Test method

Evaluation of sealability for aged rubber seals by spin–spin relaxation time

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ABSTRACT

This paper presents the applicability of proton spin–spin relaxation time, T_2, for the evaluation of the degradation of sealability for rubber seals. So far, compression set (CS) has been utilized to evaluate the degree of degradation of rubber seals. However, the reliability of CS for thin rubber seals is relatively low. Therefore, in this paper, we investigated the applicability of T_2 as a parameter for the quantitative evaluation of the degradation of sealability instead of CS. The correlations between T_2 and cross-link density, plasticizer concentration and CS for two acrylonitrile butadiene rubber (NBR) samples were discussed. The samples have different compounds and shapes: plate and O-ring. We exposed them to air and nitrogen atmospheres at high temperatures of 60, 80 and 100 °C for up to 33,000 h. The short spin –spin relaxation time, T_2^S, was shortened with aging and correlated well with the cross-link density, plasticizer concentration and CS, regardless of the atmosphere. These results revealed that T_2^S is a useful parameter for the quantitative evaluation of the degradation of sealability.

1. Introduction

Rubber seals such as O-rings are widely used for various equipment and appliances, for example, to avoid liquid or gas leakage. The lifetime of rubber seals often determines the durability of the equipment and appliances. It is important to know the lifetime of rubber seals to ensure stable and safe operation. Therefore, it is essential to evaluate the degree of degradation of the sealability quantitatively. Several factors, such as heat, ultraviolet light, oxygen or ozone, are responsible for the degradation of rubber materials [1]. Among these factors, ultraviolet degradation is not so critical for rubber seals because they are used inside the equipment and appliances. In the absence of a strong oxidant (chloride, ozone, and so on) or an oxidation catalyst such as copper, thermal degradation becomes the main cause to shorten the life time of rubber seals.

The thermal degradation of rubber seals usually proceeds with two significant phenomena. One is the decrease in plasticizer concentration as a result of volatilization and/or bleed-out. The other is the increase/decrease in cross-link density by molecular chain scission and re-bonding [2–4]. Under the combination of such degradation phenomena, some percentage of the permanent deformation against the original deflection remains after aging. The remaining deformation is, in general, called compression set (CS) and is usually employed to quantitatively evaluate the degradation process of the sealing ability [5–8]. Skidmore has reported that the increase in CS corresponds to the decrease in sealing force which directly influences the sealability of rubber seals [9].

The reliability of CS is, however, not so high for a thin or curved piece because the permanent deformation is close to the error range of the measurements [10]. On the other hand, it has already been reported by several authors that the proton spin–spin relaxation time T_2 correlates well with the molecular chain motion of polymer materials [11–18] and is sensitively affected by the plasticizer concentration and cross-link density of elastomers [19–25]. Furthermore, several authors have reported on the correlation between T_2 and polymer degradation or stability. For example, Somers et al. have reported that the T_2 values of the natural rubber samples

aged in the oven at 100 °C for up to 240 h were shortened [26]. Garbarczyk et al. have shown that the T_2 values of the acrylonitrile butadiene rubber (NBR) samples aged at 125 °C for up to 440 h decreased with aging [27]. Herberg et al. have reported that the T_2 values of damaged sections in a rubber pad with permanent deformation differed from those of undamaged sections [28]. Beck et al. measured T_2 of ethylene propylene diene rubber (EPDM) samples and found that EPDM having high mobile chains showed much higher CS values after aging for 70 h at 150 °C in air rather than that having less mobile chains [10]. Similarly, Viol et al. have also described that the higher chain mobility determined from T_2 for non-aged polyacrylate rubber samples caused higher CS values after aging for 24 h at 150 °C in air [25]. These observations suggest that the mobile chains are easily compressed during aging and such deformation remains permanently.

As mentioned above, many studies show that T_2 can be a very useful parameter for the evaluation of the rubber materials. However, the correlations between T_2 and plasticizer concentration, cross-link density and CS during very long-term have not yet been investigated. Moreover, the applicability of T_2 for the quantitative evaluation of the gradually decreased sealability of rubber materials with thermal aging has never been discussed before.

The purpose of this study is to prove the applicability of T_2 as a parameter for the quantitative evaluation of the gradually decreased sealability for rubber materials with thermal aging. We examined two different NBR samples exposed to high temperature in air and nitrogen (N_2) at constant deformation for up to 33,000 h (1375 days). The correlations among T_2, plasticizer concentration, cross-link density and CS during very long-term with aging were investigated.

2. Experimental

2.1. Test pieces

Two NBR samples (test pieces 1 and 2: TP1 and TP2) were used for evaluation. The acrylonitrile content of TP1 and TP2 were 37% and 46%, respectively. TP1 was obtained from a cylindrical rubber tube by cutting and its dimensions were 19 mm in axial length, 39 mm in circumferential length and 6.5 mm in thickness (Fig. S1-a). TP2 was an O-ring with an inner diameter of 41.7 ± 0.39 mm and a cord diameter of 3.5 ± 0.1 mm. Table 1 presents details of the samples.

2.2. Accelerated thermal aging test at constant deformation

Test pieces and spacers were sandwiched between steel plates of 10 mm in thickness. The steel plates were fastened by bolts and nuts (Fig. S1-b). The thickness of the spacers used for TP1 and TP2 were 5.85 mm and 2.80 mm, respectively. These thicknesses produced compression ratios of 10% for TP1 and 20% for TP2. All test

Table 1
Property for non-aged test pieces.

Test piece	TP1	TP2
Shape	Plate	O-ring
Hardness (equivalent to DuroA)	59.0	70.3
Base polymer	NBR	NBR
Acrylonitrile content	37%	46%
Main reinforcement filler	Carbon black	Carbon black
Cross-linking agent	Sulfur	Sulfur
Acetone soluble fraction	17%	14%
Toluene swelling ratio	215%	164%

pieces were then exposed to air in thermostatic chambers at 60, 80 and 100 °C (Fig. S1-c). Additionally, compressed TP2 test pieces were also exposed to N_2 in thermostatic chambers. The oxygen concentration in the thermostatic N_2 chambers was carefully controlled to be 0.5% or less. Several thermal aging periods were set in the range from 300 to 12,800 h for air and between 500 and 33,000 h for N_2. Details of the aging periods are listed in Table 2.

2.3. Measurements

2.3.1. Compression set: CS
Compression set (CS) was defined by the following equation:

$$CS[\%] = \frac{t_0 - t_1}{t_0 - t_S} \times 100 \qquad (1)$$

where t_0 is the original thickness, t_1 is the thickness after thermal aging and t_s is the thickness of each spacer. The t_0 value of each TP1 test piece was carefully measured with accuracy of ±0.02 mm because the TP1 test pieces had a thickness distribution of about 0.5 mm. For the TP2 test pieces, the value of t_0 was constant at 3.5 mm within the error of ±0.1 mm. After finishing the thermal aging process, the compressive load was immediately released by removal of the steel plates. The value of t_1 was measured after 30 min.

2.3.2. Spin–spin relaxation time: T_2
For measuring T_2 of TP1, we used one-third of the test piece plates after cutting the peripheral edge of the TP1 specimens to avoid the effect of heterogeneous oxidation on T_2 measurements (the heterogeneous oxidation is mentioned in Section 3.1). On the other hand, the effect of heterogeneous oxidation for TP2 should be less than for TP1 because the cord diameter of TP2 is much smaller than the dimensions of TP1. Considering this, we used one-third of TP2 without cutting off the surface for T_2 measurements. T_2 measurements were performed on a JEOL JNM-MU25 at a proton (^1H) frequency of 25 MHz and 20 °C. The solid echo pulse sequence was used to obtain T_2 with 90° pulse length of 2 μs and recycle delay times of 4 s. T_2 was expressed as the decay of the magnetization at time t, $M(t)$, with the two exponential functions expressed in the following equation:

$$M(t) = M(0) \cdot x_S \exp\left(-\frac{t}{T_2^S}\right) + M(0) \cdot x_L \exp\left(-\frac{t}{T_2^L}\right) \qquad (2)$$

where, $M(0)$ is the magnetization at time 0. The first term represents the fast relaxation component (short T_2: T_2^S). T_2^S is reflected by the low molecular mobility of cross-linked and entangled networks. T_2^L presented in the second term has a relatively large value as compared to T_2^S. This component contains the oligomer and the plasticizer with high molecular mobility. The values of x_S and x_L are ^1H molar fractions for T_2^S and T_2^L, respectively.

2.3.3. Toluene swelling ratio
The values of the swelling ratio of the TP1 and TP2 specimens were determined by the following equation:

$$S[\%] = \frac{m_1^S}{m_2^S} \times 100 \qquad (3)$$

where m_1^S and m_2^S are the wet and dry weight of each specimen after immersion in toluene, respectively. The immersion in toluene was performed at 37 ± 1 °C for 72 h. Drying was achieved in a vacuum oven at 80 °C for 19 h. We used one-third of the specimens