

Hygroscopic-Aging Behavior of Pure and NaCl-filled Polyurethane Rubber

WEN-YEN CHIU,* DING-KUO DING and CHAO-CHENG CHEN

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, Republic of China

SYNOPSIS

The aging phenomenon of highly filled rubber in humid environment was investigated. HTPBD was reacted with MDI and mixed with salt at the same time. The mixture was then hot-pressed for 24 h at 90°C to prepare the sample. The changes in mechanical properties and glass transition temperature of the sample were followed when they were subjected to different humidity at 30°C for 7 days. Furthermore, the effects of humidity on chemical structures were studied with IR.

The results showed that unfilled rubber suffered no changes in mechanical properties after 7 days in environment of high humidity (RH 97). However, for NaCl-Filled rubber, its strength decreased because of a loss of stiffness of salt after salt deliquesced. The glass transition temperature of unfilled rubber seems not to be affected by various humid conditions, but the T_g of filled rubber decreased slightly. From SEM pictures, we observed that interior holes were left after salt deliquesced. This was the main cause for the reduction in mechanical properties of filled rubber.

INTRODUCTION

Because of the widespread outdoor use of polymer-based composites, the weather resistance of composites has become a major concern in related studies. In our previous work,¹ the thermal aging of filled PU at higher temperatures was investigated. In this work, we chose humidity as the chief weather variable. The aging effects of humidity, on properties such as T_g and tensile strength, of pure and filled PU will be discussed.

Hygroscopic Aging

When the specimen is in environments of differing moisture content, moisture may diffuse into the specimen and hygroscopic aging occurs. Martin and Gardner² investigated the effects of humidity on the aging of plastics. At room temperature and high humidity, the properties were not greatly affected in the short term unless the glass transition temper-

ature was lowered by absorbed water. They argued, furthermore, that the experiment of accelerated aging in a dry environment could not simulate the aging under high humidity, and that the amount of absorbed water was not a satisfactory index for plastics used in an environment of high humidity for long term.

Gazit³ studied the moisture absorption rates of epoxy resin and its Graphite-reinforced composite. He found that the rates could be described with Fick's second law.

Dynamic Viscoelasticity

The behavior of dynamic viscoelasticity depends on temperature and frequency. The behavior is related to molecular structure and movement, to T_g , to crystal structure relaxation process, and to the morphology of fillers and matrix. Therefore, dynamic viscoelasticity is a useful tool for studying the mixing status in blends or composites.

In the curve of $\tan \delta$ vs. temperature, a transition peak can be found near T_g . The location of T_g varies with frequency. If frequency is increased 10 \times , T_g increases from about 3 to 7°C. Furthermore, the

* To whom correspondence should be addressed.

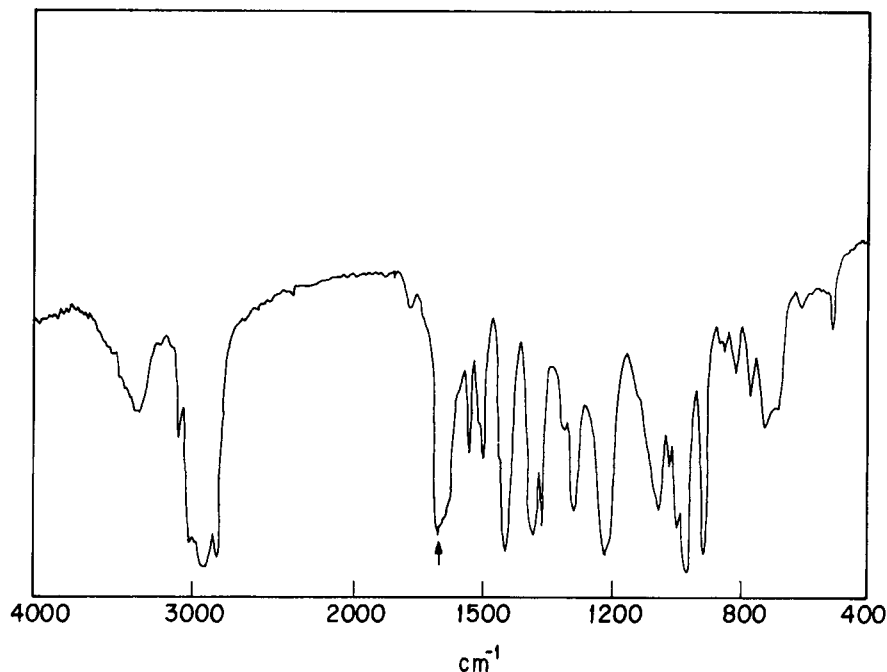


Figure 1 IR spectrum of aged PU at RH 70 for 7 days.

motion of side groups or small segments may result in peaks for secondary transition. If peaks appear at a temperature higher than T_g , the transition occurs in the crystalline phase. Otherwise, the transition occurs in amorphous phase. In addition to grafting, inner defects or fillers may cause similar transition peaks.

The interaction between polymer matrix and filler will lower the mobility of polymer segments; thus

T_g is raised. Even if there is no interaction between the two phases, the mobility and flexibility of segments near filler are still restricted simply by the existence of filler. But the effects of the existence of filler on segments are varied. Therefore, we may obtain a broad transition region. Furthermore, at the same concentration of filler, T_g is affected by the size of the particle, since it is related to the interaction area between two phases.

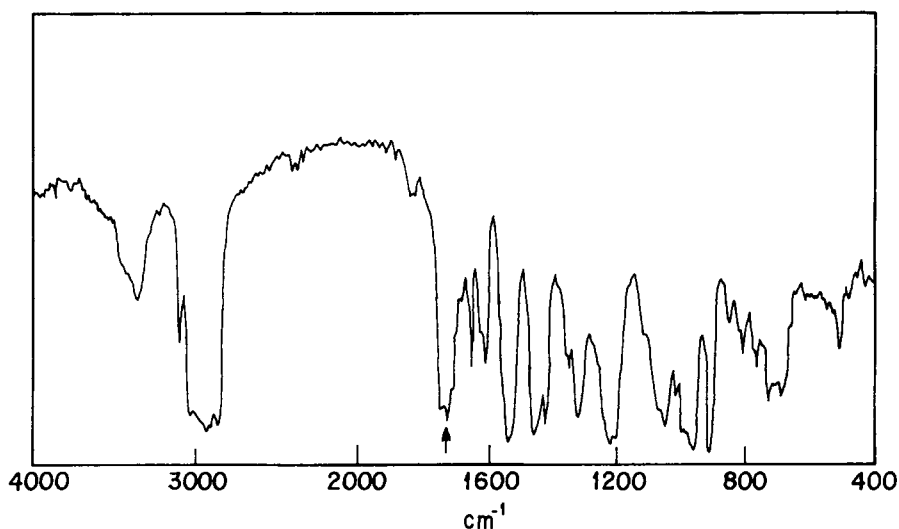


Figure 2 IR spectrum of aged Salt-PU composite at RH 97 for 1 day.

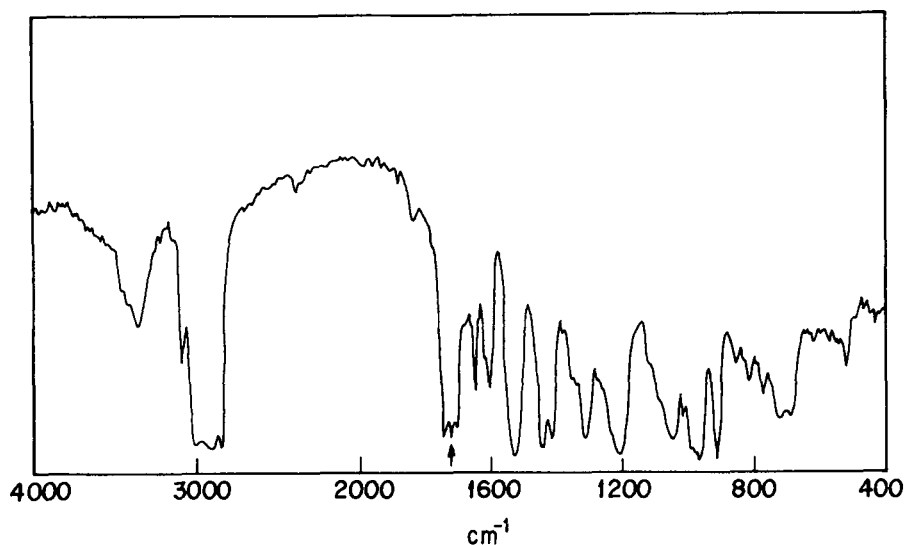


Figure 3 IR spectrum of aged Salt-PU composite at RH 97 for 7 days.

However, Kumins and Coleman⁴ found that the effect of the addition of TiO_2 into PVAc (polyvinylacetate) was just the reverse. In such cases, fillers act as plasticizers, which have the effect of lubrication and promoting the relative movement between molecules. This phenomenon may be explained in another way in that the existence of filler

decreases the interaction force between molecules or a third explanation may be that the free volume of polymer molecules is increased by filler.

EXPERIMENTAL

Polymerization of PU Rubber and Preparation of Composites

First, a given weight of NaCl and HTPBD (hydroxy-terminated polybutadiene, $\text{MW} \approx 2800$) is mixed together and a drop of catalyst, Di-*n*-butyltin Dilu-

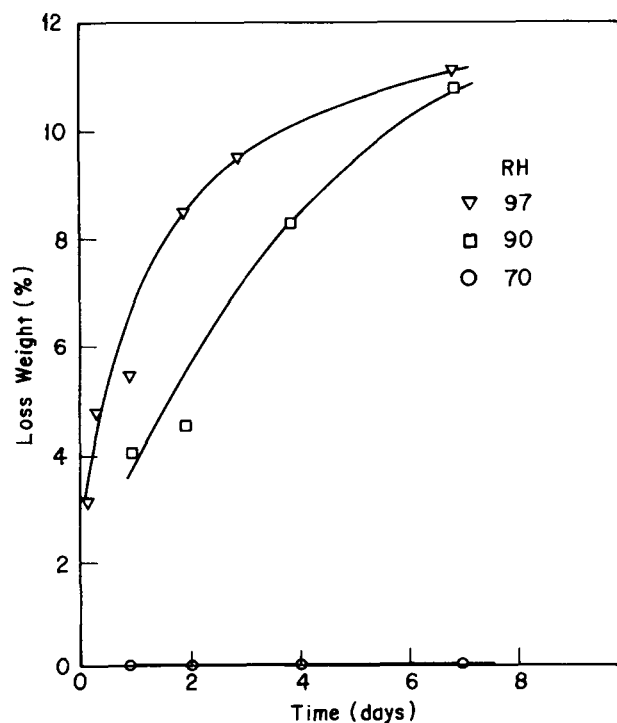


Figure 4 Weight loss of aged composite vs. aging time.

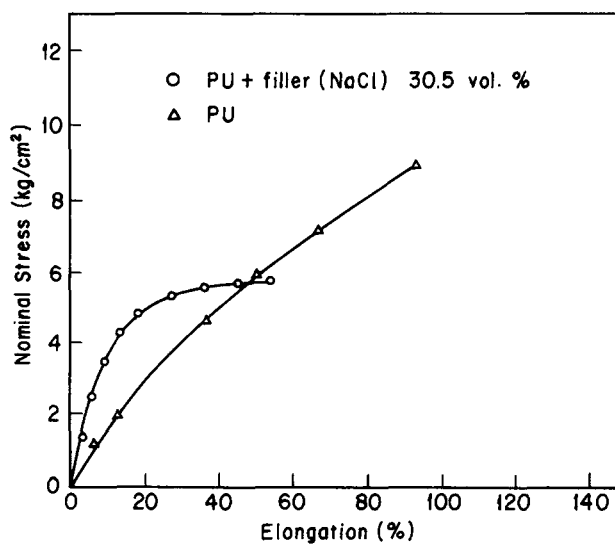


Figure 5 Stress-strain curve of PU and filled PU composite before aging.

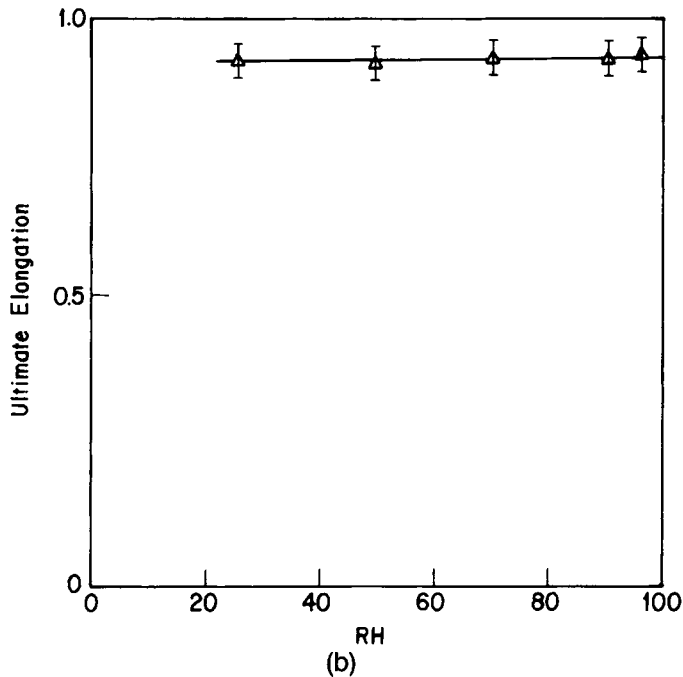
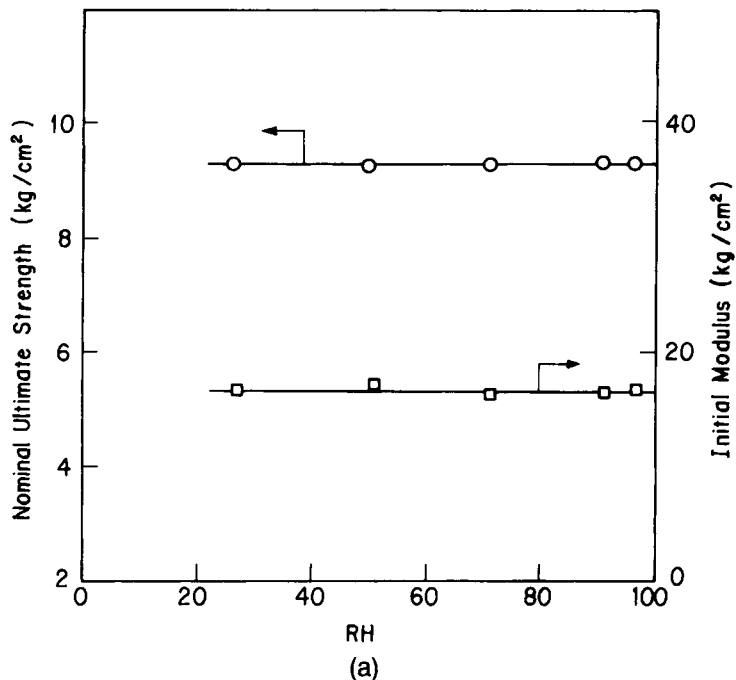


Figure 6 Mechanical properties of aged PU (7 days) vs. relative humidity.

rate, is added. Then the mixture is stirred in a suction system for 1 h. Next, calculated weight of MDI is added so that the ratio of NCO/OH ratio is controlled at 1.024. Meanwhile, stirrer and suction are on for another 2 min.

The sample is then hot-pressed under pressure of 150 Kg/cm² for 24 h. The mold is then taken out

and stored in the desiccator to let it cool to room temperature.

The procedure of preparing the specimen of pure PU rubber is the same as that of its composite except that NaCl is absent. Furthermore, it should be noted that NaCl, HTPBD, and MDI should be pretreated before use as stated in our previous paper.

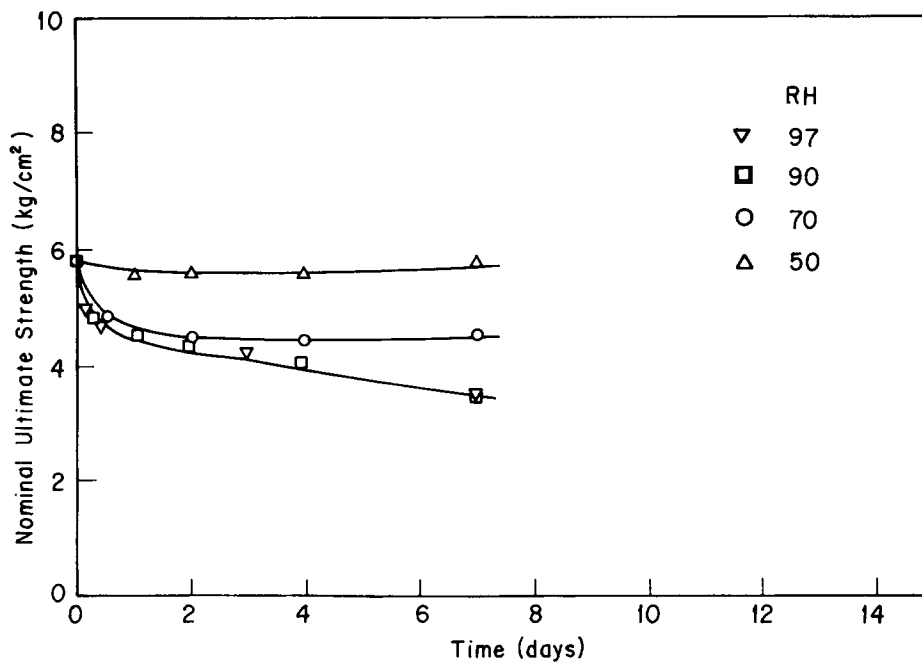


Figure 7 Ultimate strength of filled rubber vs. aging time.

Tests of Physical Properties

Specimens are first stored in desiccator for one week, then placed in environment of constant temperature (30°C) and constant humidity (RH = 50, 70, 90,

97). Specimens are taken out at constant time intervals for tests. The steps in the process follow:

1. Specimens used in test of dynamic viscoelasticity are 0.2 cm wide, 2 cm long and 0.05 cm

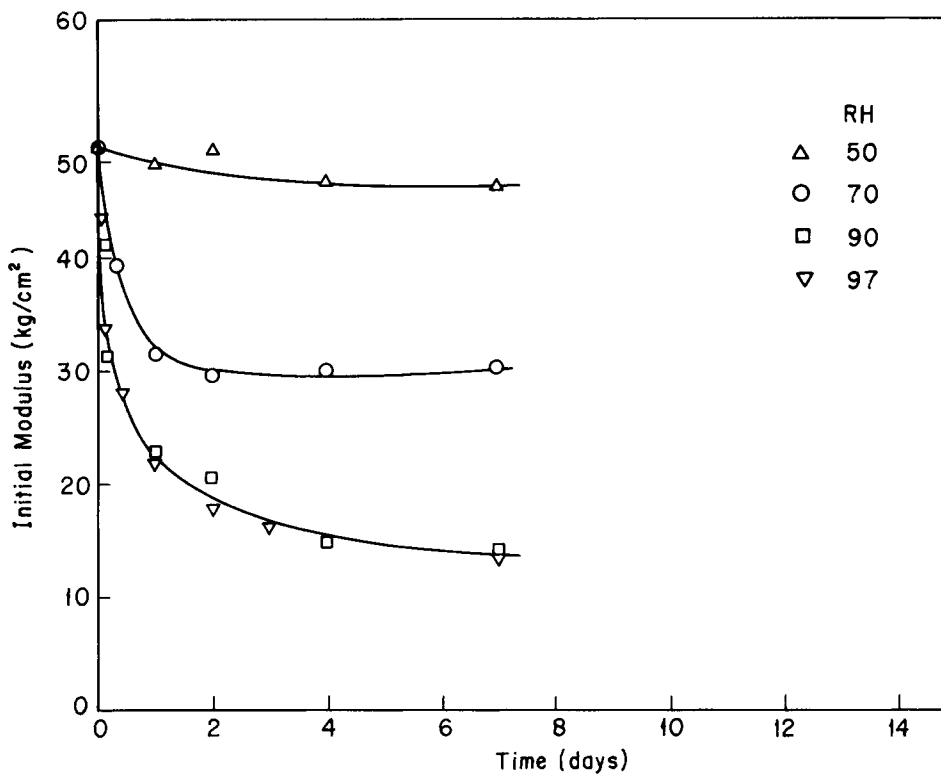


Figure 8 Initial modulus of filled rubber vs. aging time.

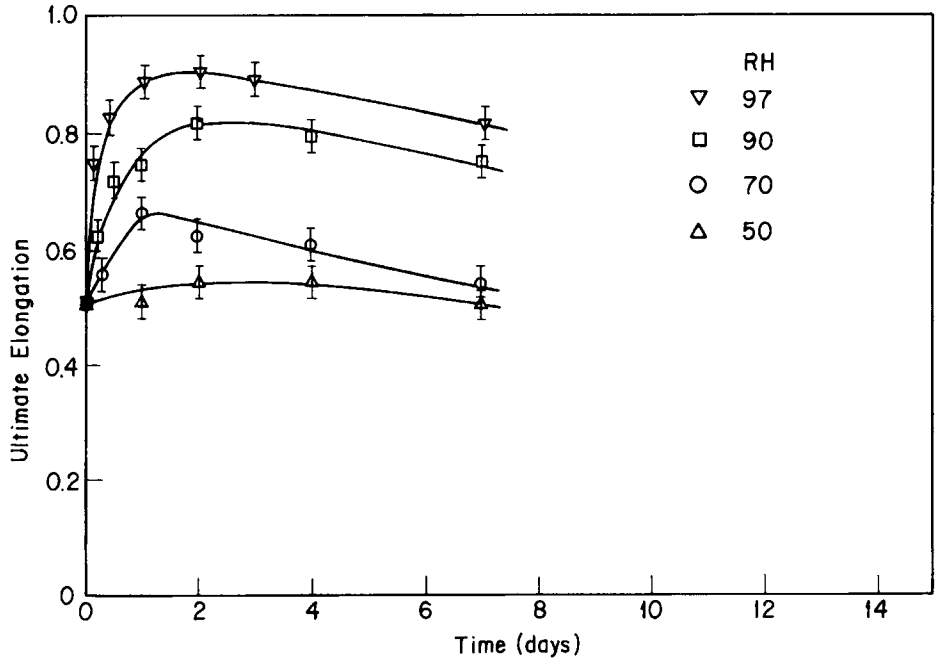


Figure 9 Elongation of filled rubber vs. aging time.

in thickness. The experimental conditions are 110 Hz of frequency, with a -150°C – 150°C and 1.5 – $2^{\circ}\text{C}/\text{min}$ heating rate.

2. The scanning range of IR spectrum is 4000 to 400 cm^{-1} .

3. The fracture surface of specimen is coated with a thin layer of conducting material (e.g., gold, silver, or carbon) for observation under SEM. The microscope is mainly used to study the shape of salt and surface of specimen.

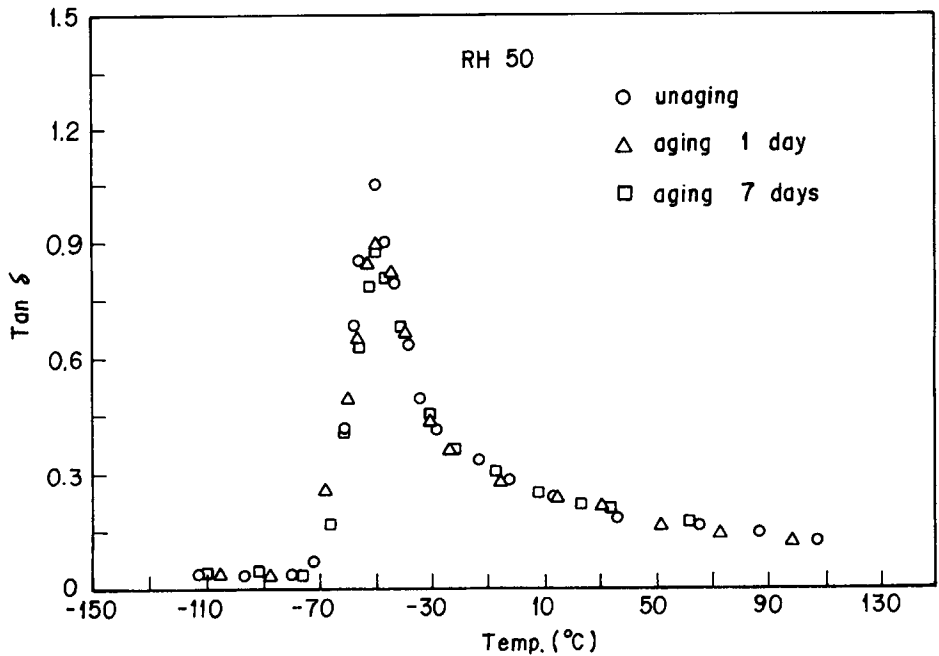


Figure 10 Loss tangent of filled rubber vs. temperature aging at RH 50.

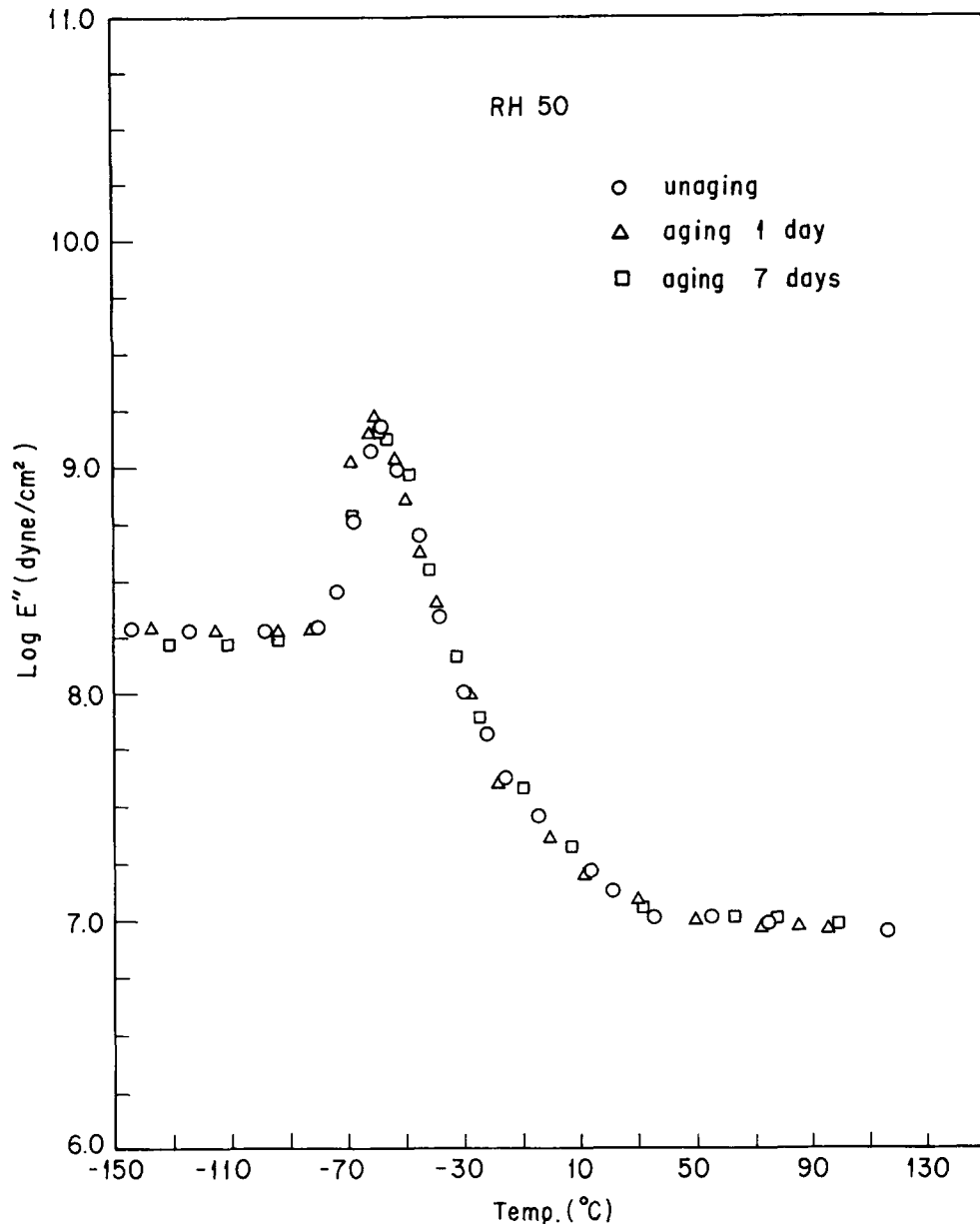


Figure 11 Loss modulus of filled rubber vs. temperature aging at RH 50.

4. The weight of the aged specimen taken from the oven with controlled temperature and humidity is recorded at constant time intervals.

RESULTS AND DISCUSSION

Analysis of IR

Films of aged pure PU rubber and PU-salt composite of 80–100 μm in thickness are used in IR analysis.

In IR spectra for pure rubber, aged at 30°C in environments of RH 70 and RH 97 respectively for one week, we find no changes in spectrum (see Fig. 1), which shows the rubber's good resistance to high humidity (at least up to one week). The IR spectra for PU-salt composite aged in environment of high humidity for one and seven days are also examined. The spectrum for composites, subject to relative humidity of RH 70, does not change after 7 days of aging. However, aging in environment of RH 97 does affect the chemical structure as seen in Figures 2

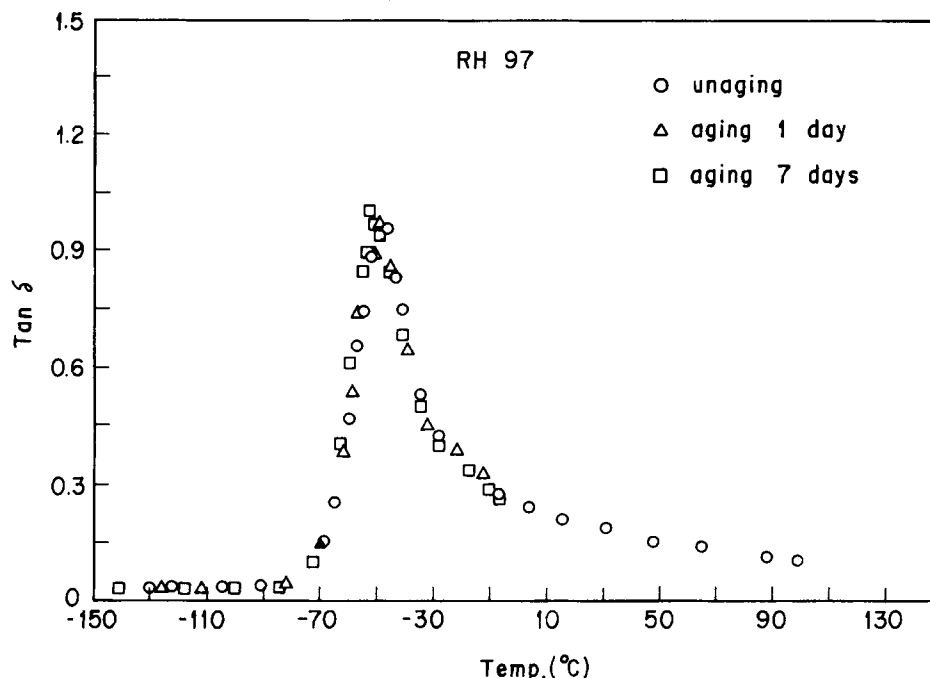


Figure 12 Loss tangent of filled rubber vs. temperature aging at RH 97.

and 3. The absorption peaks near 1720 and 1700 cm^{-1} become stronger. This strengthening may be due to the deliquescence of salt and the hydrogen bond formed by moisture with the $-\text{C}=\text{O}$ group. Consequently, the absorption peak for the $-\text{C}=\text{O}$ vibration (mainly 1740 cm^{-1}) restricted by the hydrogen bond partly moves to the lower frequency (1720 and 1700 cm^{-1}).

Weight Analysis

Figure 4 shows weight loss as a function of time of aging. Under the condition of humidity of RH 97, the weight loss is as much as 11% after 7 days. The source of weight loss is the salt which deliquesces and then moves out of the composite. Therefore, for filled rubber, the control of humidity is very important.

Table I Glass Transition Temperature (T_g) of Filled PU Aged for 7 Days at 30°C and at Various Humidity (RH)

RH	50	70	97	Unaging
T_g (°C)	-57	-59	-63	-57

Mechanical Properties

Figure 5 is a typical stress-strain curve of our system before aging. The modulus is increased by the filler, but tensile strength and elongation (at break point) are decreased.

Figure 6 shows the mechanical properties of pure rubber as having been aged for 7 days at 30°C and various humidities. In this short period, no great changes in these properties were observed. However, the long term aging properties are yet to be studied.

Figures 7-9 are plots of mechanical properties of filled rubber vs. aging time. We can see that high humidity affects tensile strength and initial modulus greatly. But at low humidity, the changes are not evident. At higher humidity, the ultimate elongation increases first but decreases later. The initial increase occurs because salt loses its stiffness after it deliquesces and the acceleration of breakage of specimen by the effect of stress concentration near the interface, caused by the difference in expansion coefficient between the two phases, is not as great. In the latter stage, however, the ultimate elongation decreases due to the holes created by the salt that has moved out.

Dynamic Viscoelasticity

From the test of dynamic viscoelasticity, the T_g of pure rubber is about -63°C and filled rubber -57°C

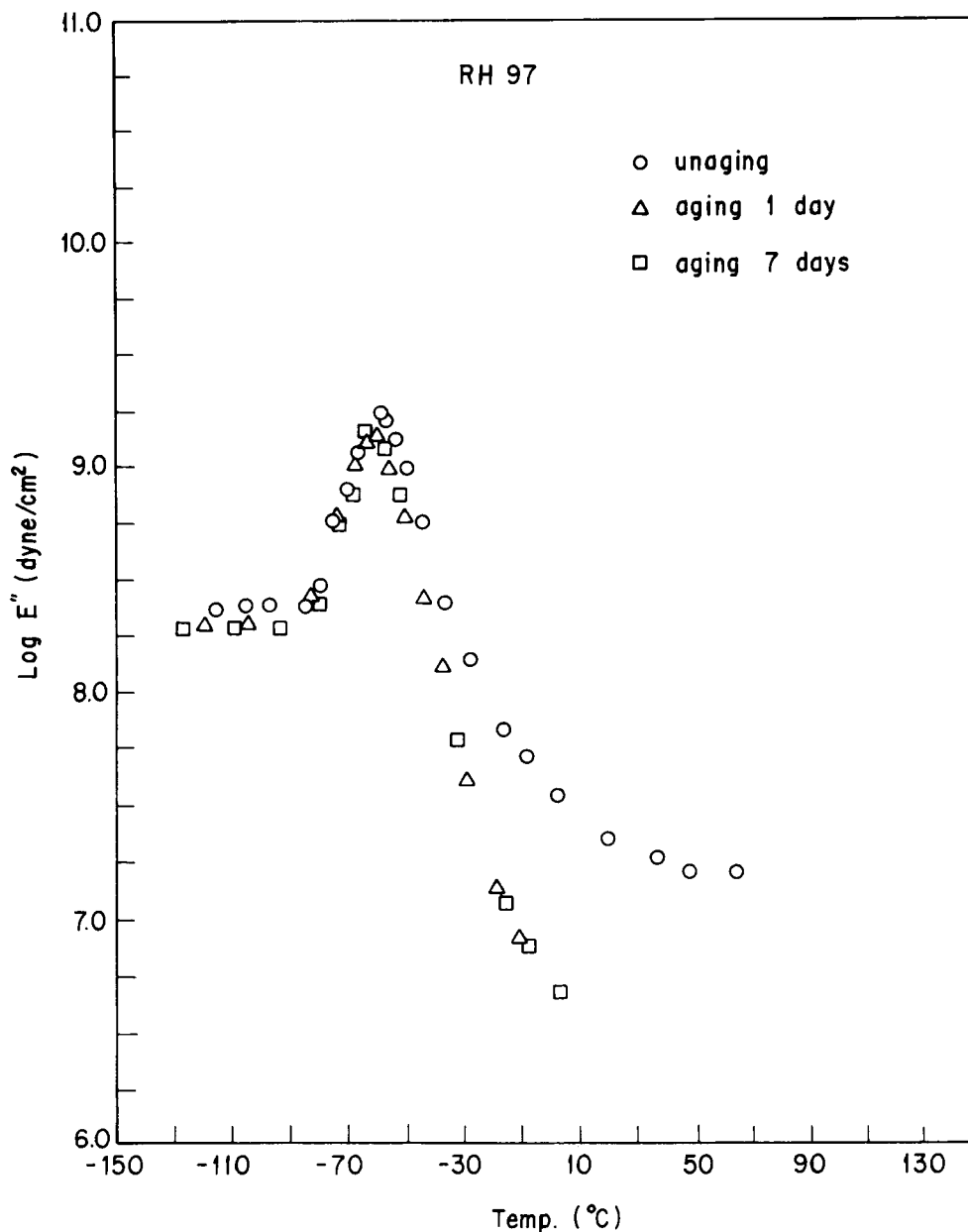


Figure 13 Loss modulus of filled rubber vs. temperature aging at RH 97.

(at 110 Hz). Since the values do not differ much from each other, chemical bonds between salt and PU rubber may not exist.

Figures 10–13 show the relations between dynamic mechanical properties and temperature for filled rubber aged at 30°C, humidity RH 50 and RH 97, for one and seven days. At lower humidity, the loss tangent and loss modulus do not show great change. At high humidity, however, T_g obviously decreases until it reaches the value of the pure rubber.

The T_g of filled rubber, having been aged for 7 days at 30°C at various humidities, are listed in Table I. The decrease in T_g occurs because the restriction on the movement of the molecular segment is released after the deliquescence of salt.

Microscope and SEM Observations

Figure 14 is the microscopic image showing the surface of the filled rubber specimen before and after

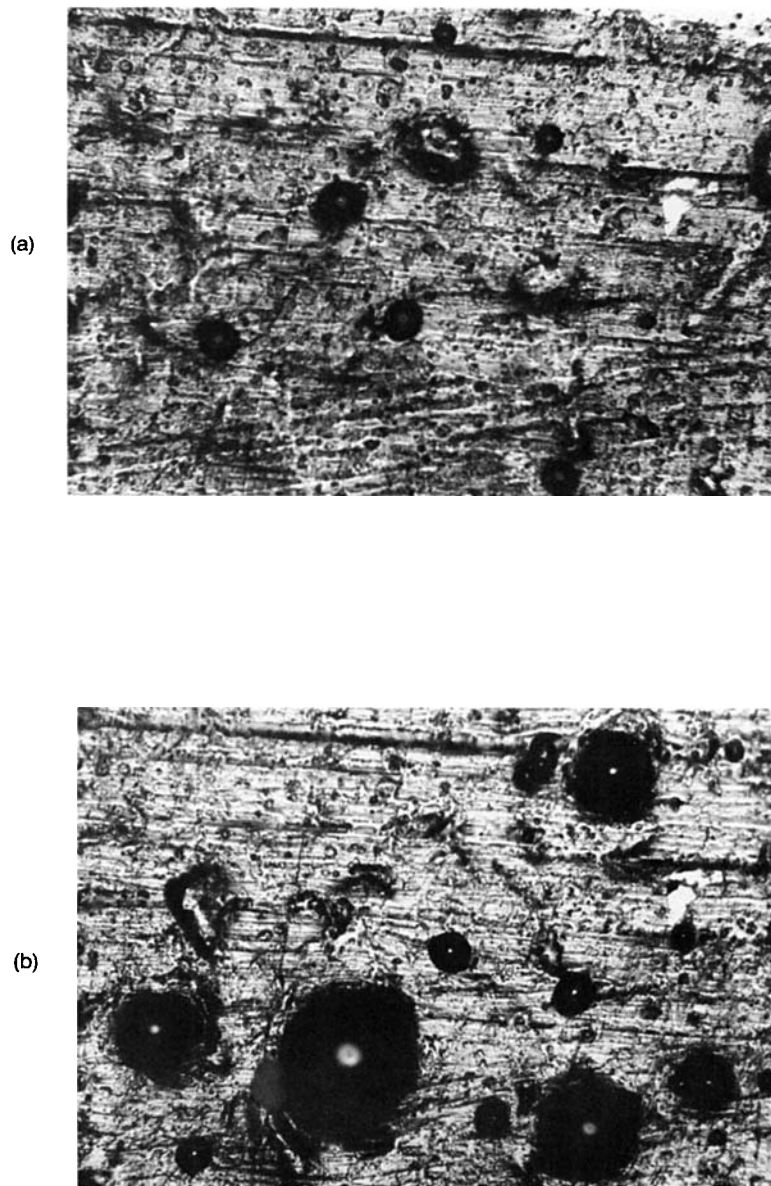
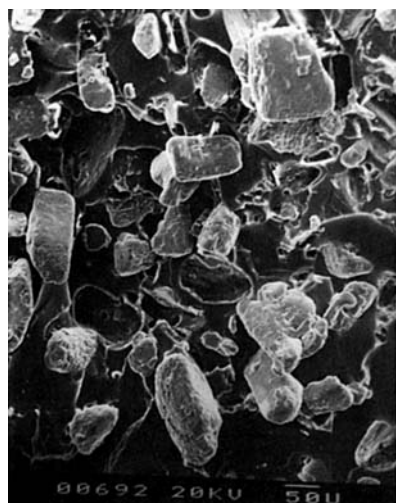


Figure 14 Micrographs of filled PU's surfaces; (a) unaged, (b) aged (2 days at 30°C and RH 97).

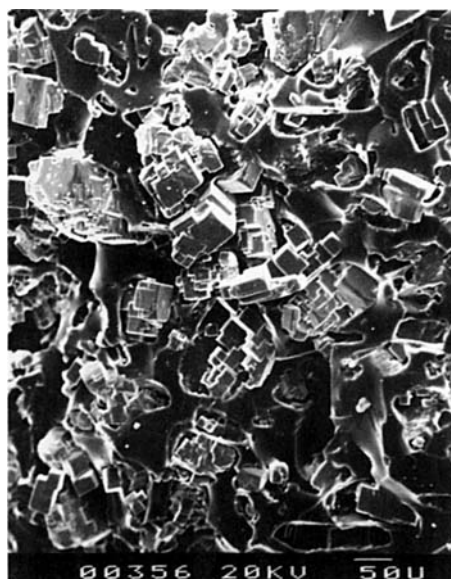
aging; the black spots represent salt. It seems that salt particles aggregate on the surface after they deliquesce and migrate to the surface.

Figure 15 (a) is the SEM picture of the tensile-fracture surface of unaged filled rubber. It can be seen that the distribution of particles is even and that the voids between salt and rubber are not great. Figure 15 (b) is the SEM picture of the central part of the tensile-fracture surface, which specimen was aged at 30°C and RH 97 for two days. Particle shape

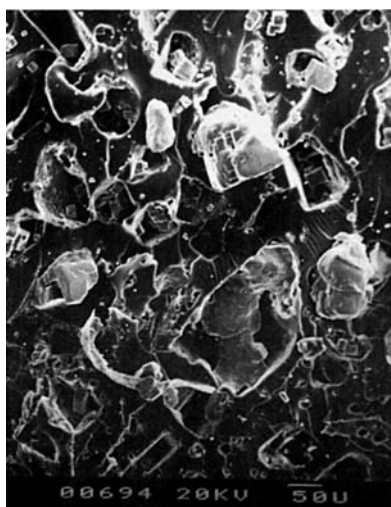
is obviously different than that shown in Figure 15 (a), and the voids are much more evident. Thus we come to the conclusion that after salt deliquesces, recrystallization and redistribution of salt occur, which increases the number of holes. Figure 15 (c) shows the SEM picture taken near the edge of the fracture surface, which specimen was aged at 30°C and RH 97 for seven days. The number of voids has increased and their size is larger due to the movement of salt.



(a)



(b)



(c)

Figure 15 SEM pictures of filled PU; (a) unaged, (b) aged (2 days at 30°C and RH 97), (c) aged (7 days at 30°C and RH 97).

REFERENCES

1. T. M. Don, W. Y. Chiu, and K. H. Hsieh, *J. Appl. Polym. Sci.*, to appear (1991).
2. J. R. Martin and R. J. Gardner, *Polym. Eng. Sci.*, **21**, 557 (1981).
3. S. Gazit, *J. Appl. Polym. Sci.*, **22**, 3547 (1978).
4. G. A. Kumins and J. Coleman, *J. Polym. Sci.*, **1-A**, 527 (1963).

Received November 27, 1990
Accepted February 1, 1991