Effects of Ultraviolet Irradiation on the Static and Dynamic Properties of Neoprene Rubbers

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ABSTRACT: Rubbers deteriorate when they are exposed to ultraviolet irradiation for long periods of time. By conducting a series of hardness measurements and simple tension tests, the static properties of neoprene rubbers before and after exposure to various durations of ultraviolet irradiation were first measured. It is found that the Shore A hardness and tensile modulus of neoprene rubbers after exposure to ultraviolet irradiation are increased but their elongation at break, tensile strength, and energy to break are significantly decreased. On the basis of a complex spring model of a vibration system, the dynamic shear properties of neoprene rubbers before and after exposure to different durations of ultraviolet irradiation were then determined from the experimental results of dynamic transmissibility tests. It is also found that the storage modulus, loss modulus, and loss factor of neoprene rubbers are drastically affected by the duration of ultraviolet irradiation they experienced. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2907–2913, 2008

Key words: degradation; mechanical properties; rubber; shear

INTRODUCTION

With the unique properties of large shear deformation, excellent energy absorption and good thermal aging resistance, neoprene rubbers are frequently used as load-bearing and earthquake-resistant components in many engineering structures such as bridges and buildings. However, the degradation of neoprene rubbers occurs when they are subjected to various environmental attacks[1,2] in service. For example, the deterioration caused by ultraviolet irradiation is normally observed and of concern in rubber component design in Taiwan because of its climate of relatively strong sunlight. Presumably, the deformation resistance and energy absorption of neoprene rubbers might be significantly reduced after exposure to some durations of ultraviolet irradiation. In some cases, the reduction of the static and dynamic properties of neoprene rubbers could cause a catastrophic failure of bridges and buildings; even they are merely subjected to some earthquakes with an intermediate intensity. When both structural integrity and durability are sought, the effects of ultraviolet irradiation on the static and dynamic properties of neoprene rubbers should be exploited in detail and then taken into account in designing rubber components for use as isolators in bridges and buildings.

Photo-degradation is most likely to occur when rubber components are exposed to strong sunlight in many practical applications, resulting in a reduction of their mechanical properties. The mechanisms of photo-oxidation in rubbers have been extensively studied by many researchers.[2–7] It was found that main chain scission, crosslinking process, and oxidation functions dominate the degradation of rubbers after exposure to some durations of ultraviolet irradiation. The main chain scission in rubbers causes first photo-dissociation and then radical formation, leading to the increase of their crosslink density.[2,7–9] On the other hand, it was verified that main chain scission and crosslinking occur simultaneously when rubbers are subjected to ultraviolet irradiation.[10,11] Inevitably, the mechanical properties of rubbers are reduced due to the changes of their molecular structure caused by photo-degradation such as main chain scission and crosslinking. Existing experimental results[12–15] confirmed that rubbers after exposure to some durations of ultraviolet irradiation deteriorate significantly. It was also reported that the tensile modulus of rubbers after exposure to ultraviolet irradiation increases slightly but their elongation at break decreases substantially; however, the tensile strength of rubbers is not appreciably affected even though many crazes appear on their surface etched by ultraviolet rays. Moreover, the antioxidant introduced in rubbers plays an important role in

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reducing their photo-degradation when they are exposed to ultraviolet irradiation in air.

Since the earthquake-resistance of bridges and buildings is primarily influenced by the dynamic response of the rubber isolators used, the effects of ultraviolet irradiation on the dynamic properties of neoprene rubbers are important and should be taken into account in rubber component design. However, the deterioration of dynamic properties of neoprene rubbers caused by ultraviolet irradiation has been paid less attention. The aim of the present work is to investigate the effects of ultraviolet irradiation on the static and dynamic shear properties of neoprene rubbers which are frequently used in Taiwan because of their good thermal-aging resistance. By conducting a series of hardness measurements, simple tension tests and dynamic transmissibility tests, the static and dynamic properties of neoprene rubbers before and after exposure to different durations of ultraviolet irradiation are first determined and then compared with each other. Consequently, the effects of ultraviolet irradiation on the deterioration of static and dynamic properties of neoprene rubbers are evaluated and presented here.

EXPERIMENTAL METHODS

Materials

All samples of neoprene rubbers reinforced with high abrasion furnace (HAF) carbon blacks were manufactured and their ingredients were measured according to Chinese National Standard by the Jih-Sheng Rubber Works, Taiwan. The formulation of the neoprene rubber is listed in Table I and expressed as parts per hundred part of rubber. Two carbon blacks with different sizes and chemical structures, N550 and N774, were added to enhance the mechanical properties of neoprene rubbers while three vulcanizing agents were used for the ease of manufacturing. Resin L-80 was used to provide a better bonding between carbon blacks and neoprene rubber. All samples of neoprene rubbers were cured at 140°C for 10 min and then tested to investigate the effects of ultraviolet irradiation on their static and dynamic properties. For simple tension tests, neoprene rubber sheets with a thickness of 2 mm were first made and then cut into dumb-bell Die C specimens as requested by ASTM D412.[16] At the same time, neoprene rubber cylinders with a diameter of 29 mm and a height of 13 mm were produced and later used in hardness measurements and dynamic transmissibility tests.

TABLE I
Formulation of the Neoprene Rubber Used

Sample ingredients	Quantity (parts per hundred part of rubber)
Neoprene W	100
Activator (WH/P)	2
Vulcanizing agent (NA-22)	2
Vulcanizing agent (DM)	2
Vulcanizing agent (S)	1
Antiozonant (OD)	2
Carbon black (N550)	20
Carbon black (N774)	20
Resin (L-80)	5
Zinc oxide	5

Ultraviolet irradiation

The exposure of neoprene rubber specimens to ultraviolet irradiation was performed in a carbon-arc standard-fade-meter (manufactured by the T-Machine Co., Taiwan) equipped with a carbon-arc lamp as the light source of ultraviolet rays. The testing conditions for the exposure of neoprene rubber specimens to ultraviolet irradiation were referred to ASTM G153[17] and ASTM D750[18]; the arc voltage of the carbon-arc lamp was in the range of 125–145 V while its arc current was 15–17 A. All neoprene rubber specimens were suspended on a specimen drum with a diameter of 530 mm around the carbon-arc lamp. Hence, ultraviolet rays with a spectral distribution of a primary wavelength of around 380 nm were generated by the carbon-arc lamp and the irradiation intensity on each neoprene rubber specimen was found to be $\sim$ 370 W/m^2. During the exposure of neoprene rubber specimens to ultraviolet irradiation, the specimen drum was rotated at a constant speed of 3 rpm around the carbon-arc lamp. As a result, the intensity and duration of ultraviolet irradiation on each neoprene rubber specimen in the carbon-arc standard-fade-meter were the same. At the same time, the temperature of black-panel under exposure was controlled to be around (52 ± 3)°C to prevent from the deterioration of neoprene rubber specimens caused by thermal aging. Before neoprene rubber specimens were mechanically tested to determine their static and dynamic shear properties at the end of ultraviolet irradiation, they were cooled for 16 h down to room temperature. Accordingly, the static and dynamic shear properties of neoprene rubber specimens after exposure to different durations of ultraviolet irradiation ranging from 100 to 1200 h were measured and then compared with each other.

Static tests

Simple tension tests of dumb-bell Die C neoprene rubber specimens were performed in an Instron 4302 tester under a crosshead speed of 500 mm/min according to ASTM D412.[16] The resulting stress–strain curves of neoprene rubber specimens before

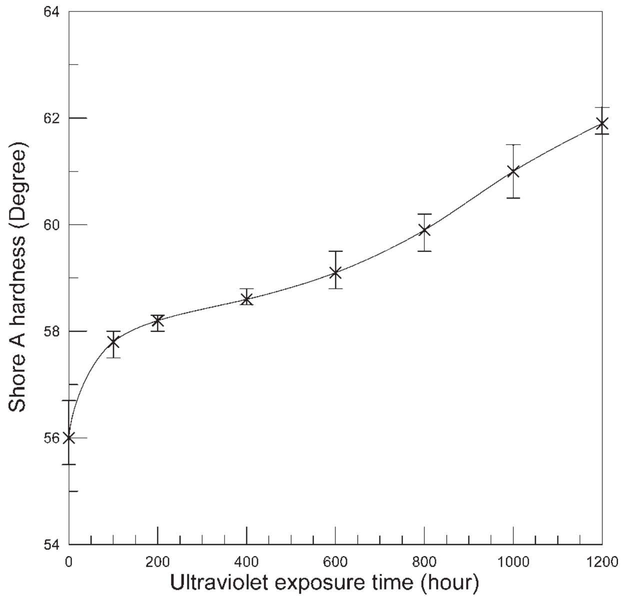

Figure 1 The variation of Shore A hardnesses of neoprene rubber specimens before and after exposure to 100, 200, 400, 600, 800, 1000, and 1200 h ultraviolet irradiation.

and after exposure to different durations of ultraviolet irradiation were first recorded. From the stress–strain curves, the tensile modulus at 25% tensile strain, elongation at break, tensile strength, and energy to break of each neoprene rubber specimen were calculated and then compared with each other. In addition, the average Shore A hardness of three neoprene rubber cylinders was determined by using a Shore A hardness tester to evaluate the degradation of neoprene rubber specimens after exposure to different durations of ultraviolet irradiation. Here, experimental results of three specimens were averaged to give their static properties.

Dynamic transmissibility tests

A series of dynamic transmissibility tests were conducted to investigate the effects of ultraviolet irradiation on the dynamic shear properties of neoprene rubber specimens. Each neoprene rubber specimen was first glued onto the surface of an aluminum plate and then fastened on the shaking table of Modalshop MB-50 vibrator. Next, a mass of 7.59 kg was glued on the upper surface of each neoprene rubber specimen. During a dynamic transmissibility test, two accelerometers were mounted separately on the mass and the shaking table of vibrator to measure their corresponding displacements. From the relative displacements between the mass and the shaking table of vibrator, the dynamic shear properties of neoprene rubber specimens before and after exposure to different durations of ultraviolet irradiation were calculated. Experimental results of five specimens were averaged and then shown in a figure to evaluate the effect of ultraviolet irradiation.

RESULTS AND DISCUSSION

From the experimental results of hardness measurements, simple tension tests and dynamic transmissibility tests, the Shore A hardness, tensile modulus, elongation at break, tensile strength, energy to break, and dynamic shear properties of neoprene rubber specimens before and after exposure to different durations of ultraviolet irradiation can be obtained and then compared with each other.

Static properties

The variations of Shore A hardness and tensile modulus at 25% tensile strain of neoprene rubber specimens before and after exposure to 100, 200, 400, 600, 800, 1000, and 1200 h ultraviolet irradiation are shown in Figures 1 and 2, respectively. From Figures 1 and 2, it is seen that both Shore A hardness and tensile modulus at 25% tensile strain of neoprene rubber specimens increase consistently as the ultraviolet irradiation time is increased. Hence, it can be said that neoprene rubbers are much stiffer and become brittle when exposed to longer duration of ultraviolet irradiation.

On the other hand, the elongation at break, tensile strength, and energy to break of neoprene rubber specimens obtained from simple tension tests are plotted in Figures 3–5 respectively. From Figure 3, it

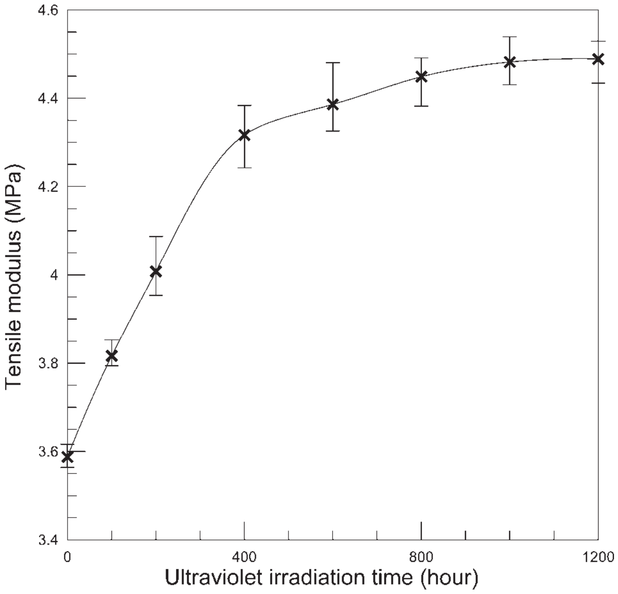

Figure 2 The variation of tensile modulus at 25% tensile strain of neoprene rubber specimens before and after exposure to 100, 200, 400, 600, 800, 1000, and 1200 h ultraviolet irradiation.

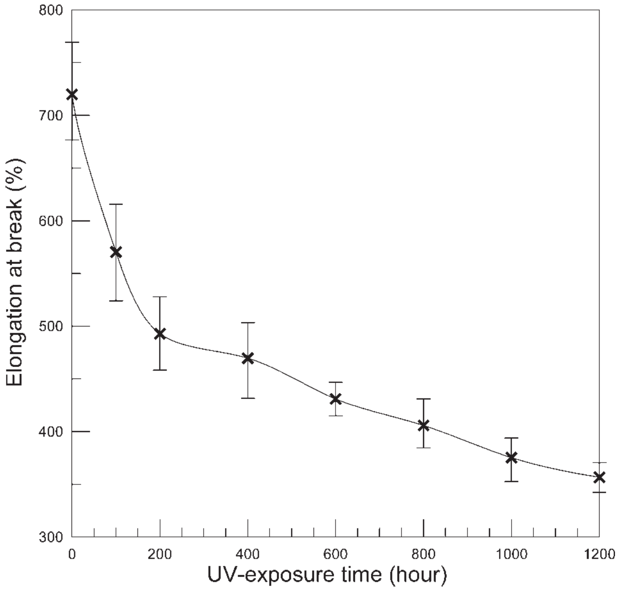

Figure 3 The variation of elongations at break of neoprene rubber specimens before and after exposure to 100, 200, 400, 600, 800, 1000, and 1200 h ultraviolet irradiation.

is clearly seen that the elongation at break of neoprene rubber specimens under tension decreases considerably with increasing ultraviolet irradiation time. Consequently, their tensile strength of Figure 4 and energy to break of Figure 5 are significantly reduced as the ultraviolet irradiation time is increased. The above findings could be attributed to the main chain scission and crosslinking in neoprene rubbers caused by ultraviolet radiation as reported in the existing literature.[2–15] As a result of that, the breakages of backbone chains in neoprene rubbers are more likely and easy to occur. Especially under larger deformation, the molecular structures of neoprene rubbers are dramatically affected, leading to the reductions of elongation at break, tensile strength, and energy to break.

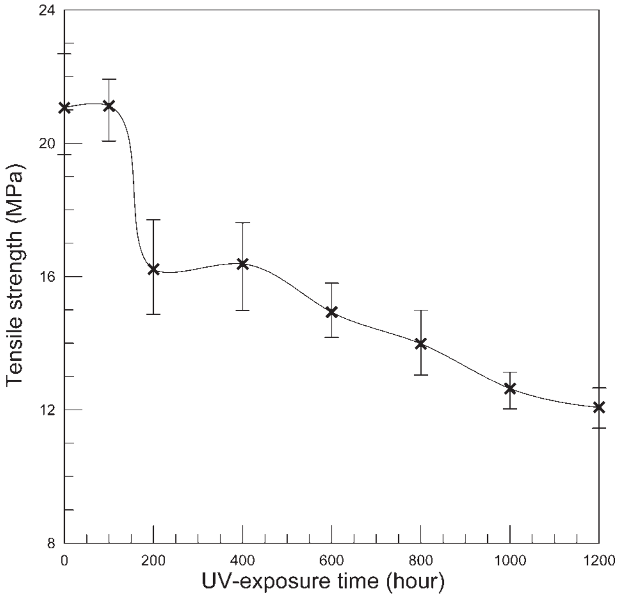

Figure 4 The variation of tensile strengths of neoprene rubber specimens before and after exposure to 100, 200, 400, 600, 800, 1000, and 1200 h ultraviolet irradiation.

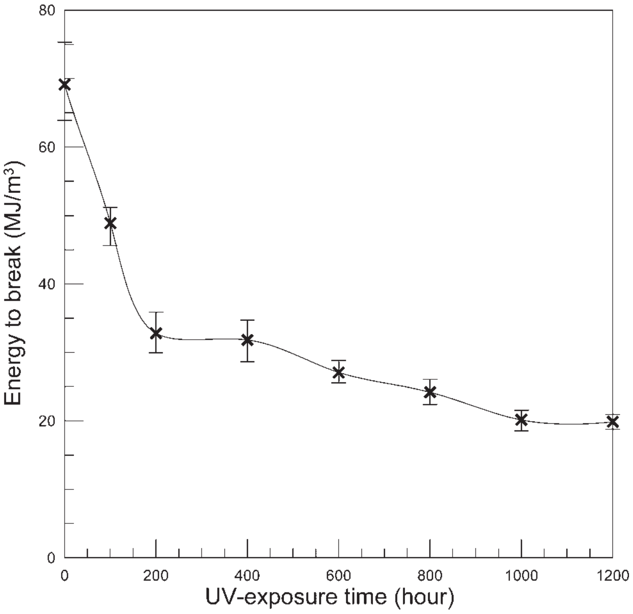

Figure 5 The variation of energies to break of neoprene rubber specimens before and after exposure to 100, 200, 400, 600, 800, 1000, and 1200 h ultraviolet irradiation.

Dynamic properties

To describe the dynamic response of neoprene rubber specimens in dynamic transmissibility tests, a complex spring model is employed and schematically illustrated in Figure 6. In the complex spring model, the equation of motion for describing the dynamic response of any neoprene rubber specimen can be expressed as

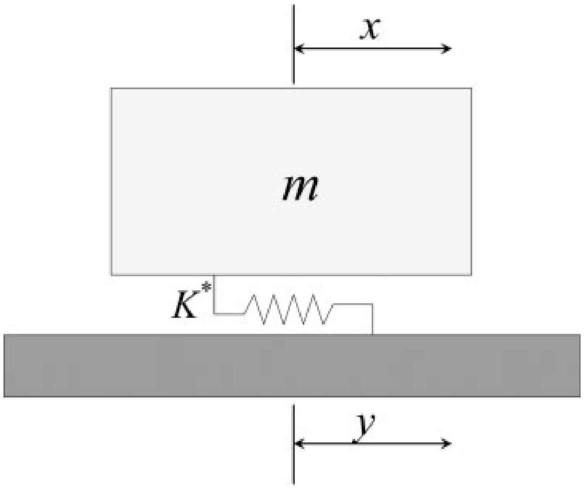

Figure 6 A complex spring model of a vibration system is employed for dynamic transmissibility tests.

$$m\ddot{x} = K^{*}(y - x) \tag{1}$$

wherein, y is the displacement of the shaking table of vibrator and x is the corresponding displacement transmitted from the shaking table through the neoprene rubber specimen to the upper mass m at any instant. The complex stiffness of the neoprene rubber specimen K^* can be written as: $K^* = K' + iK'' = |K^*|e^{i\delta}$. Here, δ is the phase angle between stress and strain, K' is the dynamic stiffness and K'' represents the energy absorption of the neoprene rubber specimen.

By setting $x = Xe^{i\omega t}$ and $y = Ye^{i\omega t}$ and then substituting them into eq. (1), the transmissibility ratio X/Y can be expressed as

$$\frac{X}{Y} = \frac{K' + iK''}{(K' + iK'') - m\omega^2} = \left|\frac{Y}{X}\right| e^{i\Phi} \tag{2}$$

where

$$\tan\Phi = \frac{-K''m\omega^2}{K'^2 - K'm\omega^2 + K''^2} \tag{3}$$

In the above equations, X and Y are the amplitudes of the upper mass and the shaking table of vibrator, respectively; Φ is the phase angle between X and Y with a frequency of ω. Moreover, the loss factor η of the neoprene rubber specimen is found to be

$$\eta = \tan\delta = \frac{K''}{K'} = -\frac{\tan\Phi}{\frac{|X/Y|}{\cos\Phi} - 1} \tag{4}$$

By substituting $\eta = K''/K'$ into eq. (3), the dynamic parameters K'' and K' can be further written as:

$$K'' = \frac{(\tan\Phi - \eta)m\eta\omega^2}{(\eta^2 + 1)\tan\Phi} \tag{5}$$

$$K' = \frac{K''}{\eta} = \frac{(\tan\Phi - \eta)m\omega^2}{(\eta^2 + 1)\tan\Phi} \tag{6}$$

It is noted that both Φ and X/Y can be measured directly from dynamic transmissibility tests. As a result, the dynamic parameters of the neoprene rubber specimen η, K'', and K' can be calculated from experimental results through eqs. (4)–(6). Furthermore, the complex shear modulus G^* including the storage modulus G' and the loss modulus G'' is given

$$G^{*} = G' + iG'' = \frac{h}{A}(K' + iK'') \tag{7}$$

here h and A are the height and cross-sectional area of the neoprene rubber specimen, respectively.

In conducting dynamic transmissibility tests, a pseudo random noise was first input to the vibrator and a random vibration was then imposed on the shaking table. During dynamic transmissibility testing, the accelerations of the upper mass and the shaking table were measured simultaneously by using two accelerometers. The measured accelerations of the upper mass and the shaking table were transformed to a frequency domain using the method of fast Fourier transformation. Thus, the transmissibility ratio X/Y and Φ under a loading frequency of ω were computed from a series of spectrum analyses. Through eqs. (4)–(7), the dynamic properties of the neoprene rubber specimen G', G'', and tan δ were eventually obtained.

The dynamic shear properties G', G'', and tan δ of neoprene rubber specimens before and after exposure to various durations of ultraviolet irradiation were determined from dynamic transmissibility tests under a loading frequency of 10 20, 30, 40, and 50 Hz, respectively. The variations of the storage modulus G', loss modulus G'', and loss factor tan δ of neoprene rubber specimens are shown in Figures 7–9, respectively. From Figure 7, it is seen that the storage modulus G' under each loading frequency increases gradually with increasing ultraviolet irradiation time. At the same time, the loss modulus G'' of neoprene rubber specimens in Figure 8 increases at first and then drops slightly after reaching a maximum when the duration of ultraviolet irradiation is increased. From Figure 9, it is found that the loss factor tan δ of neoprene rubber specimens under a

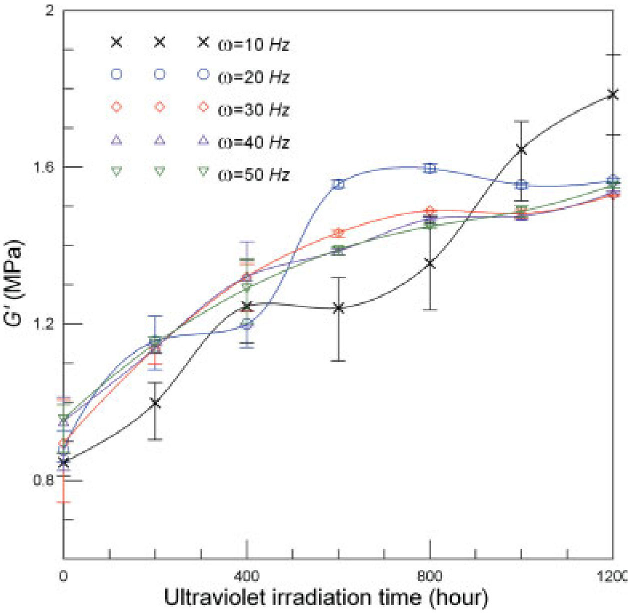

Figure 7 The variation of storage modulus G' with respect to ultraviolet irradiation time for neoprene rubber specimens under a loading frequency of ω = 10, 20, 30, 40, and 50 Hz, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

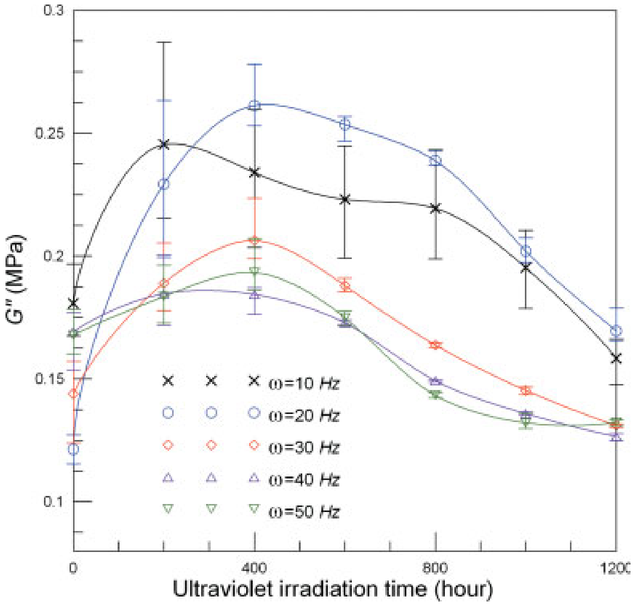

Figure 8 The variation of loss modulus G'' with respect to ultraviolet irradiation time for neoprene rubber specimens under a loading frequency of $\omega = 10$, 20, 30, 40, and 50 Hz, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

lower loading frequency of 10, 20, or 30 Hz increases at the beginning and then decreases after reaching a peak value as the ultraviolet irradiation time is increased. However, the loss factor tan δ of neoprene rubber specimens under a higher loading frequency of 40 or 50 Hz decreases consistently after exposure to different durations of ultraviolet radiation. The reason for the increases of G'' and tan δ at the beginning could be attributed to the formation of some derivatives such as hydroxyl, carbonyl products, and ester groups caused by photo-oxidation.[2,5,6] As a result the viscosity of neoprene rubber specimens becomes higher for the first 200 h. It is also found that some spots formed on the surfaces of neoprene rubber specimens after exposure to ultraviolet irradiation. As the ultraviolet irradiation time is increased, the effect of crosslinking caused by ultraviolet irradiation on the dynamic shear properties of neoprene rubber specimens is more significant and thus they become brittle. Figure 10 shows the experimental results of FTIR spectrometer on neoprene rubber specimens before and after 800 h ultraviolet irradiation. It is seen that the transmittance decreases at 1680–1630 cm^{-1} (C=C stretching) and 1100–1004 cm^{-1} (C—C stretching),[1] which indicates the increase of crosslink density. On the other hand, some derivatives at 1340 cm^{-1} (CH_2 wagging), 1420 cm^{-1}, and 1470 cm^{-1} (CH_2 deformation) are also formed after exposure to 800 h ultraviolet irradiation.

The increase of storage modulus G' of neoprene rubber specimens after 1200 h ultraviolet irradiation can be substantially increased up to 110% when they are under a loading frequency of 10 Hz. On the contrary, the reductions of loss modulus G'' and loss factor tan δ of neoprene rubber specimens after 1200 h ultraviolet irradiation are more than 25% when $\omega = 40$ Hz and 50% when $\omega = 10$ Hz, respectively.

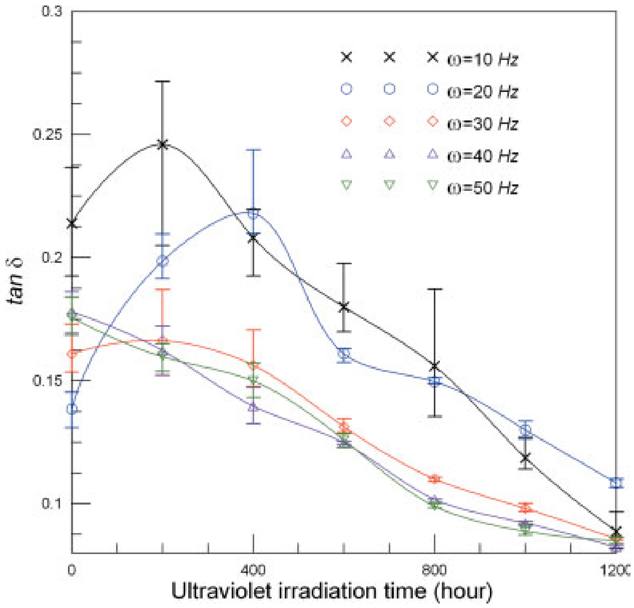

Figure 9 The variation of loss factor tan δ with respect to ultraviolet irradiation time for neoprene rubber specimens under a loading frequency of $\omega = 10$, 20, 30, 40, and 50 Hz, respectively. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

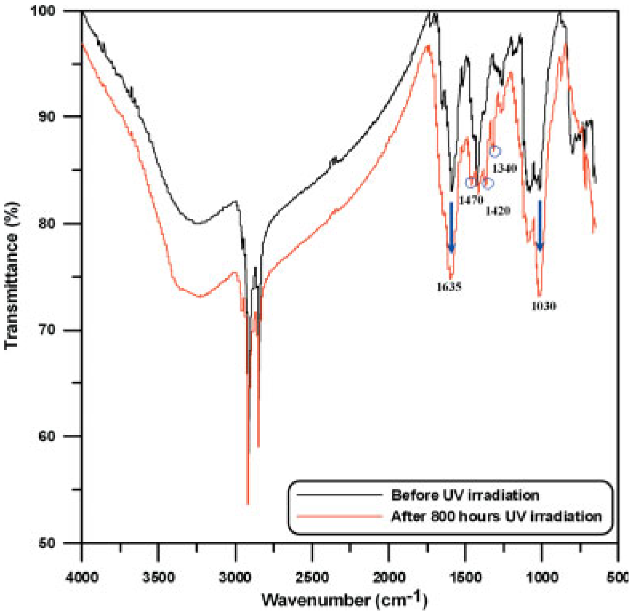

Figure 10 Experimental results of FTIR spectrometer on neoprene rubber specimens before and after 800 h ultraviolet irradiation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

These experimental results of Figures 7–9 indicate that the dynamic shear properties of neoprene rubbers deteriorate gradually from a visco-elastic damping material to an elastic brittle material due to their molecular structures such as crosslink density and main chain scissions caused by ultraviolet irradiation. In other words, the dynamic functions of neoprene rubbers used in many engineering applications such as impact reduction, vibration prevention, and energy absorption are thus reduced significantly after exposure to a longer duration of ultraviolet irradiation. Other than ultraviolet irradiation, temperature cycles and relative humidity are also two important factors in evaluating the deterioration of neoprene rubbers in Taiwan caused by its climate of relatively higher temperature and humidity. It is expected that the degree of crosslinking and resulting mechanical properties of neoprene rubbers are affected by the environmental attacks of temperature cycles and relative humidity. Future research could be directed to a series of experimental tests to investigate the effects of temperature cycles and relative humidity on the static and dynamic shear properties of neoprene rubbers.

CONCLUSIONS

By conducting a series of hardness measurements, simple tension tests and dynamic transmissibility tests, the static and dynamic properties of neoprene rubber specimens before and after exposure to various durations of ultraviolet irradiation are measured and compared with each other. It is found that the Shore A hardness and tensile modulus at 25% tensile strain of neoprene rubber specimens after exposure to ultraviolet irradiation is increased. But, their elongation at break, tensile strength and energy to break are significantly decreased. The above findings could be attributed to the change of molecular structure in neoprene rubber specimens caused by ultraviolet irradiation. At the same time, the dynamic shear properties of neoprene rubber specimens after exposure to various durations of ultraviolet irradiation deteriorate due to the changes in their molecular structure. The storage modulus G' increases but the loss modulus G'' and the loss factor tan δ increases initially and decrease significantly after reaching a maximum as the duration of ultraviolet irradiation is increased. On the basis of the experimental results obtained here, it can be said that neoprene rubbers after exposure to ultraviolet irradiation become harder and are transformed from a damping visco-elastic state to a brittle elastic state. Therefore, the deterioration of static and dynamic properties of neoprene rubbers caused by ultraviolet irradiation cannot be neglected and should be taken into account in designing load-bearing and earthquake-resistant rubber components used in bridges and buildings.

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