MODIFICATION OF POLYURETHANE ELASTOMER BY USING A REACTIVE SILICONE

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SUMMARY

Surface characteristic of polyurethane elastomer (PUE) was ameliorated by reacting the prepolymer with the reactive silicone (Si-NCO), one side of which was terminated with isocyanate group, in the presence of 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA). Tackiness and surface energy of the modified FUE decreased with an increase in Si-NCO content. Abrasion resistance was enhanced by adding Si-NCO in a noticeable manner. However, the addition of more than a certain amount of Si-NCO diminished the resistance partly due to a deterioration of mechanical properties. The optimum modification of PUE surface was achieved by adding around 3phr (parts per hundred parts of rubber) of Si-NCO, where the tackiness was able to decrease without significantly sacrificing the mechanical strength.

INTRODUCTION

Polyurethane elastomer (PUE) is a polymer obtained by the reaction of polyurethane, both sides of which are terminated with isocyanate group, with suport material (diamine). A variety of combinations of these materials provide PUE with an excellent physicoproperty. Especially, PUE has elasticity in spite of the high hardness. Therefore, PUE not only exhibits unusual mechanoproperties such as abrasive resistance, tensile strength, tear strength, and so on, but is exellent in oil resistance, vibration protectivity, and low temperature property. These outstanding properties make PUE useful as a special rubber in various branches of industry.

PUE is very often used for a roll which is directly in contact with paper. However, the surface tackiness of PUE causes the rolling up of paper and the lowering of friction factor of the roll because of adhesion of paper powder to it, and it fails to bring its function into full play. In order to improve this defect, KUROSE tried to improve surface characteristic of PUE by blending silicone oil with PUE[1]. But, the poor compatibility between silicone oil and PUE gave rise to the phase separation. Subsequently he examined the modification by a chemical reaction, that is, he tried to ameliorate the compativity by the use of reactive silicones, both sides or one side of which are terminated with isocyanate group. He found that the use of one-side terminated silicone made it possible to modify PUE successfully.

Based on KUROSE's results, we examined the effect of the amount of Si-NCO on the degree of surface modification in datail. Fric-
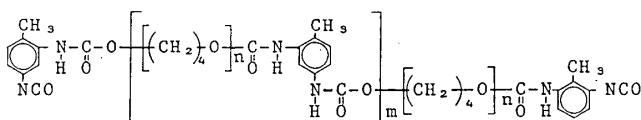
tion, tackiness, surface energy (contact angle with water, wettability) and other properties were investigated by changing the amount of Si -NCO. In this paper we report the interesting results obtained here.
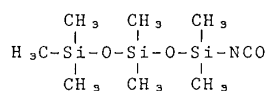
ENPERIMENTAL

Materials

Polyurethane prepolymer [I] used in this work was polyuretane terminated both sides with isocyanate group, which was comprised of PTMG (polytetramethylene glycol) and TDI (tolylenediisocyanate). The structure of silicone in order to modify PUE is illustrated below, which was end-capped one side with isocyanate group. MOCA (3,3'-dichloro-4,4' -diaminodiphenylmethane) was used as a polymer-chain extender.
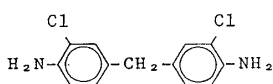
a) Prepolymer [I]

b) One-side Terminated Silicone (Si-NCO) [II]

$$H_3C-Si-O-Si-O-Si-NCO$$

c) Chain Extender [III]

3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA)

Preparation of Specimen

Preparation procedure according to conventional PUE process is shown in Fig. 1. Prepolymer and Si-NCO were previously deformed at 80°C in vacuo for 1hr. MOCA and various amounts of Si-NCO as listed in Table 1 were mixed with the prepolymer. After stirring for
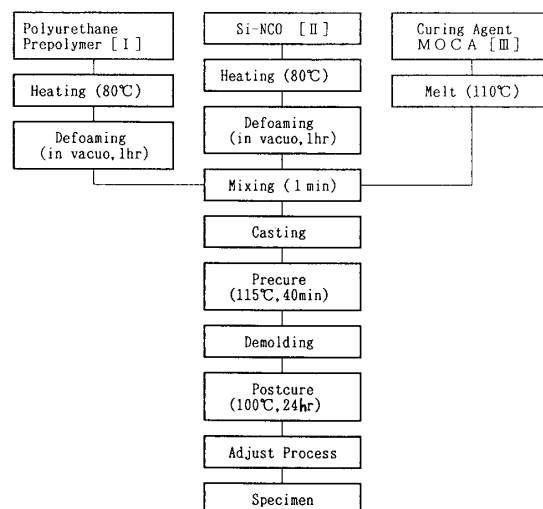

Fig. 1 Preparation procedure of a specimen

Table 1. The amount of each component (phr*)

Specimen No.	1	2	3	4
Prepolymer [I]	100	100	100	100
Si-NCO [II]		3	6	9
MOCA [III]	12.5	12.5	12.5	12.5

phr* : parts per hundred parts of rubber

about 1 min without mingling bubbles, the mixture was placed into a mold and precured at 115°C for 40 min. The hardened material was took out from the mold and then postcured at 100°C for 24 hr in an oven.

Curing Condition

Conventional curing condition was as follows; precuring at 115°C for 40 min and postcuring at 100°C for 24hr. The possibility that the addition of Si-NCO might change the hardening degree made us reexamine the optimal curing condition. Tg and mechanical propeties of the specimens prepared at different postcuring time were measured in the cases of 0 phr and 3 phr of Si-NCO contents.

Physical Properties

Surface property is most important for the specimen prepared in this study, although abrasion and mechanical properties were also investigated. Abrasion property was evaluated by using an NBS abrasion test machine. Mechani-
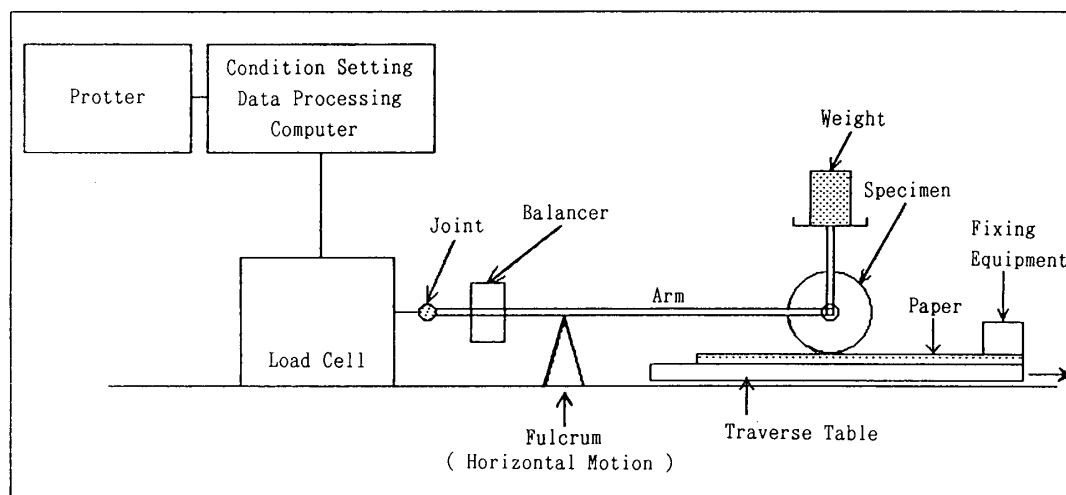
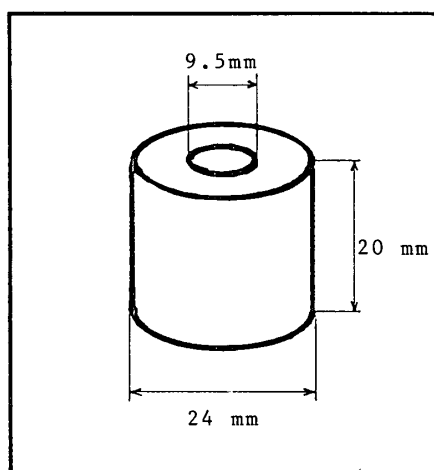Fig. 2 Surface analysing instrument (HEIDON MODEL-14)

Fig. 3 Specimen for friction and
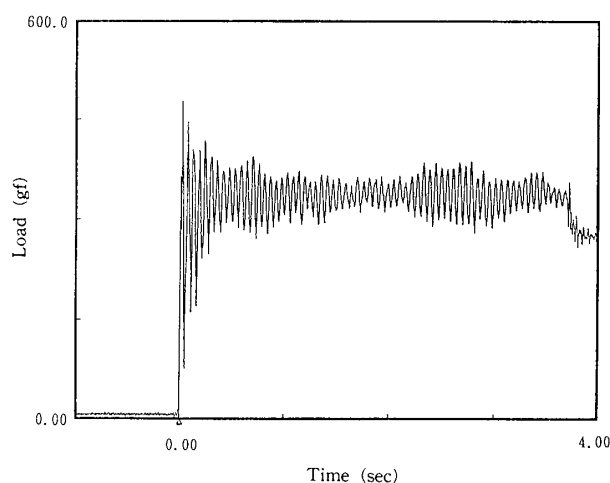tackiness measurements

Fig. 4 A chart obtained by HEIDON MODEL-14

cal properties were estimated with regard to hardness, tensile strength, elongation at break, tear strength, and compression set in accordance with JIS K6301. In addition, changes of these properties after heating the specimen or dipping it into hot water were examined.

1) Friction Factor

Friction factor against paper was measured by a HEIDON MODEL-14 surface analysing instrument shown in Fig. 2. Each specimen was processed in size illustrated in Fig. 3, which was fixed to a steel shaft, and mounted in the instrument. An example of the chart obtained in this measurement is shown in Fig. 4. Static friction

factor can be calculated from the initial large peak. We adopted the maximum height of the peak at steady state for the calculation of kinetic friction factor, although the average value between top and bottom of the peak is generally used.

2) Tackiness

Tackiness against paper was also examined in the similar manner by using the same instrument and specimen. The specimen was loaded with a weight of 1 kg for 5 min, and after removing the weight tackiness was investigated.

3) Surface Energy

Two methods, measurement of contact angle

Table 2. Surface Tension of n-paraffin (20°C)

n-Paraffins	Surface Tension (dyn/cm)
n-Hexane	18.42
n-Heptane	20.31
n-Octane	21.76
n-Nonane	22.92
n-Decane	23.92
n-Dodecane	24.51

with water and that of wettability, were adopted in order to evaluate surface energy. Change of surface energy of the specimen by varying the Si-NCO content was examined. The influence of surface roughness was too large to compare sarface energy of the specimen one another. Therefore, we used the specimens prepared anew by casting on teflon seats, and measured surface energy of the air-contacted side.

① Contact Angle

Contact angle measurement was carried out by a Goniometer-type instrument after 5 min from the surface-washing with ethanol. The value of contact angle was given as the average of ten points.

② Wettability

Wettability was estimated according to JIS K6768. Solvents which have different surface tensions were spread over the whole surface of a solid. When the surface was uniformaly wetting with a solvent, the value of surface tension of the solvent was regarded as wettability index of the solid. The present method using the index makes it possible to estimate the whole surface, although the contact angle method is made in limited area of the solid.

Solvents having different surface tensions (30 -56 dyn/cm) were prepared by mixing formamide with ethylcellosolve (ethyleneglycol monoethylether) at the various ratios. n -Paraffins were used as the solvent having

surface tension less than 30 dyn/cm (see Table 2). After surface of the specimen was washed with ethanol, wettability was measured 3 times for each specimen.

4) Abrasion Index

Several methods estimating abrasion index of a solid, such as NBS method, have been known. NBS's abrasion test according to ASTM D1630 was adopted in the present work. Abrasion index is expressed in percentage by comparing the abraded rate of the sample with that of natural rubber (NR : standard).

$$\text{Abrasion Index } (\%) = (R_1/R_2) \times 100$$

R$_1$: the average number of rotations abrading a sample by 2.5mm

R$_2$: that abrading NR by 2.5mm

5) Mechanical Properties

These were related to hardness (Hs), tensile strength (T_B), elongation at break (E_B), tear strength ($T_R(B)$), and compression set (CS), which were measured according to JIS K6301.

6) Aging Test

After heating the specimens in an oven at 70° C or dipping them into hot water (70°C) for the prescribed time (2, 2.5, 5, 10, and 15 day) the mechanical properties described above were estimated again and the changes of them between before and after heating or aging were investigated.

Measurements

The friction factor and tackiness was measured on a SHINTO KAGAKU surface analysing instrument Model HEIDON-14. The 3 -Dimension roughness was recorded on a KOSAKA LABORATORY 3-D roughness measuring instrument Model SE-30K. The contact angle measurement was made on a KYOWA KAGAKU goniometer-type contact angle measuring instrument Model CA-P. The tensile strength, the tear strength, and the elongation at break were measured on a SHIMAD-
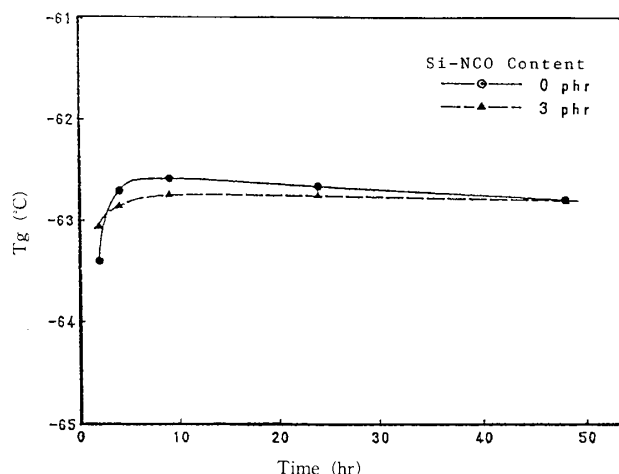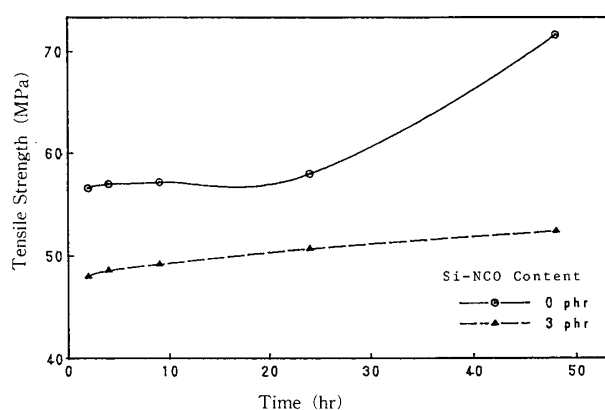
Fig. 5 Effect of postcure time on Tg

Fig. 6 Relationship between postcure time and tensile strength

Fig. 7 Relationship between postcure time and elongation at break

Fig. 8 Relationship between postcure time and tear strength

Fig. 9 Relationship between postcure time and hardness

ZU autograph Model DSS-2000. The abrasion was estimated by using an NBS abrasion testing machine according to ASTM D1630.

RESULTS AND DISCUSSION

Postcure Conditions

It has been known that the cured state was closely related to the glass transition temperature (Tg)[2]. Based on this fact, we investigated the effect of postcure time on Tg value (Fig. 5). In addition, the relationships between postcure time and tensile strength (Fig. 6), elongation at break (Fig. 7), tear strength (Fig. 8), hardness (Fig. 9), and compression set (Fig. 10) were examined.

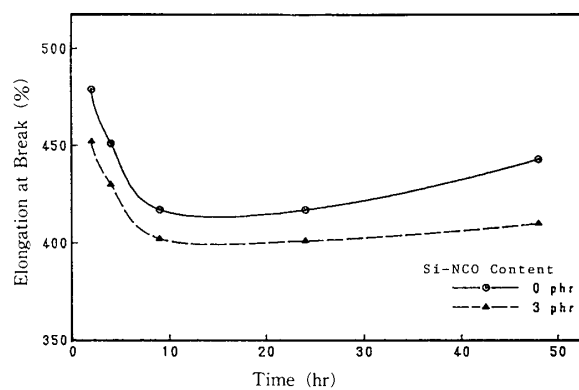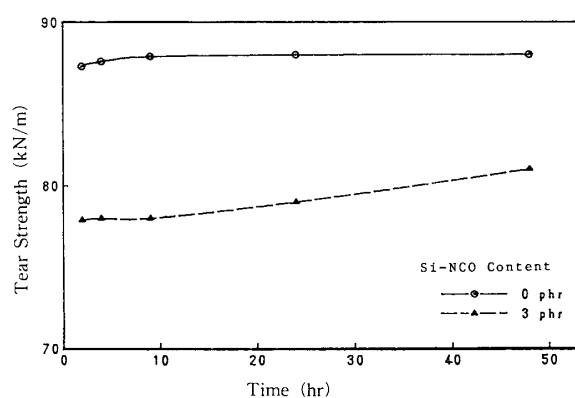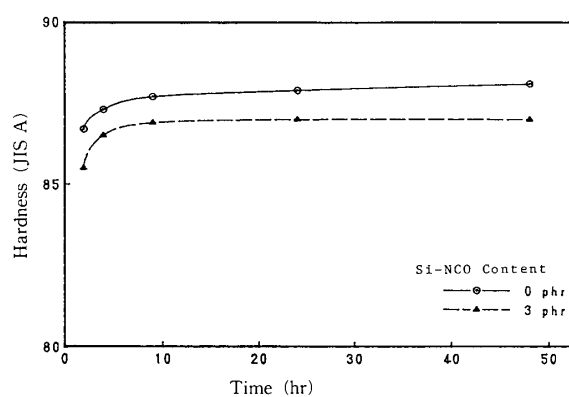As can be seen from Fig. 5, the influence of an amount of Si-NCO on Tg is negligibly small. The result that the Tg values became constant after 24 hr revealed that postcure process was completed at this time. Figs. 6-10 show that the other values become also steady after 24 hr.
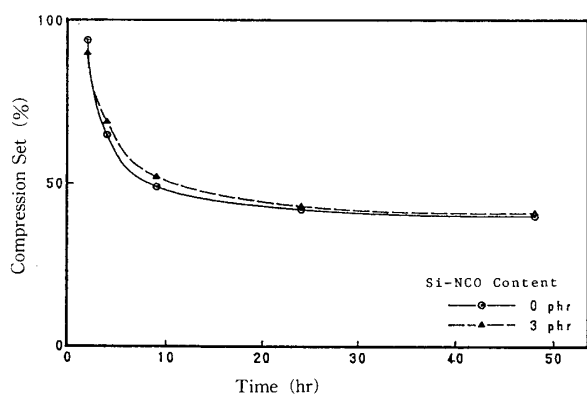
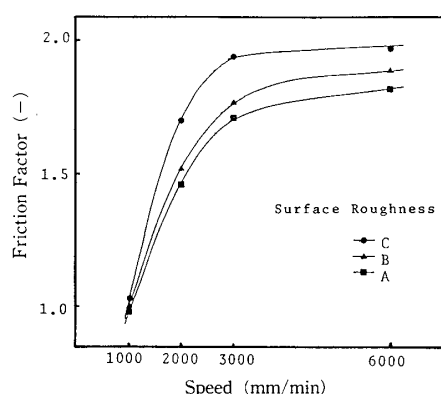**Fig. 10**　Relationship between postcure time and
compression set

Fig. 11　Effect of roughness on static friction factor
(rate dependence, 300gf)

Fig. 12　Effect of roughness on static friction factor
(weight dependence, 3000mm/min)

Fig. 13　Relationship between Si-NCO content and
friction factor

Influence of Surface Roughness on Friction Factor

It is well known that the grinded state of surface affects the friction factor in a striking manner. The same grinding condition does not necessarily give the same surface roughness owing to the differences in Si-NCO content. We studied the influence of grinding condition on surface roughness by using a 3-dimension surface analyzer. Samples were prepared by grinding No. 1 specimen (Table 1) coasely (A), moderately (B), finely (C). Relationships between static friction factor and the grinding conditions are shown in Fig. 11 and 12. It is clear that the static friction factor decreases with increasing in surface roughness and in slide speed, and with decreasing in loaded weight on the sample.
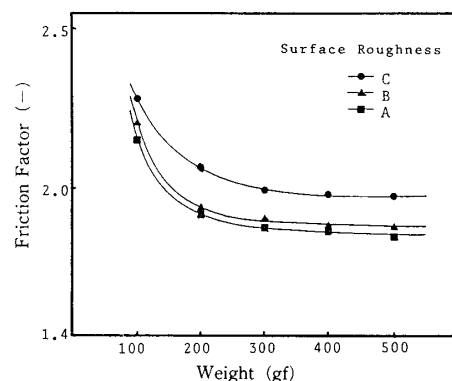
Friction Factor

Dependence of an amount of Si-NCO on the friction factor is shown in Fig. 13. The static friction factor decreased with an increase in Si-NCO content. It is probably due to a decrease in the surface tackiness by adding of Si-NCO. The kinetic friction factor of the sample without Si-NCO was smaller than those of the samples containing 3 and 6 phr of Si-NCO. It can be considered that paper powder tacked on the surface of the sample without Si-NCO made the kinetic friction factor decrease.

Tackiness

Change of tackiness by adding Si-NCO is shown in Fig. 14. The tackiness is reduced in a striking manner by adding Si-NCO.
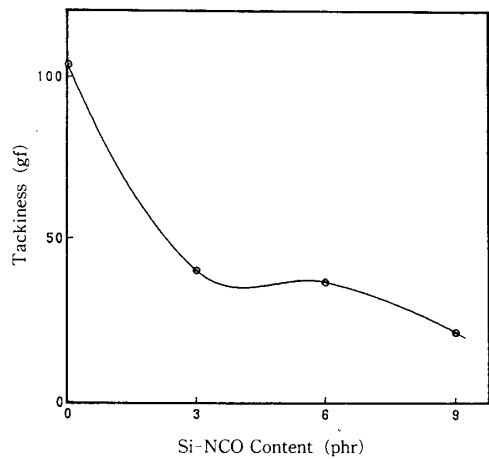
Fig. 14 Relationship between Si-NCO content and tackiness

Table 3 Contact Angle with Water

Si-NCO Content (phr)	Contact Angle (degree)
0	80.6°±2.0
3	103.6°±1.2
6	104.2°±1.7
9	104.4°±2.3
Paper	107.8°±1.3

Table 4 Wettability

Surface Energy (dyn/cm)		Si-NCO content (phr)			
		0	3	6	9
18.42	⟨n-Hexane⟩	○	○	○	○
20.31	⟨n-Heptane⟩	○	○	○	○
21.76	⟨n-Octane⟩	○	○	○	○
22.92	⟨n-Nonane⟩	○	○	○	△
23.92	⟨n-Decane⟩	○	△	×	×
24.51	⟨n-Dodecane⟩	○	×	×	×
30		○	×	×	×
31		○	×	×	×
32		○	×	×	×
33		○	×	×	×
34		△	×	×	×
35		×	×	×	×
36		×	×	×	×
37		×	×	×	×

○ : Wetting
△ : Partly Wetting
× : Not Wetting

Table 5 NBS Abrasion Resistance Index

Si-NCO Content (phr)	0	3	6	9
NBS abrasion resistance index (%)	175	956	740	587

Table 6 Mechanical Properties

Si-NCO Content (phr)	0	3	6	9
Hardness (JIS A)	87.9	87.0	86.5	85.7
Tensile Strength (MPa)	58.0	50.0	34.5	26.0
Elongation at Break (%)	437	420	398	381
Tear Strength (kN/m)	85.7	72.4	71.4	70.4
Compression Set (%)	28	30	30	31

Contact Angle with Water

Contact angles of the specimens and paper with water are listed in Table 3. Contact angle was remarkably enhanced with an increase in Si-NCO content. The addition of Si-NCO made surface energy go down.

Wettability

Wettability of the specimens used in this work is listed in Table 4. The surface energy which was estimated by the wettability index was decreased by adding Si-NCO, and was increased with an increase in Si-NCO content. This result is the same as that obtained by the contact angle method.

Abrasion

Abrasion resistance indexes of the specimens evaluated according to NBS are listed in Table 5. The addition of Si-NCO led to a marked enhancement of the index. In the cases of the Si-NCO containing specimens, slide or slip between the specimen and the abrading instrument might occur due to a decrease in the static friction factor. However, the index decreased with an increase in Si-NCO content partly because mechanical properties, particularly, tensile strength and tear strength were damaged by the addition of Si-NCO.

Mechanical Properties

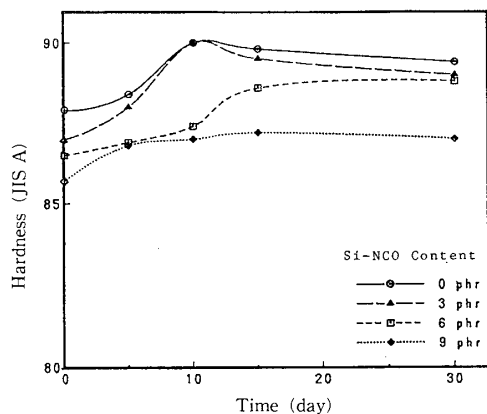As can be seen from Table 6, the addition of Si-NCO deteriorated the mechanical prop-
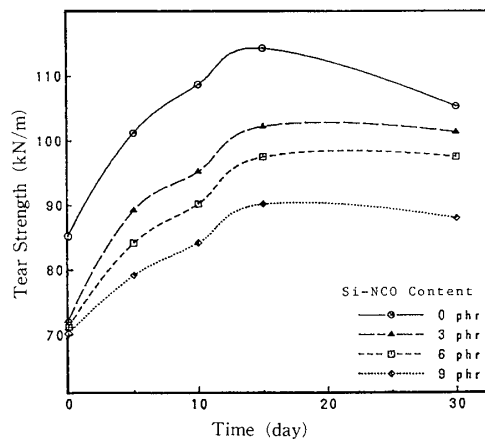
Fig. 15   Influence of heating on hardness
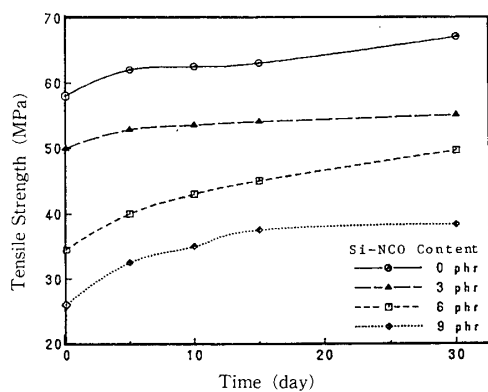

Fig. 16   Influence of heating on tesile strength
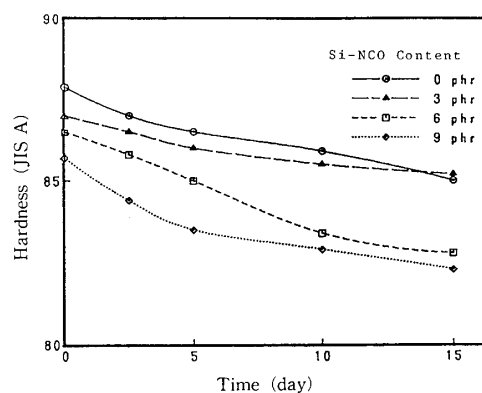

Fig. 17   Influence of heating on elongation at break

Fig. 18   Influence of heating on tear strength

Fig. 19   Effect of hot-water aging on hardness
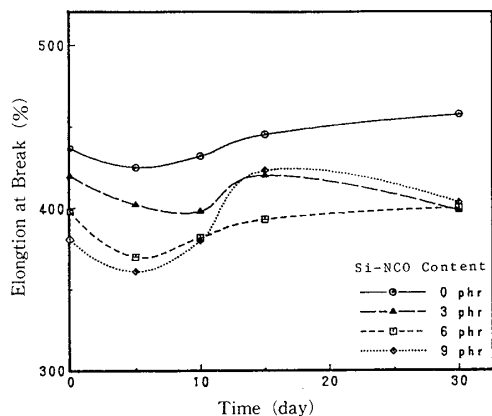
heating in a oven at 70°C are shown in Figs. 15 -18. The prolonged heating time augmented hardness and tensile strength to some extent, and enhanced tear strength remarkably. Changes of the properties by dipping into hot water (at 70°C) were also investigated, and are shown in Figs. 19-22. An increase in dipping time diminished hardness and tensile strength considerably, and tear strength to a certain degree, although it enlarged elongation at break.

CONCLUSION

Surface modification of a conventional polyurethane elastomer (PUE) was examined by reacting the prepolymer with 3,3'-dichloro -4,4'-diaminodiphenylmethane (MOCA) and silicone (Si-NCO), one side of which was ter-

erties, and particularly the lowering of tensile strength in the cases of 6 and 9 phr was distinguished. An increase in Si-NCO content was liable to decrease hardness, elongation at break, and tear strength.

Aging Effects on Mechanical Properties
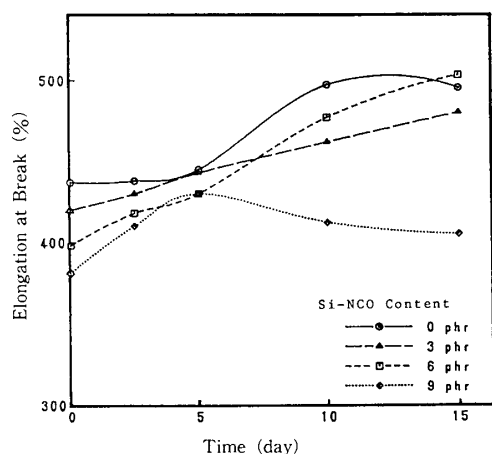
Changes of the mechanical properties by

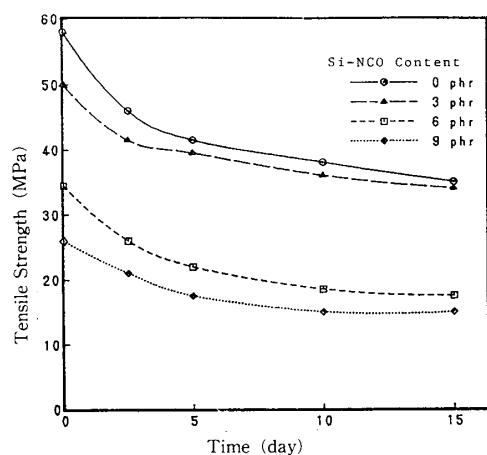Fig. 20 Effect of hot-water aging on tensile strength

Fig. 21 Effect of hot-water aging on elongation at break

minated with isocyanate group. The tackiness and the surface energy of the modified PUE
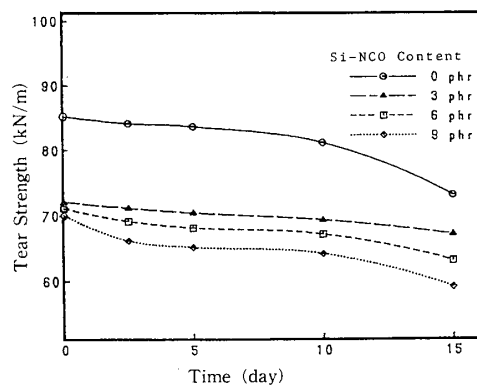

Fig. 22 Effect of hot-water aging on tear strength

decreased with an increase in Si-NCO content. The abrasion resistance was enhanced in a noticeable manner by adding Si-NCO. However, the addition of Si-NCO more than a certain amount diminished the resistance owing to a deterioration of mechanical properties. The optimum modification of PUE surface was achieved by adding around 3phr of Si-NCO.

REFERENCES

1) H. Kurose, *Meiji Rubber and Chemical Company Technical Report*, 11, No. 1, 45 (1989).

2) L. Little, *"Rapid and Reliable State of Cure Determinations of Elastomeric Seals"*, SAE Technical Paper Series, 880308 (1988).