

Effects of Carbon Blacks on Viscoelastic Behavior of Natural Rubber Melt

Shinyoung Kaang[†], Soo Shin, Chang Nam Choi and Changwoon Nah*

Faculty of Applied Chemistry, College of Engineering, Chonnam National University, Kwangju 500-757, Korea

*Department of Polymer Science and Technology, College of Engineering

Chonbuk National University, Chonju, Chonbuk 506-756, Korea

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천연고무 용융체의 점탄성적 거동에 대한 카본블랙의 영향

강 신 영[†] · 신 수 · 최 창 남 · 나 창 운*

전남대학교 응용화학부, *전북대학교 고분자공학과

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ABSTRACT : Effect of carbon blacks (CBs) on the stress relaxation and the elastic recovery of uncrosslinked natural rubber (NR) was examined. It was found that if the type of CB is characterized by smaller size and higher structure, the stress relaxation is more delayed and the elastic recovery becomes more active. These results are attributed to the degree of bound rubber, i.e., the interaction between NR and CB.

요약 : 미가교 천연고무의 응력완화와 탄성복원에 대한 카본블랙의 영향을 조사하였다. 카본블랙의 형태가 보다 작고 높은 구조의 특징을 가질 때 응력완화는 더 지연되었고 탄성복원은 더 활발하였다. 이 결과는 결합고무의 크기, 즉 천연고무와 카본블랙의 상호작용의 크기에 기인하였다.

Keywords : stress relaxation, elastic recovery, bound rubber, natural rubber melt.

I. Introduction

Rubber processing features such as die swell, green strength, tack strength, and shrinkage are governed by the elastic behavior of the rubber melt. Treloar¹ carried out pioneer work in the

area of elastic recovery and plastic flow in raw rubber, in which he indicated the role of mechanical entanglements in the delayed elasticity of the raw rubber. Djiauw and Gent² examined the effects of time, temperature, and the amount of extension on the elasticity of green rubbers. Kaang and coworkers^{3,4} recently investigated the effects of molecular weight on the stress relaxation and

[†]대표저자(e-mail : kaang@chonnam.ac.kr)

the elastic recovery of natural rubber melt. Kilian and Kaang⁵ again described these experimental results on the stress relaxation and elastic recovery of the entanglement melts with the aid of the aggregate model.

Reinforcement of rubber by fillers and its mechanisms have been the topics of numerous researches. In general, however, attention has been given on the physical properties of filled vulcanizates rather than those of uncrosslinked rubber melts. Even though significant works has been focused to elucidate the reinforcement mechanisms in filled rubber melts,⁶⁻¹⁰ further work is necessary to the filled rubber melt to find out how elastic responses of the melt would be affected by fillers. In this study, therefore, we examined the effects of various carbon blacks on the stress relaxation and the elastic recovery of uncrosslinked natural rubber.

II. Experimental

Natural rubber (NR, Standard Malaysian Rubber-Constant Viscosity 60) was used and only carbon black (CB) was mixed in. No other additives were used in these experiments. The CBs selected to examine the effects of their sizes and structures were N103, N326, N358, N550, and N990. Nitrogen adsorption and DBP absorption number for the selected CBs are shown in Table 1. NR was mixed with 50phr of CB in the Banbury internal mixer (Farrel, Model No. 82, USA) at 120°C for 4.5min, and the milling using a laboratory two-roll milling machine (Brabender, PM-3000, USA) at 70°C for 5min followed.

Stress relaxation and elastic recovery were mea-

Table 1. Nitrogen Adsorption and DBP Absorption Numbers of Various Carbon Blacks Used

ASTM Designation	Nitrogen adsorption* (m/g ²)	DBP absorption number* (target values) (cm ³ /100g)
N103 ⁺	142	130
N326	84	72
N358	87	150
N550	42	121
N990	9	43

*ASTM D1765-91

⁺Technical report from Korea Steel Petrochemical Co. Ltd., Korea

sured using green NR sheets with a thickness of 2mm, which were prepared by pressing the green rubber between Mylar films using a hot press (Dake, model # 44-251, USA) at 100°C for 2 hrs. After molding, the rubber sheet was cooled at room temperature, and allowed to fully relax at least 48 hrs before beginning the tests. Rubber strips 10mm wide and 120mm long were cut from the sheets using a razor blade. The Mylar films were removed from both sides of the strip just before testing.

After annealing about 20min at the test temperature, the clamped strip, one end of which was gripped to the load cell of a universal tensile tester (Shimadzu, AGS-500D, Japan), was suddenly extended to 100% elongation and the change in the tensile force at constant elongation was automatically recorded versus time. The test temperatures employed were between -15°C and 100°C in a thermostatic chamber. For recovery experiments, the rubber strip was fixed between two clamps with a 100% elongation in a temperature-controlled water bath. This strip was quickly released by cutting through it just above the bottom clamp after a cer-

tain holding time, t_s , called the 'relaxation time', which was prolonged from 2min to 600min. The test temperature employed was 30°C.

III. Results and Discussion

1. Bound rubber

The determination of the amount of bound rubber is one of the ways to evaluate the interaction between rubber and CB. The bound rubber could be determined for all CBs except N990. The mixed compounds were extracted with toluene using a glass filter cage at room temperature for 7days. Toluene was renewed after 3 days. The samples were dried for 24 hrs in air at room temperature, and then for another 24 hrs in a vacuum oven at 105°C. The bound rubber was obtained using the following equation from the measured weight of the specimen :⁹

$$\text{B. R.} = \frac{W_{ig} - W\{m_f/(m_f+m_p)\}}{W\{m_p/(m_f+m_p)\}} \times 100 \quad (1)$$

where W is the weight of the specimen, W_{ig} the weight of CB and gel, m_f the weight of CB in the compound, m_p the weight of NR in the compound. As shown in Table 2, the experimental results clearly depend on the type of CB. The order of the

Table 2. Experimental Results of the Bound Rubber for Natural Rubber Mixed with Various Carbon Blacks

Carbon black	Bound rubber(%)
N103	41.22(±1.85)
N326	27.46(±2.79)
N358	35.11(±3.96)
N550	22.03(±1.11)
N990	N/A

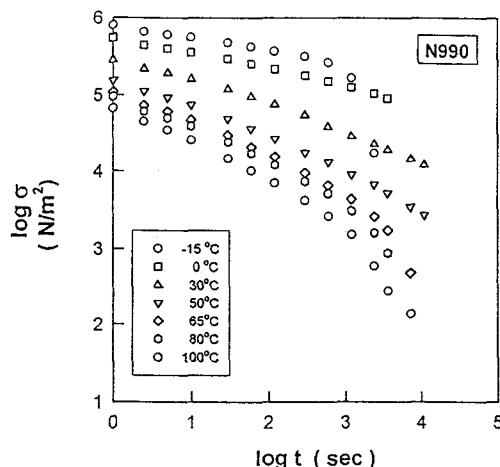


Fig. 1. The relation between stress relaxation, σ , and relaxation time, t , at various temperatures for uncrosslinked natural rubber mixed with N990.

bound rubber was found to follow $N103 > N358 > N326 > N550$. The bound rubber increased as the size of CB decreased and its structure was more developed for CBs having a similar size.

2. Stress relaxation

The temperature dependence of the relaxation behavior was investigated for NR mixed with a variety of CBs, principally via the method of time-temperature superposition. The relaxation function can be represented solely as a function of time at a particular temperature since the behavior at other temperatures follows directly from the WLF relation.¹¹ Isothermal stress relaxation data were obtained at various temperatures between -15°C to 100°C over a time scale of a few seconds to 10⁴ seconds. A typical result on the relaxation is represented in Figure 1, showing the relation between stress and relaxation time at various temperatures for NR compound mixed with N990 using a log-log scale. By using a scale factor (a_T) to deter-

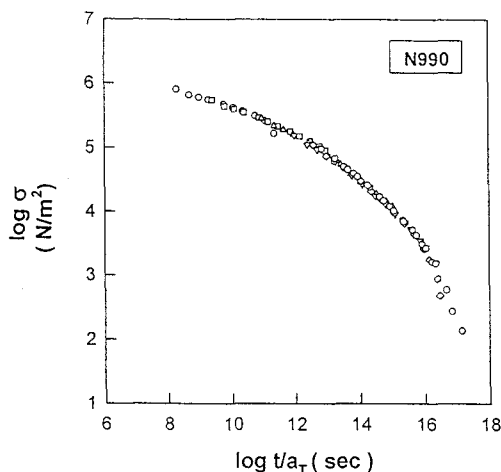


Fig. 2. Master curve of stress relaxation at T_g (-64°C) for uncrosslinked natural rubber mixed with N990.

mine the effective time, t/a_T , at the glass transition temperature (T_g), measurements at different temperatures can be brought into agreement. The scale factor is obtained by WLF equation :

$$\log a_T = \frac{-17.4(T - T_g)}{51.6 + (T - T_g)} \quad (2)$$

The stress isotherm-segments were horizontally shifted into superposition using the standard empirical techniques. Figure 2 shows the resulting master curve for NR compound containing CB of N990 at -64°C , which is the glass transition temperature of the compound. The observed superposition is quite satisfactory with the precision of data. All of the isotherm stress relaxation curves reflected a gradual decrease with the effective time. In the same way, master curves of the stress relaxation were constructed for each of the other compounds mixed with various CBs, as shown in Figure 3. The dependence of the stress relaxation on the types of CB looks obvious. The stress relaxation was extremely delayed when N103 was

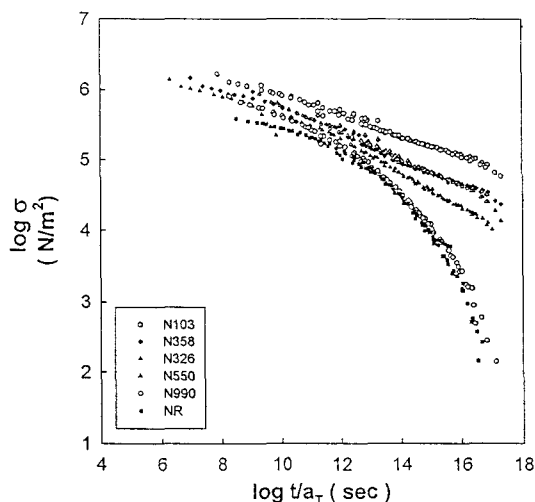


Fig. 3. Master curves of stress relaxation at T_g (-64°C) for uncrosslinked natural rubber mixed with various carbon blacks.

added, on the other hand, no effect on the delay of the stress relaxation was observed for N990. The degree of delay varied according to the characteristics of CB. The smaller size and the more developed structure of CBs are more effective in delaying the stress relaxation. The order was the same as the bound rubber. The driving force for delaying the stress relaxation would be a strong interaction between NR and CBs.¹²

3. Recovery behavior

The sample was stretched to 100% elongation and held for various relaxation times. The fractional residual deformation, $S(\%)$, remaining at a time t after liberation from restraint was calculated by the following equation :²

$$S(\%) = \frac{(l_t - l_0)}{(l_s - l_0)} \times 100 \quad (3)$$

where l_0 and l_s are the lengths between two marks on the testpiece in the unstretched and initially

stretched states, and l_t is the length of the testpiece measured at time t . The fractional residual deformation was plotted against the log-time. The results for the recovery response of NR compound mixed with CB of N990 are shown in Figure 4. The fractional residual deformation gradually diminished with time. It should be noted that the testpiece with the shorter relaxation time showed a highly elastic recovery returning to its original dimensions, while the testpiece with longer relaxation time showed slow elastic recovery and will have no further recovery after the theoretical infinite time. This experimental observation can be explained by the theoretical assumption that the stress relaxation is attributed to the disentangling of those molecular chains that formed a transitory elastic network at the time the deformation was imposed.¹³ Therefore, the fractional stress remaining after a time, t , is assumed to be proportional to the fractional number of those entanglements remaining.

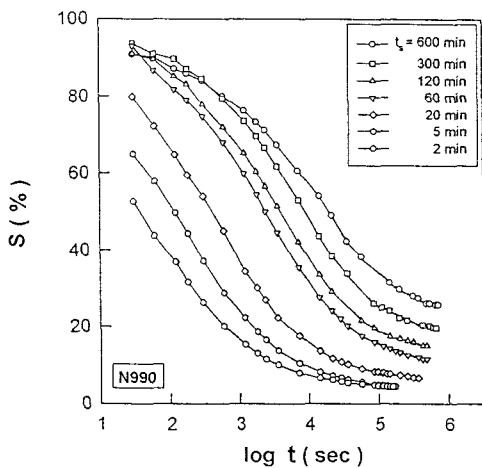


Fig. 4. The recovery after various relaxation times, t_s , for uncrosslinked natural rubber mixed with N990 from 100% elongation at 30°C.

The fractional residual deformation was plotted against the logarithm of time and the segments of each relaxation time were horizontally shifted into superposition using empirical techniques to form a master curve. The fractional residual deformation, $S(\%)$, was plotted against the logarithm of a reduced time scale, t/t_s . The resulting master curve for NR compound containing CB of N990 at 30°C is shown in Figure 5, and the recovery behavior obtained for each of the other compounds mixed with various CBs are shown in Figure 6. Each of master curves show single curves for each CB, which clearly affected the elastic recovery behavior as is seen in the resulting comparison between various CBs. Each master curve indicated similar trends in the elastic recovery. However, the recovery was clearly encouraged as the size of CB was decreased and its structure was more developed. The stronger interaction between NR and CB would contribute to the higher elastic recovery to its initial state.

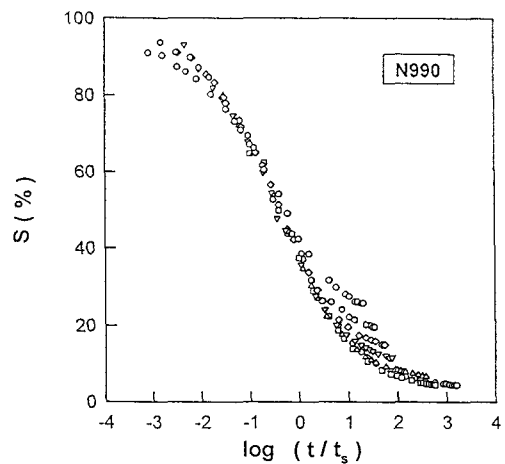


Fig. 5. Master curve of elastic recovery for uncrosslinked natural rubber mixed with N990 at 30°C.

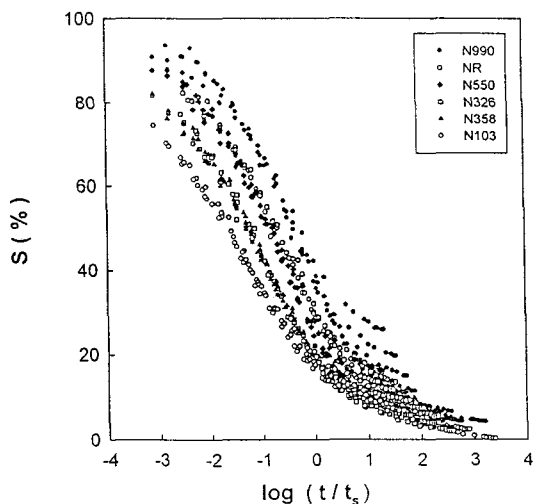


Fig. 6. Master curves of elastic recovery for uncrosslinked natural rubber mixed with various carbon blacks at 30°C.

4. Melt viscosity

Apparent viscosity, i.e., apparent shear stress per apparent shear rate, for NR melt containing various CBs was obtained using Monsanto processability tester (Monsanto, K-18, USA) having capillary die L/D of 20. The experimental results are presented in Figure 7, in which apparent viscosity is plotted against apparent shear rate in log-log scale. The apparent viscosity decreased with shear rate within a given range, indicating a typical shear-thinning behavior of NR compounds.¹⁴ The apparent viscosity of NR melt was obviously increased approximately 20 times by mixing with CB. Though the effect of CB types on the apparent viscosity are not great, a slight difference between the compounds containing various CBs was observed: the viscosity increased as the size of CB decreased and its structure was more developed, which is the same order as the bound rubber.

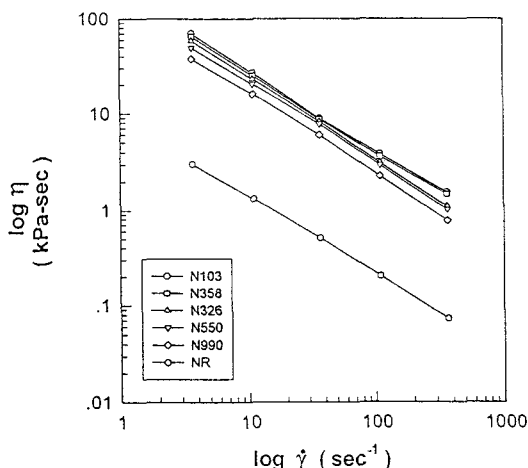


Fig. 7. The relation between apparent viscosity, η , and apparent shear rate, $\dot{\gamma}$, for uncrosslinked natural rubber mixed with various carbon blacks.

IV. Conclusion

We have attempted to show the effect of CB on the stress relaxation and the elastic recovery of uncrosslinked NR. The interaction between CB and rubber evaluated by the determination of bound rubber. The order of the bound rubber was $N103 > N358 > N326 > N550$, and depends on the surface area rather than the structure of CB. The higher structure of CB provided the more bound rubber in the case where the size of CB was similar. The stress relaxation of NR melt was found to be related in accordance with the WLF time-temperature equivalence principle. The stress relaxation was clearly delayed as the interaction between rubber and CB increased, which was ordered $N103 > N358 > N326 > N550 > N990$. The values of the elastic recovery of NR melt were found to follow substantially similar time dependence. The single recovery curve, plotted against the reduced time scale t/t_s , serves to characterize de-

layed elastic recovery. The degree of elastic recovery was enhanced as the interaction between rubber and CB increased, which was ordered N103 > N358 > N326 > N550 > N990.

Acknowledgments

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