Study on Variation of Structure and Properties of Natural Rubber During Accelerated Storage

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ABSTRACT: The dynamic variations of molecular structure and properties of natural rubber (NR) during the accelerated storage have been studied. The results showed that, with the prolonging of the storage time, the average molecular weight and the gel content increased, the width index of molecular weight distribution decreased, the gel size increased gradually, but the crosslinking density of gel fluctuated only within a narrow range. Besides, the initial plasticity increased, whereas the plasticity retention index decreased. The studies with thermal analyses and infrared spectroscopy showed that the thermal degradation temperature dropped, the thermal degradation rate increased, and the thermal stability has decreased after the storage of NR. The molecular structure and properties of NR are in a state of dynamic variation during accelerate storage. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1779–1783, 1998

Key words: natural rubber; accelerated storage; structure; properties

INTRODUCTION

The natural rubber, which has a good elasticity, hardens gradually with the prolonging of storage time.[1] This problem has been taken into consideration in rubber industry. Some workers suggested that the hardening is related to the crosslinking of the carbonyl group in NR molecular chain.[1] But other workers thought that the hardening of NR was led by the other functional groups such as epoxy group,[2,3] and only the reactions of carbonyl or epoxy groups with the amino acid in the latex can result in crosslinkage.[4] Many reports has been published on this problem. But the reports on the variation of structure and properties of NR during storage are very few. This report studies and discusses the relation between molecular structure and properties of NR during the accelerated storage and the pattern of their dynamic variation. The variation pattern coincides virtually with that of NR during the storage in the warehouse.[5–7]

EXPERIMENTAL

Get some fresh NR latex from the local field of NR plantation and coagulate the latex with 5% acetic acid and press the coagulum to about 2 mm thick with sheeting mill. Heat in an oven of 70°C until the rubber sheet becomes transparent so as to make a NR thin sample.

Put the NR thin sample (about 2 mm of thickness) into a sealed container containing the desiccant P_2O_5. Heat the container in the oven of 70°C. The heating time of sample 1, sample 2, sample 3, sample 4 and sample 5 are 0, 6, 12, 24, and 48 h, respectively.[5]

The molecular weight was determined by using of GPC.[8]

The gel content was determined by using of screen filtration method. The size of the large,

Figure 1 Molecular weight distribution of NR in different accelerated storage time.

Figure 2 Relation between gel content and accelerated storage time.

medium and small gel are >175 μm, 40 to 175 μm, and 15 to 40 μm, respectively. The gel crosslinking density was determined by using of swelling method.[5]

The initial plasticity (P_0) was determined according to GB 3510-83; the plasticity retention index (PRI) was determined according to GB 3517-83.[5]

RESULTS AND DISCUSSION

Figure 1 shows the molecular weight distribution curves of NR in different accelerated storage time. It can be seen from Figure 1 that the molecular weight distribution curves of NR become gradually narrow with the increasing of storage time, the high molecular portion increases, and the low molecular portion decreases. The distribution curve is bimodal before storage, and the peak of high molecular portion increases, whereas that of low molecular portion decreases gradually with the prolonging of the storage time. The peak of low molecular portion almost disappeared by the storage of 48 h (sample 5).

The data of the Table I show that both the weight-average molecular weight ($\overline{M}_w$) and the number-average molecular weight ($\overline{M}_n$) of NR increase with the prolonging of the storage time, but the width index of the molecular weight distribution ($\overline{M}_w/\overline{M}_n$) decreases.

Figure 2 shows the gel size distribution curves of NR in different storage time. It can be seen from Figure 2 that the gel has been formed owing to the crosslinking of NR molecules, and the total gel content increased during accelerated storage. The large gel content increased with the prolonging of the storage time and fluctuated within a narrow range after 24 h. The medium and small gel contents decreased with the prolonging of the storage time and became almost unchanged after 24 h.

The variation of the gel size of NR is apparent during accelerated storage, but the variation of the crosslinking density is not evident (see Fig. 3).

Table I Average Molecular Weight and Width Index of Molecular Weight Distribution of NR in Different Accelerated Storage Time

	$\overline{M}_w \times 10^{-4}$	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$
Sample 1	71.0	5.1	13.9
Sample 3	82.0	6.7	12.2
Sample 4	102.0	18.5	5.5
Sample 5	135.0	44.0	3.1

Figure 3 Relation between gel crosslinking density and accelerated storage time.

Figure 4 Relation between p_0 and accelerated storage time.

Figure 6 TG and DTG curves of sample 1 and sample 4 in air (the heating rate is 30°C/min).

The technical properties of the standard NR consist of six items: dirt content, ash content, nitrogen content, volatile matter content, initial plasticity (P_0), and plasticity retention index (PRI). The first four items reflect the purity of NR, P_0 indicates the plasticity and reflects the mechanical property, and PRI shows the aging property of NR. P_0 of NR changed greatly after a certain period of accelerated storage and increased rapidly with the prolonging of storage time (see Fig. 4), but the increment of P_0 decreased after 24 h. The variation pattern of PRI of NR is just in contrary with P_0, the PRI decreased apparently with the prolonging of the storage time but approached to constant after 24 h (see Fig. 5).

Figure 6 shows the thermogravimetric analysis (TG) and derivative thermogravimetry (DTG) curves of samples 1 and 4. The initial temperature of weight loss (T_0) and the temperature at the maximum weight loss rate or the peak temperature of the DTG curve (T_p), obtained by bi-tangent method from the TG curve, are as follow:

sample 1—T_0 = 318°C, T_p = 349°C; sample 4—T_o = 316°C, T_p = 344°C.

The results show that the thermal degradation temperature or thermal stability of NR decreased after storage.

Figures 7 and 8 are the infrared differential spectra of thermal degradation of samples 1 and 4, respectively. It can be seen from the figures that the thermal degradation products of both

Figure 5 Relation between PRI and accelerated storage time.

Figure 7 FTIR differential spectrum of sample 1 in air of 145°C in 1, 2, and 3 h.

Figure 8 FTIR differential spectrum of sample 4 in air of 145°C in 1, 2, and 3 h.

sample 1 and sample 4 are alike, they are hydroperoxyl, hydroxyl, and carbonyl compounds. The absorption peaks of carbon–carbon double bond (835 cm^{-1}) and methylene group (1450 cm^{-1}) of NR decreased, apparently during thermal degradation, but that of the carbonyl group (1715 cm^{-1}) and hydroxyl group (3500 cm^{-1}) obviously increased. The difference of the two samples is the intensity variations of the special absorption peaks or the degrees of the reaction. The degree of reaction of sample 4 in 1 h equals to that of sample 1 in 3 h. This shows further that the thermal degradation rate of NR increases or the thermal stability decreases after the storage.

There are "unnormal groups" such as carbonyl and epoxy in the NR molecules. These groups undergo condensation reaction by the action of nonrubber constituents during accelerated storage, which leads to the increasing of the NR molecular weight and the crosslinking of NR molecules. In the meanwhile, the condensation reaction results in the increasing of the gel content and the changing of the gel size from small to large. The variation of the gel crosslinking density is not apparent; this may be due to the small number of the "unnormal groups," so the crosslinks are also few.

Figure 9 Relation between $\overline{M}$ and P_0.

The variation of the NR molecular structure affects the other properties of NR directly. P_0 has a fine positive relationship with the average molecular weight (see Fig. 9); so does the large gel content (see Fig. 10), but the large gel content has a negative relationship with the PRI (see Fig. 11). Thus, the dynamic variation of the NR molecular structure during storage causes the change of NR properties directly. This is one of the main reasons that the homogeneity of the NR properties is poor.

CONCLUSIONS

Our experiment shows that the structure and properties of NR changed during storage. With the prolonging of the storage time, the molecular weight increased continuously, the molecular weight distribution curve varied from bimodal to

Figure 10 Relation between P_0 and large gel content.

Large gel content(%)

Figure 11 Relation between PRI and large gel content.

unimodal, the width index of molecular weight distribution decreased continuously, the gel size changed from small to large, the total gel content increased gradually, and the gel crosslinking density fluctuated in a narrow range. The variation of structure resulted in the apparent variation of P_0 and PRI. P_0 is directly proportional to storage time, and PRI is inversely proportional to the storage time. At the same time, the thermal deg-

radation temperature dropped, the thermal degradation rate increased, and the thermal stability decreased. These results have a practical meaning for the guidance of the variation of NR properties during storage in the warehouse.

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