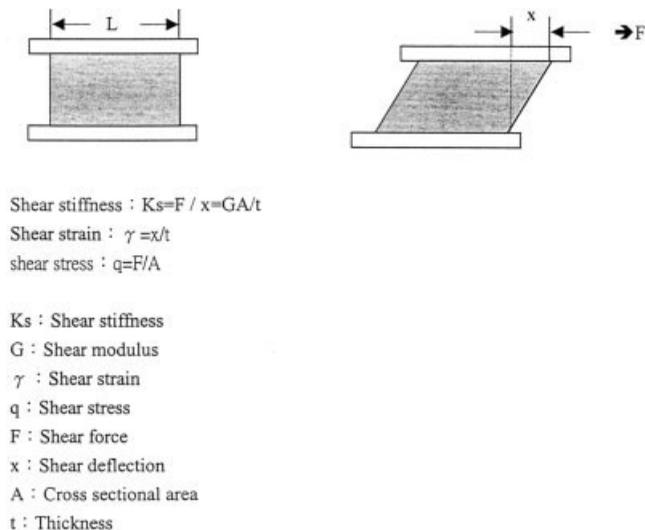


Figure 2 The rubber block in shear.

FTIR in this research. The IR spectrum is shown in Figure 3. It is known that the absorption peak of silicone (SPE100, where the three numbers indicate the

respective silicone, PU, and EP content) reaches 3600 cm^{-1} (Si—OH); 1080 cm^{-1} (Si—O—Si); and $2958, 1245, \text{ and } 802\text{ cm}^{-1}$ (Si—CH₃). The absorption peak of PU (SPE 010) reaches $3400, 1700, \text{ and } 2250\text{ cm}^{-1}$ for —NH, —CO, and —NCO, respectively. For EP (SPE001), the absorption climax of C(CH₃)₂ and C—OH comes at $1381 \text{ and } 3500\text{ cm}^{-1}$, respectively. From the FTIR spectrum of silicone/EP (SPE101), we found that the Si—OH of silicone and C—OH of EP form a copolymer of Si—O—C through dehydration and a wavelength of 1104 cm^{-1} is absorbed by the Si—O—C linking key. It is concluded that a reaction exists between silicone and EP, and its structure is shown in Scheme 1. On the other hand, it can be observed from the FTIR spectrum of silicone/PU (SPE110) that the absorption peak of the functional group with a wavelength of 3600 cm^{-1} (OH) for silicone and 2250 cm^{-1} (NCO) for PU disappears, which indicates that a chemical reaction occurs between the OH of silicone and the NCO of PU. Its structure is shown in Scheme 2. For the FTIR spectrum of PU/EP (SPE011), we discovered that the functional group absorption peaks of EP with a wavelength of 3484

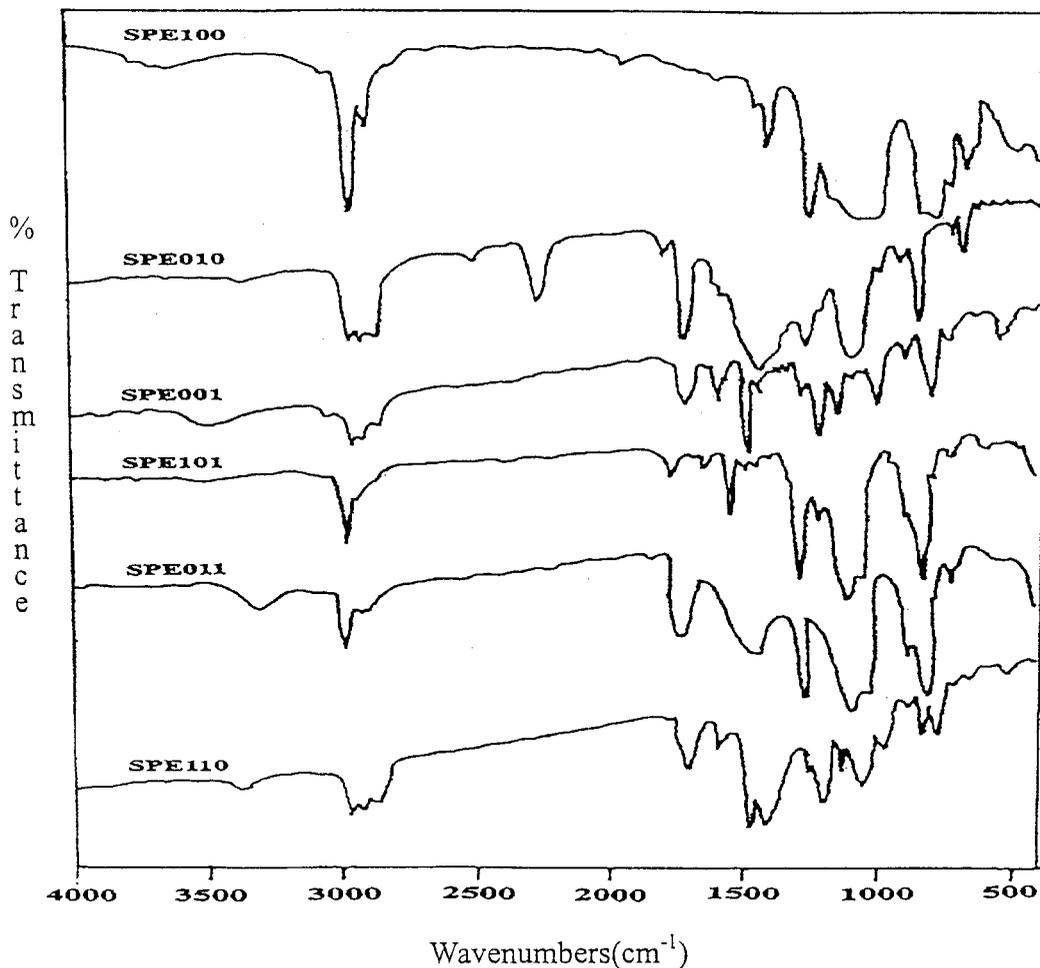
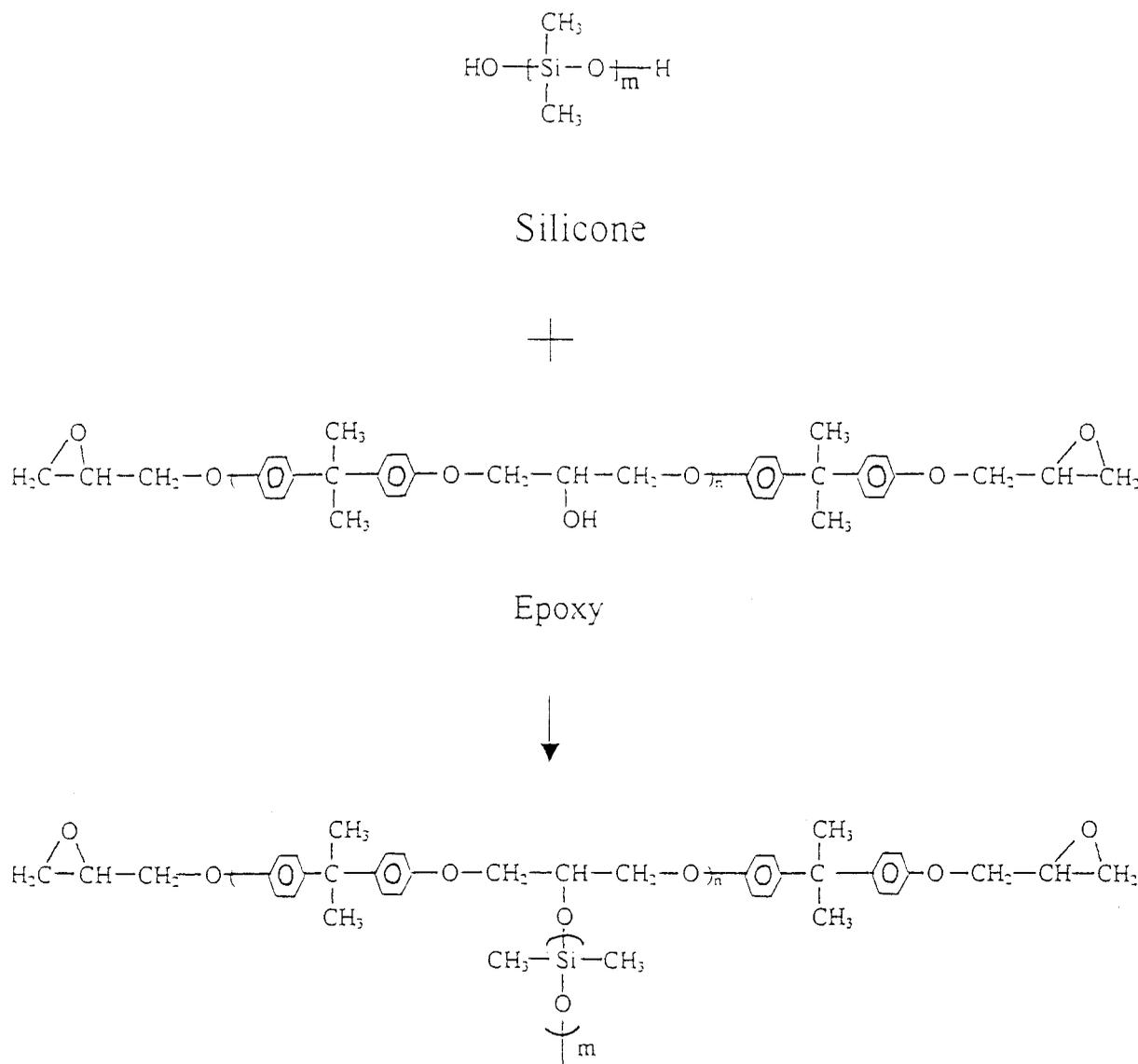


Figure 3 The FTIR evaluation of silicone rubber/PU/epoxy blends.



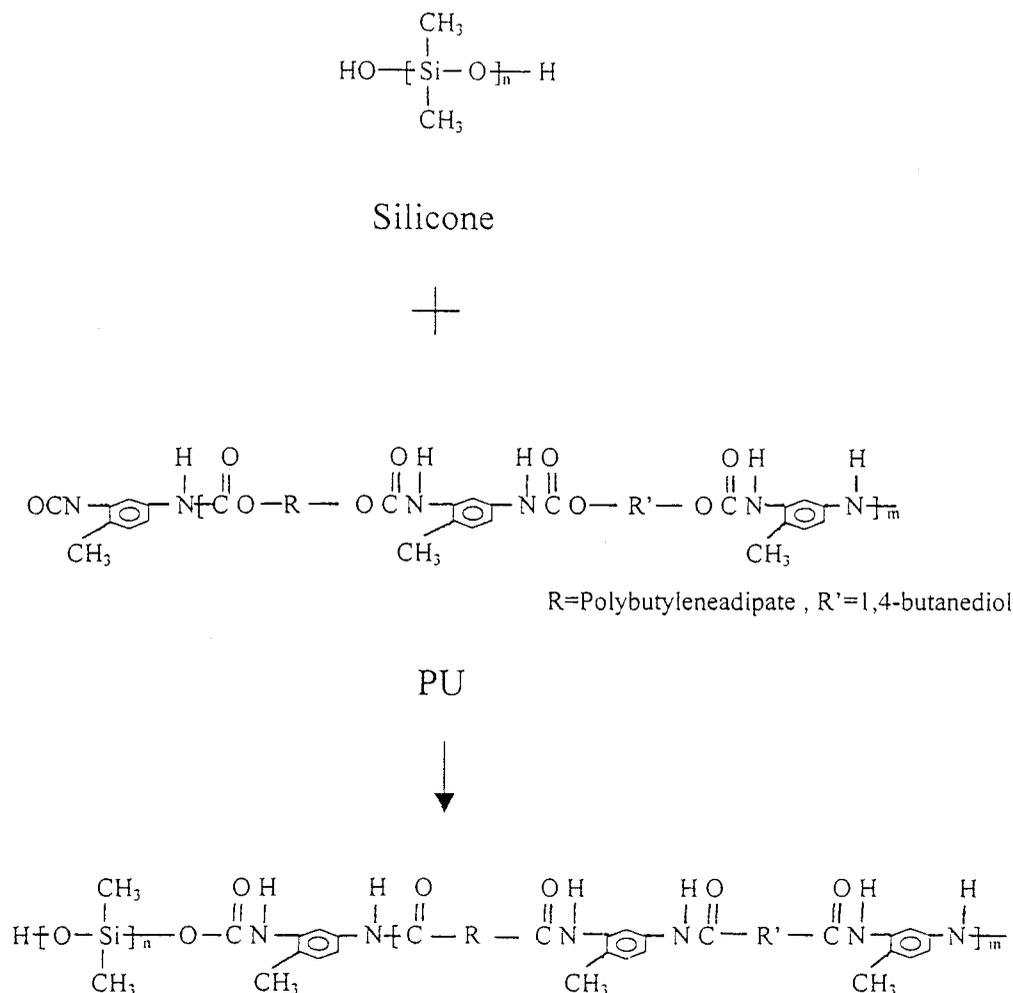
Scheme 1 The structure of the silicone rubber/epoxy blend.

cm^{-1} (OH) and PU with a wavelength of 2250 cm^{-1} (NCO) are gone, which reveals that a chemical reaction exists between the NCO in PU and the OH in EP. Its structure is shown in Scheme 3. From the results discussed above it is obvious that an intermolecular reaction between silicone, PU, and EP really exists.

Intermolecular interaction in SPE

Effective information on the aggregate structure of the polymer blend can be observed through the intermolecular interaction in the DMA.³⁷⁻³⁹ Figures 4 through 10 contain the DMA curves of various blends measured with a frequency of 1 Hz. First, for the material of the single-phase system, it is derived from the DMA information in Figure 4 that the glass-transition tem-

perature (T_g) peak of pure silicone is at -133.8°C , the T_g peak of pure PU in Figure 5 is at about -63.2°C , and that of pure EP in Figure 6 is approximately 83.9°C . Second, for the material of the two-phase system, in Figure 7 the silicone peak of silicone/PU increases from -133.8 to -118°C and the PU peak decreases from -63.2 to -67.5°C . Figure 8 shows that the silicone peak of silicone/EP increases from -133.8 to -117°C and the EP peak decreases from 83.9 to 39°C . In Figure 9 the PU peak of PU/EP increases from -63.2 to -48°C and the EP peak decreases from 83.9 to 52°C . It is thus known that when materials of two phases are blended, a graft interpenetrating polymer network structure (graft-IPN) results that is due to the peak movement caused by the reaction of the functional group in silicone/PU, silicone/EP, and PU/EP.



Scheme 2 The structure of the silicone rubber/PU blend.

To investigate the intermolecular interaction of the three-phase SPE, SPE721 was chosen as the target to conduct DMA, and the results are shown in Figure 10. An analysis and comparison of the location of each T_g peak in Figures 4–10 demonstrates that the silicone peak moves from -133.8 to -131.8°C , the PU peak moves from -63.2 to -101.1°C , and the EP peak moves from 83.9 to -45.1°C . With a range of about 128°C , which is due to the intermolecular reaction in SPE, an IPN structure is formed while crosslinking.

In addition, part of the silicone reacts to PU and part of it reacts to EP in SPE721. Thus, the portion of the PU reacting to EP forms a new molecular chain. Excess silicone forms a crosslink. This type of structure renders an independent EP peak. Furthermore, because it combines with silicone and PU molecules, the molecular chain tends to be soft, which forces it to move toward a low temperature. As part of the PU reacts to silicone, which makes the molecular chain become even softer, the temperature decreases about 38°C . Excess silicone is affected by the PU and

EP components, which increases the temperature slightly. As a result, under the intermolecular interactions among the three networks, the PU and EP peaks move toward low temperatures; however, the silicone peak moves toward a high temperature.

From the analysis above we know that the distance between crosslinking points can be changed through the functional group changes of silicone/PU, silicone/EP, and PU/EP when blending these three materials. The rigidity of the target performance can be achieved through control of the alterations of the component proportions. In addition, the IPN structure formed by silicone/PU, silicone/EP, and PU/EP can also effect the performance adjustment. Consequently, the intermolecular interaction in the three-phase SPE is apparent and the three-phase SPE blend has a semi-IPN structure. The shockproof and energy absorption characteristics of materials can be improved via appropriate proportions of the three-phase elements. Until then, performance and heat resistance can be expected as well.

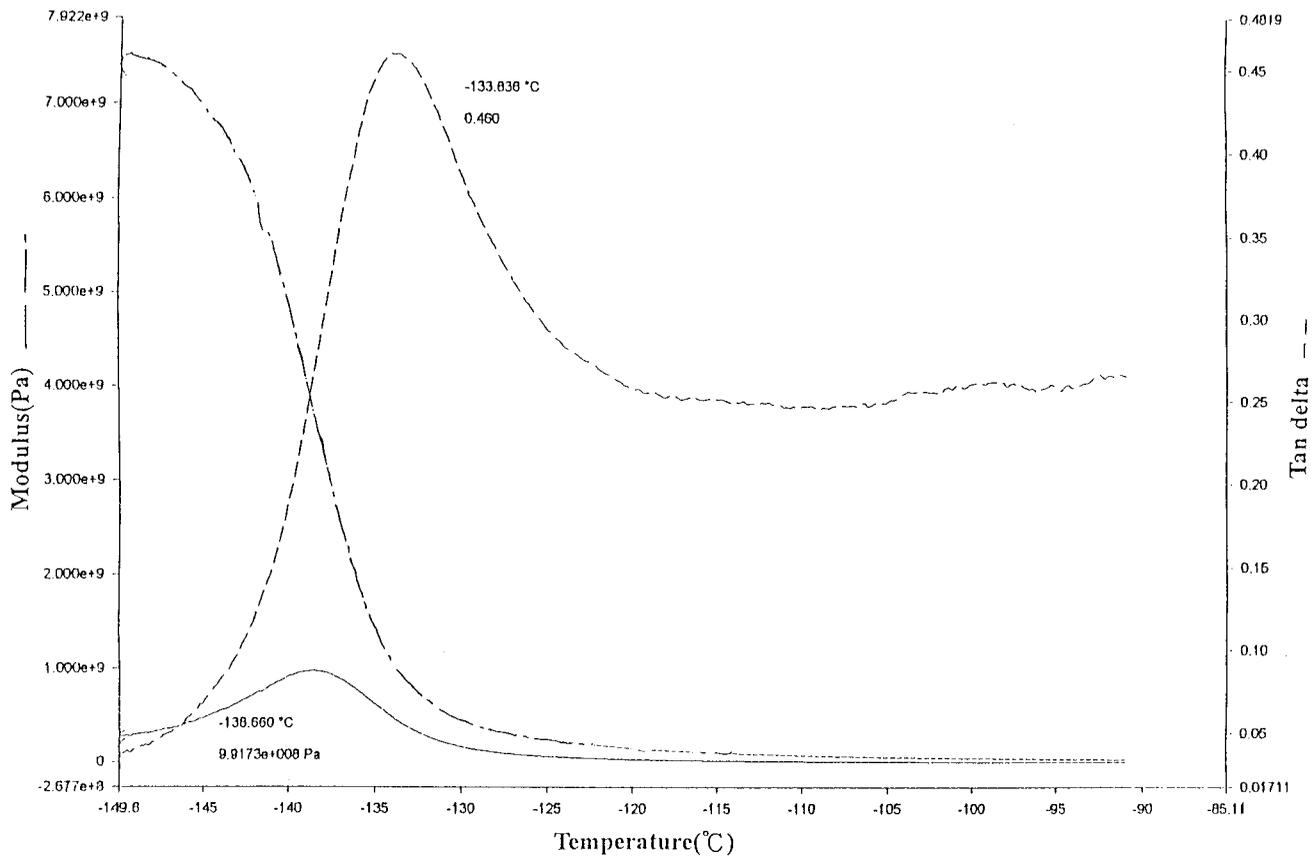


Figure 4 The effect of temperature on the storage modulus, loss modulus, and damping (tan δ) of silicone rubber.

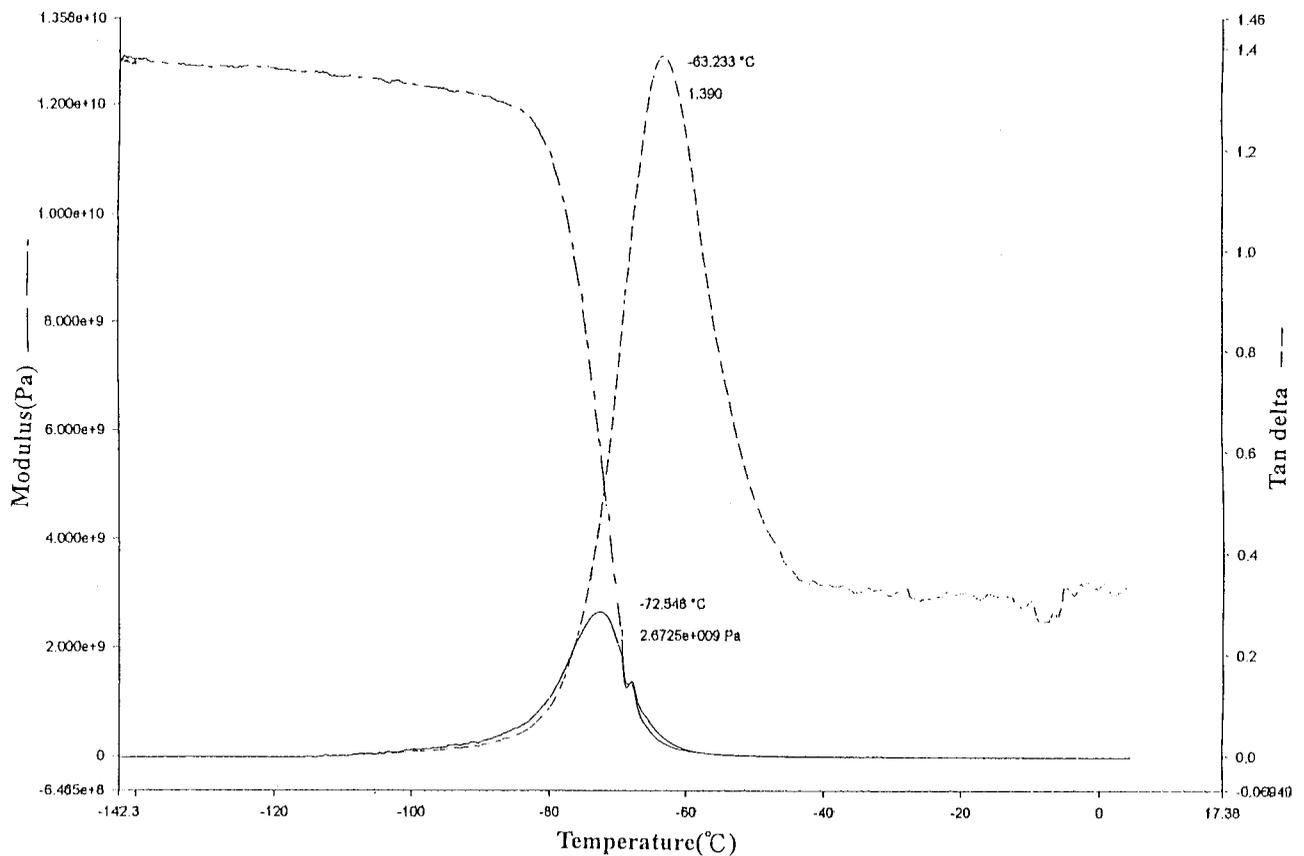


Figure 5 The effect of temperature on the storage modulus, loss modulus, and damping (tan δ) of PU.

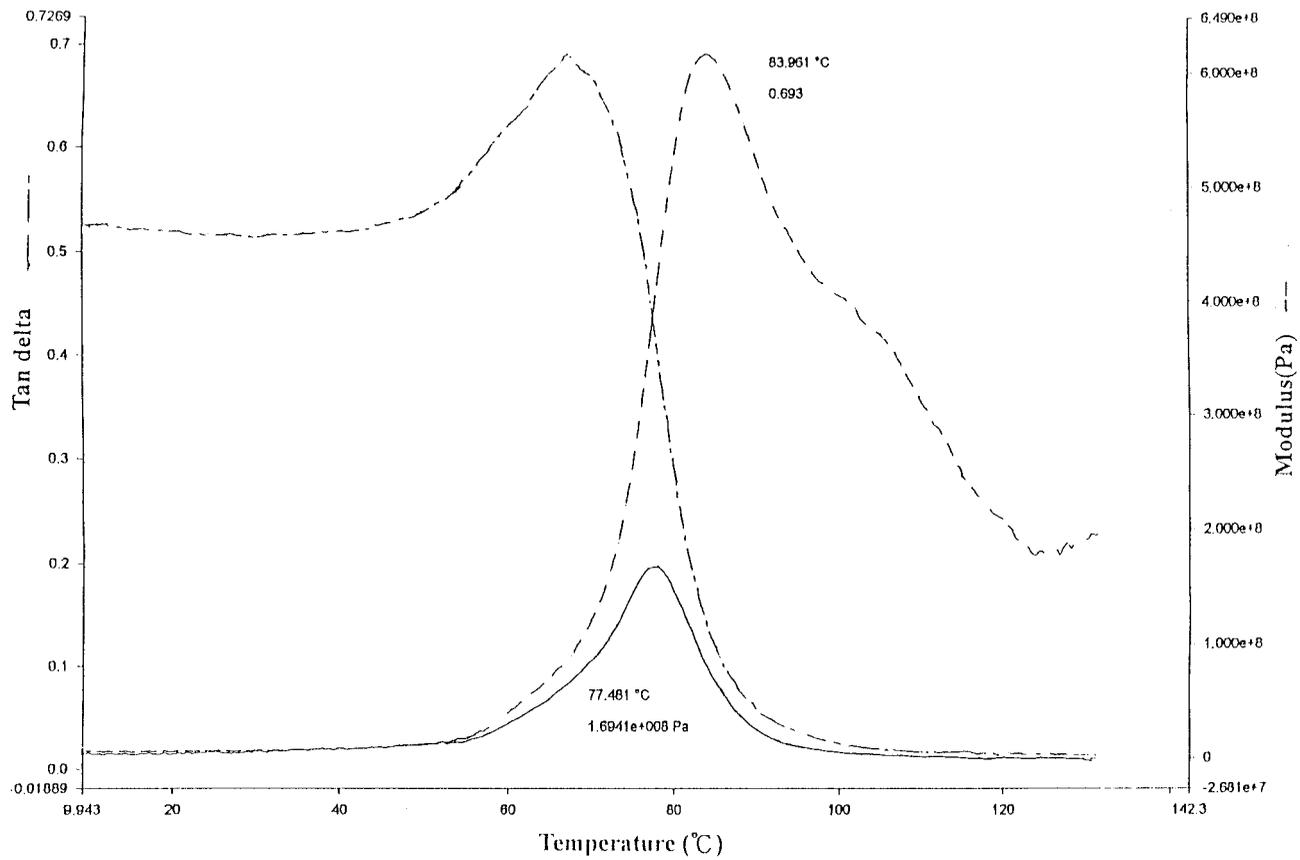


Figure 6 The effect of temperature on the storage modulus, loss modulus, and damping ($\tan \delta$) of epoxy.

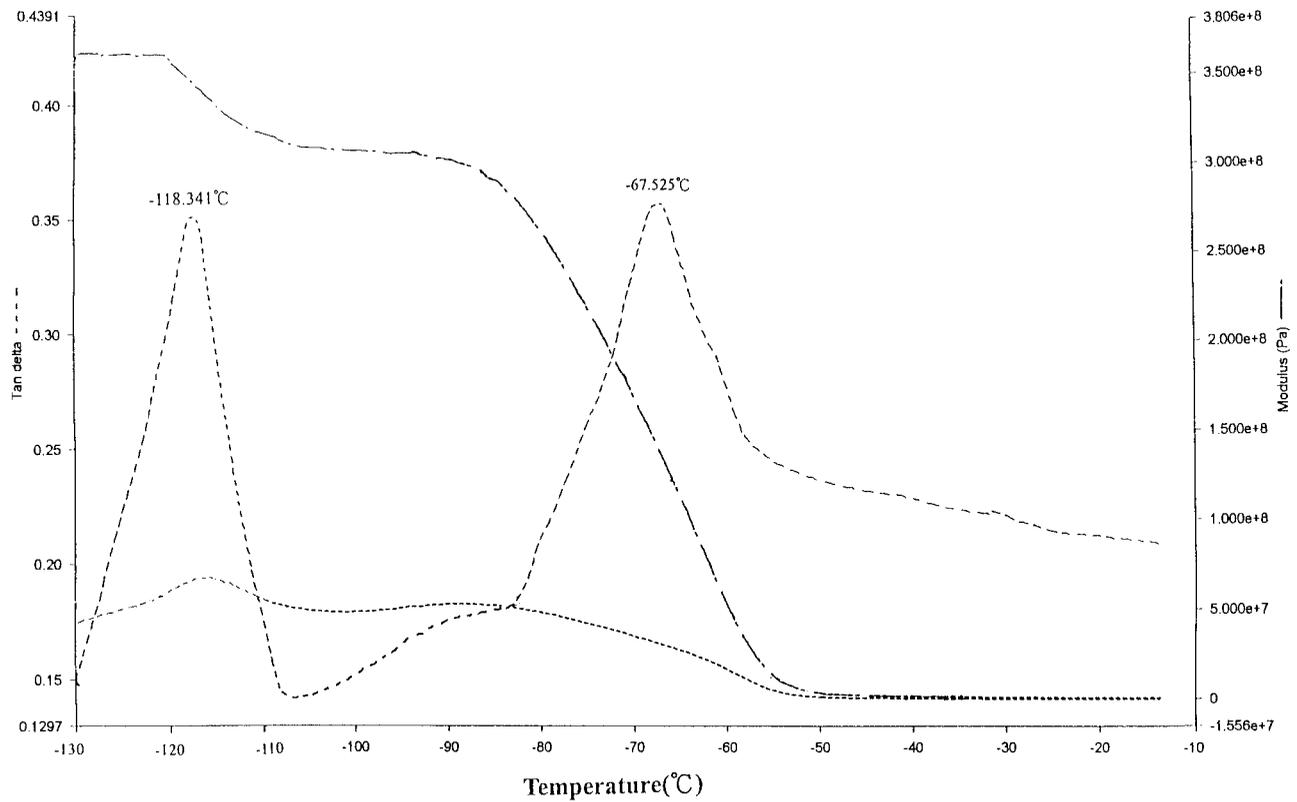


Figure 7 The effect of temperature on the storage modulus, loss modulus, and damping ($\tan \delta$) of silicone rubber/PU blends.

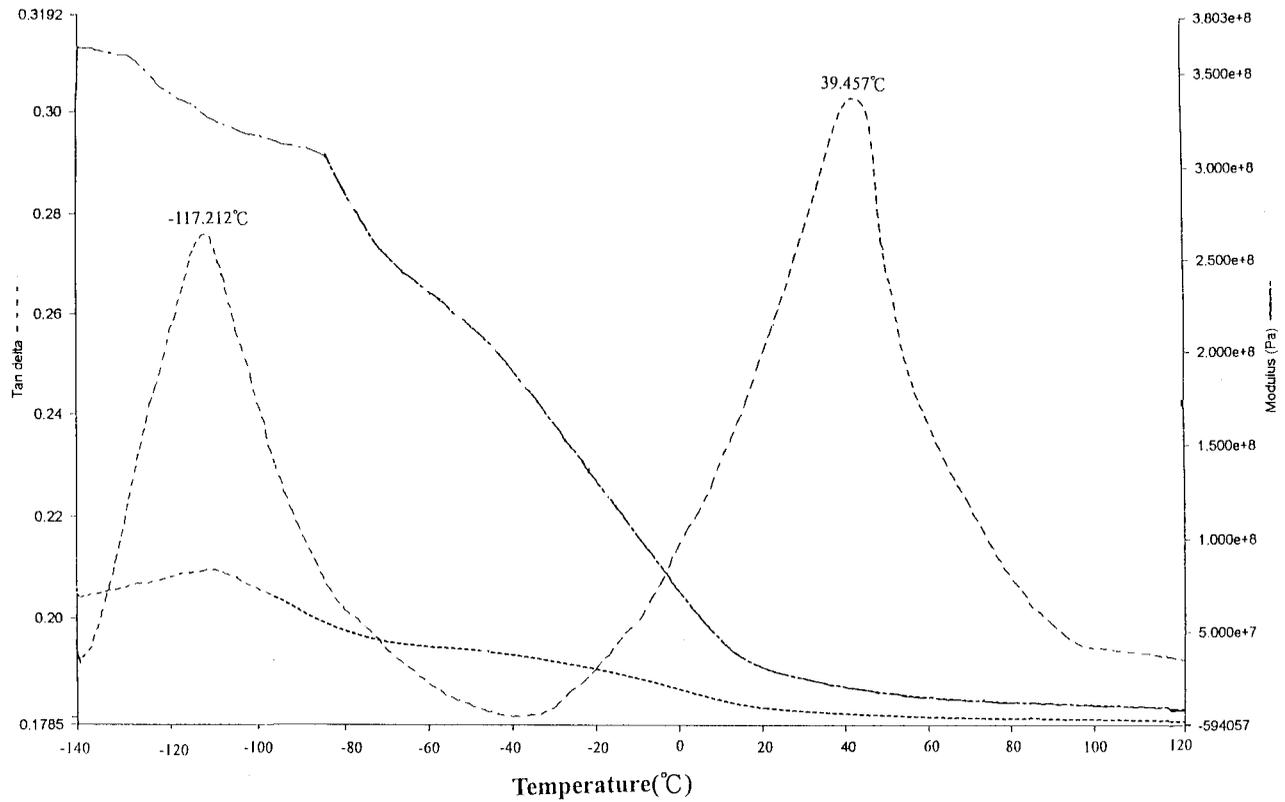


Figure 8 The effect of temperature on the storage modulus, loss modulus, and damping ($\tan \delta$) of silicone rubber/epoxy blends.

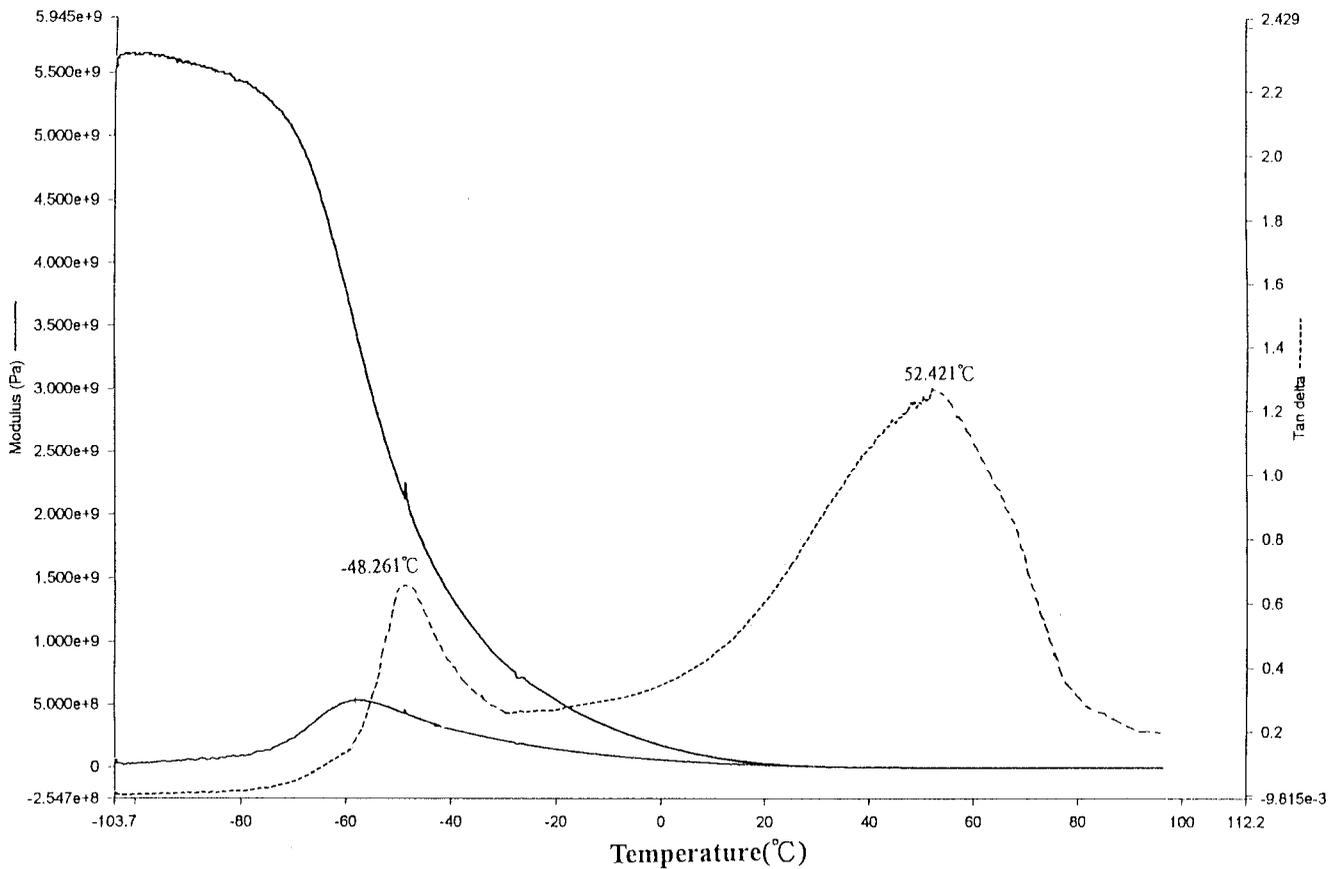


Figure 9 The effect of temperature on the storage modulus, loss modulus, and damping ($\tan \delta$) of PU/epoxy blends.

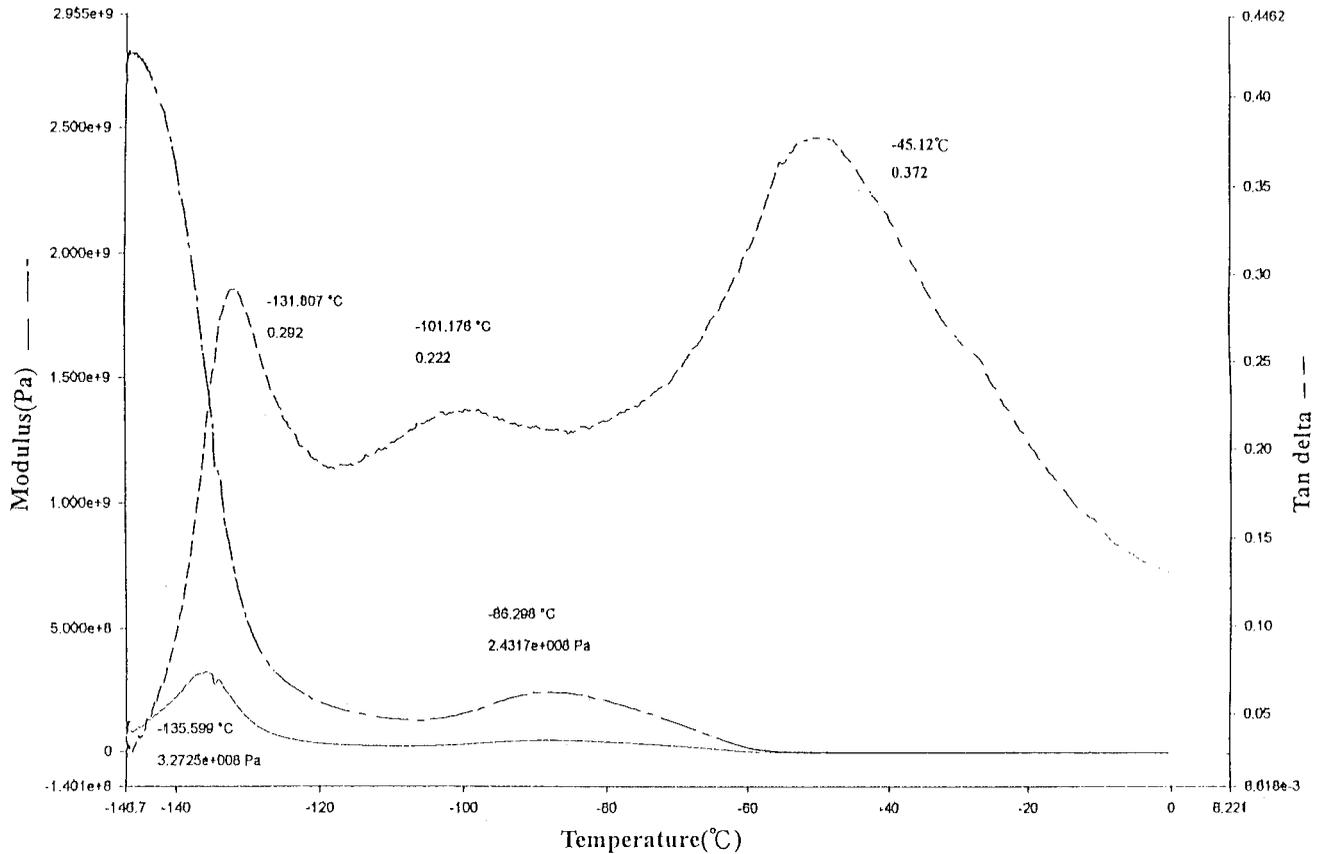


Figure 10 The effect of temperature on the storage modulus, loss modulus, and damping ($\tan \delta$) of silicone rubber/PU/epoxy blends.

Analysis of mechanical properties of SPE blends

Figure 11 is a bar chart of the tensile stress for various SPEs. The EP on a brittle material has the greatest strength; and in regard to the rubber properties of silicone and PU, silicone has more strength than PU. When two phases are blended, the crosslinking distance of the molecular chain for SPE703 is enlarged because 30 wt % EP added to the silicone, the C—OH in EP reacts to Si—OH in the silicone, and there are crosslinks between the molecular chains of silicone. Therefore, an aggregate structure of the larger net-

work is formed and the strength of SPE703 is less than that of pure silicone or EP.

On the other hand, for the two-phase SPE730, an aggregate structure with a larger network is established, which is due to the reaction between the NCO in PU and the OH in silicone. Because the silicone network is not as soft as the PU network, the strength of SPE730 falls between silicone and PU.

Based on the reasons above, 30 wt % PU is replaced by 10 wt % EP for SPE721 and the reactions between silicone/PU, silicone/EP, and PU/EP enlarge the distance between crosslinking points,

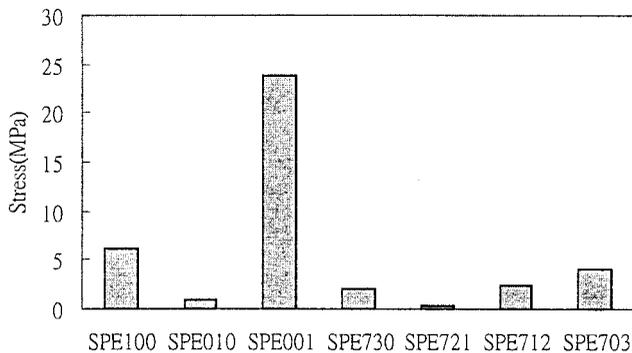


Figure 11 The stress of silicone rubber/PU/epoxy blends.

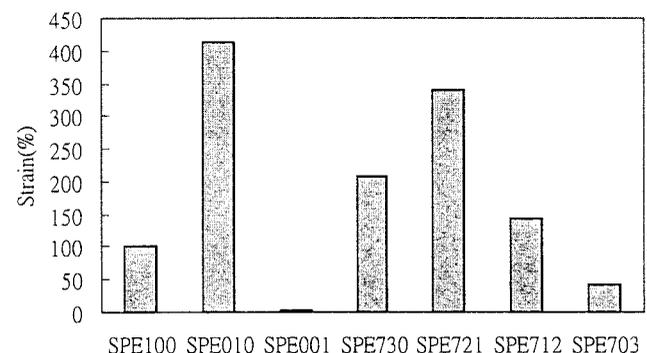


Figure 12 The strain of silicone rubber/PU/epoxy blends.

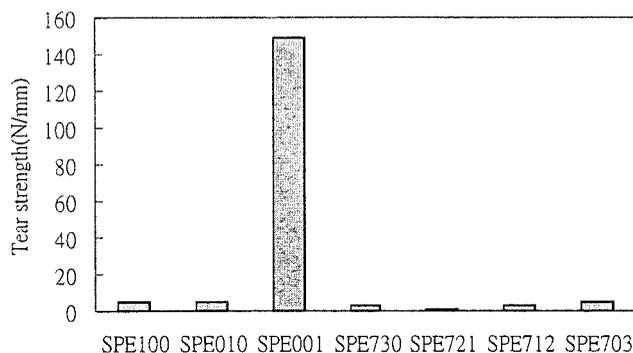


Figure 13 The tear strength of silicone rubber/PU/epoxy blends.

which results in an IPN structure. Therefore, SPE721 is not as strong as SPE730. In addition, the increased proportion of EP in SPE712 is because of the greater rigidity of the molecule chain. From the experiment we know that the crosslinking density can be changed through different levels of reactions, as well as blending of the rigidity of the molecular chain, in addition to introducing the aggregate structure of the IPN in order to control the properties of the polymer. Figure 12 contains the percentages of strain drawing of various SPE polymers. It is derived that strain has a corresponding relation with stress. The SPE with greater strength has a relatively lower tensile stress. Figure 13 shows the tear strength in contrast to the changes in the blending proportions. From the figure we know that PU has a smaller resistance capacity; therefore, the tear strength decreases after adding PU.

For statics, the rigidity feature of the rubber material can be divided into the stiffness under compression (K_c) and the shear stiffness (K_s). Generally speaking, the modulus obtained through compression is greater than that via shear. This is because, when compression stress imposes on a rubber material, it is increased because of the existing defects and submicroscopic cracks that tend to enclose it.⁴⁰ Figures 14 and 15 reveal the relationships between the compression rigidity, shear rigidity, and blending proportions of various SPEs. We concluded that the compression and

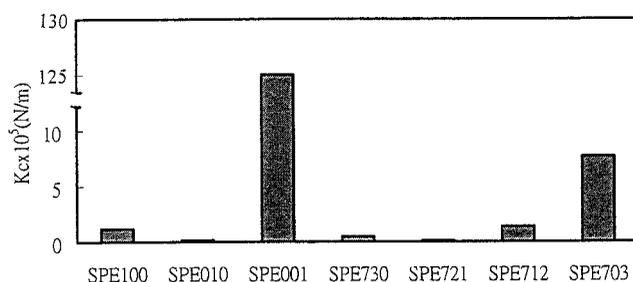


Figure 14 The compression stiffness of silicone rubber/PU/epoxy blends.

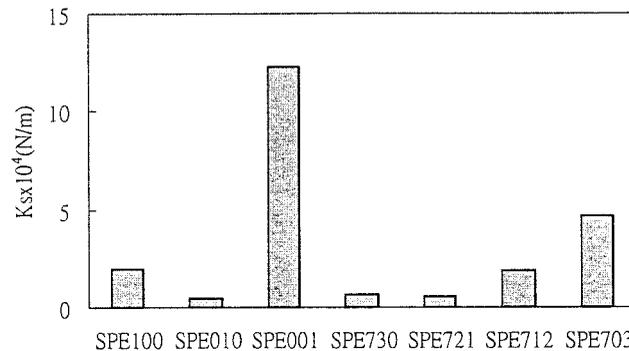


Figure 15 The shear stiffness of silicone rubber/PU/epoxy blends.

shear rigidities have the same tendencies as the tensile strength.

CONCLUSIONS

Specific conclusions can be made from the experimental results

1. According to the analysis of the IR, the absorption peak of the polymer changes with different blending proportions. The chemical structure changes because of the reactions between the silicone, PU, and EP, which influences the crosslinking network of the aggregate structure.
2. The DMA results verify that the three-phase polymer blends of silicone, EP, and PU have a semi-IPN structure. Interactions between silicone/PU, silicone/EP, and PU/EP really exist, which forces the PU and EP peaks to dramatically move toward low temperatures.
3. Due to the reaction between Si—OH and PU—NCO in two-phase polymer blends of silicone/PU, Si—OH and C—OH in two-phase polymer blends of silicone/EP, and PU—NCO and C—OH in two-phase polymer blends of PU/EP, the crosslinking distance is enlarged, which significantly decreases the mechanical properties of the three-phase SPE system.
4. In the two-phase polymer blends of silicone/PU, silicone/EP, and PU/EP, the graft-IPN structure makes the mechanical properties of silicone/PU/EP polymer blends incline toward a compound rule.

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