

Research Article

Use of Rubber Process Analyzer for Characterizing the Molecular Weight Parameters of Natural Rubber

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The aim of this work is to introduce a simple and rapid method for characterizing the molecular weight parameters and other molecular structure parameters of natural rubber (NR) using a rubber process analyzer (RPA). In this work, NR of different molecular weights was prepared by milling. Molecular weight parameters were measured by gel permeation chromatography coupled with laser light scattering (GPC-LLS) for comparison with RPA results. It was verified that increasing of milling time leads to a decrease of the number-average molecular weight (\bar{M}_n), weight-average molecular weight (\bar{M}_w), and molecular weight distribution (MWD). The dynamic and rheological properties were evaluated on RPA by tests of strain sweep, frequency sweep, and stress relaxation. These results were used to characterize the average molecular weight, MWD, and viscosity of NR and were found to agree with those from GPC-LLS. This convenient and rapid technology for characterizing NR molecular weight parameters would be especially useful in the elastomer industry.

1. Introduction

Molecular weight is an important parameter for natural rubber (NR) characterization. A series of NR parameters (e.g., molecular weight, molecular weight distribution (MWD)) are commonly measured by gel permeation chromatography (GPC), laser light scattering (LLS), and nuclear magnetic resonance (NMR) [1–3]. Because these technologies are complicated and time consuming, an alternative simple and rapid technology is desired.

Mooney viscosity is a significant parameter that can be used to characterize the average molecular weight of raw rubber crudely. In the rubber industry, Mooney viscosity is a standard for evaluating raw rubber under ASTM D 1646 and ISO 289 [4] and has been used for characterizing raw rubber and mixed stocks for more than 70 years. Researches had shown that two styrene-butadiene rubber samples with different dynamic properties can have the same Mooney viscosity [5]. Therefore, this measurement alone

cannot be used to characterize the elastomer molecular weight.

Polymer dynamic properties and rheological behavior are influenced by molecular weight, MWD, and long chain branching (LCB). Guimarães and coworkers [6] found that the rheological properties of high-density polyethylene/poly(ethylene-co-octene) metallocene elastomers (HDPE/EOC) blends are influenced significantly by the proportion of LCB and the molecular weight of the metallocene elastomer. Conversely, viscosity, elastic modulus, loss factor, and so forth can be used to give information about the molecular structure of polymer material. Zero-shear viscosity (η_0) is influenced by molecular weight, while η_0 and the relaxation spectrum can be used to calculate the molecular weight of polyethylene (PE) [7]. The shear-thinning phenomenon is very sharp in LCB polymers. Compared with linear molecular counterparts with the same molecular weight, LCB-PE has a higher shear viscosity at a low shear rate and a lower shear viscosity at high shear rate [8]. Azizi and coworkers [9] concluded that the melt flow index increased

TABLE I: Molecular weight parameter of natural rubber with different milling times.

	5	10	15	20	25	30
\overline{Mn}	2.808×10^5	2.163×10^5	1.613×10^5	1.272×10^5	1.137×10^5	1.106×10^5
\overline{Mw}	3.736×10^5	2.754×10^5	2.039×10^5	1.601×10^5	1.417×10^5	1.370×10^5
$\overline{Mw}/\overline{Mn}$	1.330	1.273	1.264	1.259	1.246	1.239

and the complex viscosity decreased with a decrease in polypropylene (PP) molecular weight. Moreover, the molecular weight and MWD were calculated from dynamic rheological data. In general, many studies have focused on the relationship between molecular structure and dynamic behavior.

The rubber process analyzer (RPA) is a dynamic mechanical rheological tester and it is universally used for characterizing raw elastomers and unvulcanized compounds [10]. Over the past 20 years, since the RPA was invented by Alpha Technologies, it has been used to characterize dynamic properties [11, 12], rheological properties [13], and the network structure [14] of elastomers. The blending of different elastomers and their compatibility [15], the dispersion of nanofillers in polymer matrices, and compatibility between filler and elastomers [16] are a major topic for application of the RPA to elastomers.

In summary, many studies have dealt with the characterization of polymer molecular structure by measurement of dynamic properties and rheological behavior, but limited research has focused on elastomers. Quite a few papers report that elastomer molecular weight and MWD characterization by RPA had been done.

In this work, NR with a series of different molecular weights was prepared by milling, and molecular weight parameters were measured by GPC-LLS. These parameters were then used as a reference standard for comparison with those obtained from RPA. The complex viscosity, relaxation times, elastic modulus, viscosity modulus, and loss factor measured by RPA were used to determine average molecular weight, MWD, and viscosity for NR with different milling times. Through this study, the molecular weight, MWD, and rheological properties of NR were characterized qualitatively using RPA.

2. Experimental

2.1. Material and Sample Preparation

2.1.1. Material. Natural rubber was purchased from Hainan Rubber Industry Group, China. Other chemicals were all of commercial grade.

2.1.2. Sample Preparation. Raw NR (300 g) was milled 5, 10, 15, 20, 25, and 30 times using a two-roller mill with 2 mm spacing. The milling temperature was 60°C. Milling was done in open air.

2.2. Measurements

2.2.1. Molecular Weight Analysis. Molecular weight was determined by GPC-LLS (GPC, Waters Corporation, USA). The GPC-LLS equipment consisted of an online degasser, an Agilent 1100 Series pump, a multiangle scattering detector (DAWN HELEOS, Wyatt Technology, Santa Barbara, CA, USA), online viscosity detector (Viscostar, Wyatt Technology, Santa Barbara, CA, USA), and refractive index detector (Optilab rEX model, Wyatt Technology, USA). The columns were two PL-MIXED-BL mixed bed columns (10 μm , 300 mm \times 7.8 mm inner diameter) (Agilent). The columns were maintained at 30°C. The mobile phase, tetrahydrofuran (THF) (200 μL), was injected at a flow rate of 1.0 mL/min.

2.2.2. Mooney Viscosity [ML(1+4)100°C]. The ML(1+4)100°C was determined using a Mooney Viscometer (UM-2050, U-CAN, Taiwan) according to Chinese standard: GB/T 1232.1-2000.

2.2.3. RPA Analysis. An RPA2000 (Alpha Technologies, Akron, OH, USA) was used for dynamic and rheological measurements. The samples were cut from milled NR of about 6 g and placed into moulding chamber. A strain sweep was carried out at 1 Hz and 100°C. The frequency sweep was carried out at a strain of 14% and at 100°C. The stress relaxation was measured at a strain of 40% and at a temperature of 100°C, with a 2 min test time.

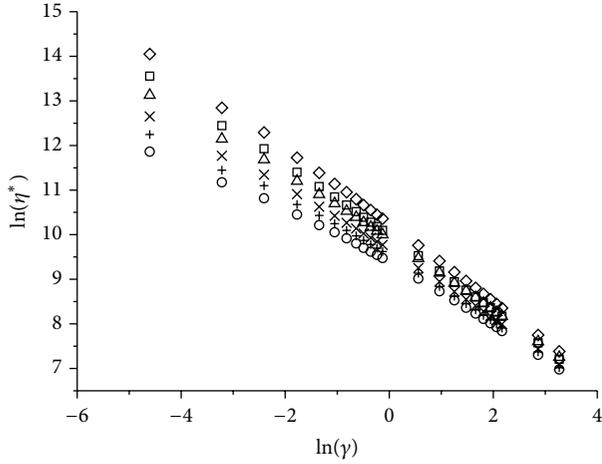
3. Results and Discussion

3.1. Molecular Weight. Gels are important components in NR but cannot be characterized by GPC and LLS. About the measurement method of molecular weight of NR, we often remove the gel portion and the sol portion is analyzed to determine the molecular weight. In general, the molecular weight measured by GPC-LLS represents the molecular weight of the sol portion. Table I shows the molecular weight averages and molecular weight distribution of NR milled a different number of times. With an increase in milling time, \overline{Mn} and \overline{Mw} decreased. The MWD decreases as the milling time increases, indicating that there is narrowing of the MWD as the milling time increases. It is proposed that the mechanical action decreases the molecular weight.

3.2. Mooney Viscosity. The Mooney viscosity is a basic parameter for characterizing NR and is used to evaluate the average molecular weight of the rubber material. Table 2

TABLE 2: Mooney viscosity of natural rubber with different milling times.

	5	10	15	20	25	30
ML(1+4)	86.63	72.50	52.49	43.04	36.12	29.50

FIGURE 1: Relationship between $\ln(\eta^*)$ and $\ln(\dot{\gamma})$ under frequency sweep (\diamond : milled 5 times; \square : milled 10 times; \triangle : milled 15 times; \times : milled 20 times; $+$: milled 25 times; \circ : milled 30 times).

shows the ML(1+4) of NR milled 5, 10, 15, 20, 25, and 30 times. The greater the milling time, the lower the ML(1+4). The mechanical action therefore decreases the molecular weight and leads to a decrease in ML(1+4).

3.3. Viscosity. The complex viscosity obtained using the RPA is considered to be the apparent viscosity, because it corresponds closely to the apparent viscosity value measured using a capillary rheometer [13]. Equation (1) describes the relationship between apparent viscosity and shear rate, where k and α are rubber constants and η and $\dot{\gamma}$ are the apparent viscosity and shear rate, respectively. Equation (2) is the natural logarithm of both sides of (1). A linear relationship exists between $\ln(\eta)$ and $\ln(\dot{\gamma})$. Consider

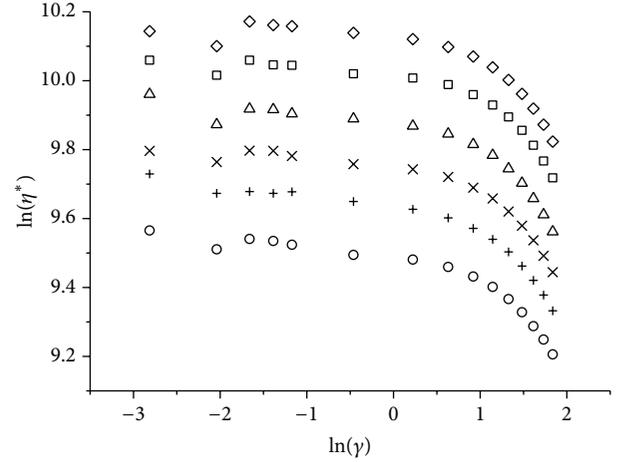
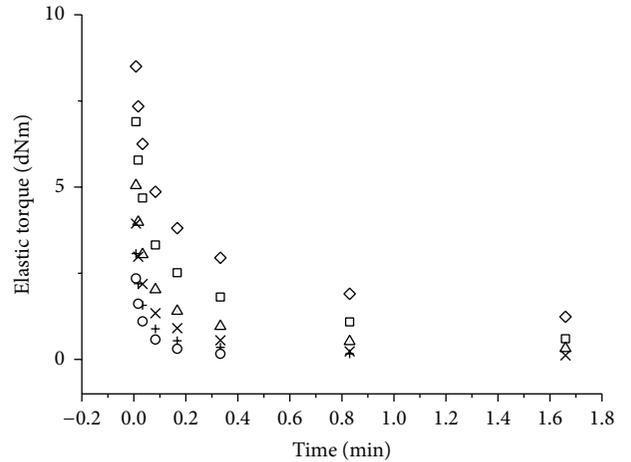
$$\eta = k \cdot \dot{\gamma}^{\alpha-1}, \quad (1)$$

$$\ln(\eta) = \ln(k) + (\alpha - 1) \cdot \ln(\dot{\gamma}). \quad (2)$$

Figure 1 shows a plot of complex viscosity versus shear rate for a frequency sweep test. An inverse linear relationship exists between $\ln(\eta^*)$ and $\ln(\dot{\gamma})$. The gradient of the straight line decreases with an increase in milling time.

Figure 2 shows a plot of complex viscosity versus shear rate for a strain sweep test. Two stages exist on the curves: a straight line parallel to $\ln(\dot{\gamma})$ axis and another similar to the frequency sweep.

For the stage parallel to $\ln(\dot{\gamma})$ axis, the constant (α) is approximately equal to 1, and this represents a Newtonian behavior. For the other stage at higher strain, η^* decreases with increased shear rate for the strain sweep. This is a shear-thinning behavior, a feature of non-Newtonian behavior,

FIGURE 2: Relationship between $\ln(\eta^*)$ and $\ln(\dot{\gamma})$ under strain sweep (\diamond : milled 5 times; \square : milled 10 times; \triangle : milled 15 times; \times : milled 20 times; $+$: milled 25 times; \circ : milled 30 times).FIGURE 3: Stress relaxation curves of natural rubber at 100°C (\diamond : milled 5 times; \square : milled 10 times; \triangle : milled 15 times; \times : milled 20 times; $+$: milled 25 times; \circ : milled 30 times).

and is caused by the higher strain that destroys the molecular structure of the NR.

There is an obvious effect on the complex viscosity of NR with a different milling time. The value of $\ln(\eta^*)$ decreases with an increase in milling time.

The value of zero-shear viscosity (η_0) of the NR cannot be calculated for different milling times. The value of η_0 is assumed to decrease with an increase in milling time, based on the drop of (η^*) expressed by the straight line in Figures 1 and 2. The decrease in (η_0) is caused by a decrease in molecular weight of the NR.

3.4. Stress Relaxation. Figure 3 shows the stress relaxation of NR for different milling times. With an increase in milling time, the value of the elastic torque (S') decreases at the same relaxation time. Relaxation time is a polymer parameter used to characterize molecular motion and molecular

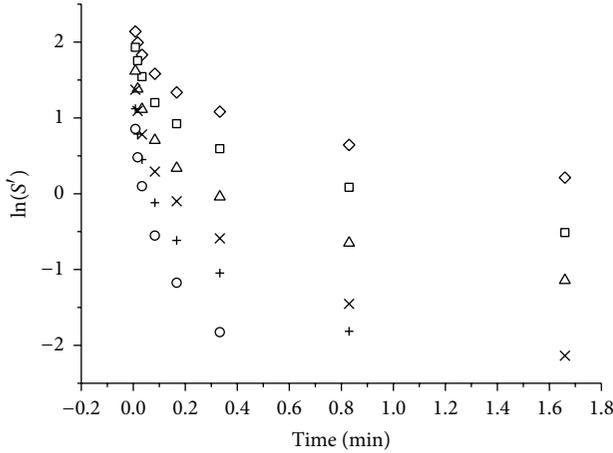


FIGURE 4: Relationship between time and $\ln(\sigma_0)$ (\diamond : milled 5 times; \square : milled 10 times; \triangle : milled 15 times; \times : milled 20 times; $+$: milled 25 times; \circ : milled 30 times).

TABLE 3: Parameter of stress relaxation of natural rubber with different milling times.

	$1/\tau$	τ	$\ln(\sigma_0)$	σ_0	r
5	1.0662	0.93791	1.7702	5.872028	0.918041
10	1.3421	0.745101	1.4651	4.327976	0.919456
15	1.5059	0.664055	1.0053	2.732727	0.892805
20	1.9429	0.514695	0.6682	1.950723	0.912031
25	3.17	0.315457	0.4898	1.63199	0.892525
30	7.006	0.142735	0.4697	1.599514	0.943133

r : correlation coefficient.

structure. It not only depends on temperature and external force, but is also affected by the molecular structure and internal network of the polymer. Equation (3) expresses the relationship between stress relaxation time (τ) and stress (σ), where σ_0 is the initial stress. The elastic torque obtained from the stress relaxation measured by RPA is used as stress in this work. Equation (4) is obtained by rearranging (3) and shows the linear relationship between $\ln \sigma$ and time (t), where $(-1/\tau)$ is the slope of the straight line in (4). A plot of $\ln \sigma$ versus time (t) yields the linear relationship in Figure 4 with parameters in Table 3 calculated using (4). According to the results, the relaxation time and initial stress decrease in proportion to an increase in milling time. In general, with an increase in milling time, the relaxation time and initial stress decrease. The mechanical action causes the molecular weight to decrease, reduces molecular entanglement, and leads to ease of motion of the molecular chain. Hence,

$$\sigma = \sigma_0 \cdot e^{-t/\tau}, \quad (3)$$

$$\ln \sigma = \ln \sigma_0 - \frac{t}{\tau}. \quad (4)$$

3.5. Molecular Weight and Molecular Weight Distribution. The elastic modulus (G') and viscosity modulus (G'') are two important parameters for characterizing the dynamic properties of the elastomer. G'' represents the internal friction

of the molecules in an elastomer. Under an external force, molecular chain orientation is caused by internal friction. When the elastomer molecular weight is lower than a certain value, there is a crossover point between the curves of G' and G'' , which means that there is a balance in state of internal friction and disorientation [17]. With an increase in molecular weight, the crossover point moves to lower frequency because of restricted disorientation. The lower frequency allows for sufficient time for molecular orientation. The higher molecular weight molecules therefore need more time for molecular orientation. According to (5), G_x is the crossover point which is in inverse proportion to the polydispersity [18]. In summary, data for the crossover point demonstrate that the molecular weight decreases with an increase in frequency and polydispersity increases with a decrease in G_x . The lower frequency therefore corresponds to a higher molecular weight, and the higher modulus corresponds to lower polydispersity. Therefore,

$$G_x = 8.4 \times 10^5 \left(\frac{Mw}{Mn} \right)^{-1.385}. \quad (5)$$

Figure 5 shows the curves of elastic modulus (G') and viscosity modulus (G'') in response to the frequency sweep of NR for different milling times. Six graphs are shown of NR for milling times of 5, 10, 15, 20, 25, and 30. A crossover point [$G_{(\text{milling times})}(f, G)$] exists in the graph when the milling time is more than 15. The crossover points are $G_{(20)}(0.01, 13.9)$, $G_{(25)}(0.05, 21.3)$, and $G_{(30)}(0.1, 22.2)$. The existence of a crossover point indicates that frequency and modulus increase with milling time. For milling times less than 15, no crossover point exists because the higher molecular weight NR requires a smaller frequency for molecular orientation.

4. Conclusions

NR molecular weight and MWD as characterized by dynamic properties and rheological behavior correspond with those measured by GPC-LLS. With an increase in milling time, \overline{Mn} , \overline{Mw} , and MWD decrease. The complex viscosity of NR decreases with an increase in shear rate, and the increase in molecular weight increases the zero-shear viscosity. The relaxation parameter is calculated from $\sigma = \sigma_0 \cdot e^{-t/\tau}$, which is measured by RPA under stress relaxation. The average molecular weight and MWD are obtained from a crossover point between the curves of G' and G'' under a frequency sweep. The crossover point represents the modulus and frequency, where lower frequency means a higher molecular weight, and higher modulus means lower polydispersity. This work provides a relationship between the dynamic properties and rheological behavior and molecular structure parameters of NR, offers a convenient and fast technique for the characterization of NR molecular structure, and is well suited to the elastomer industry.

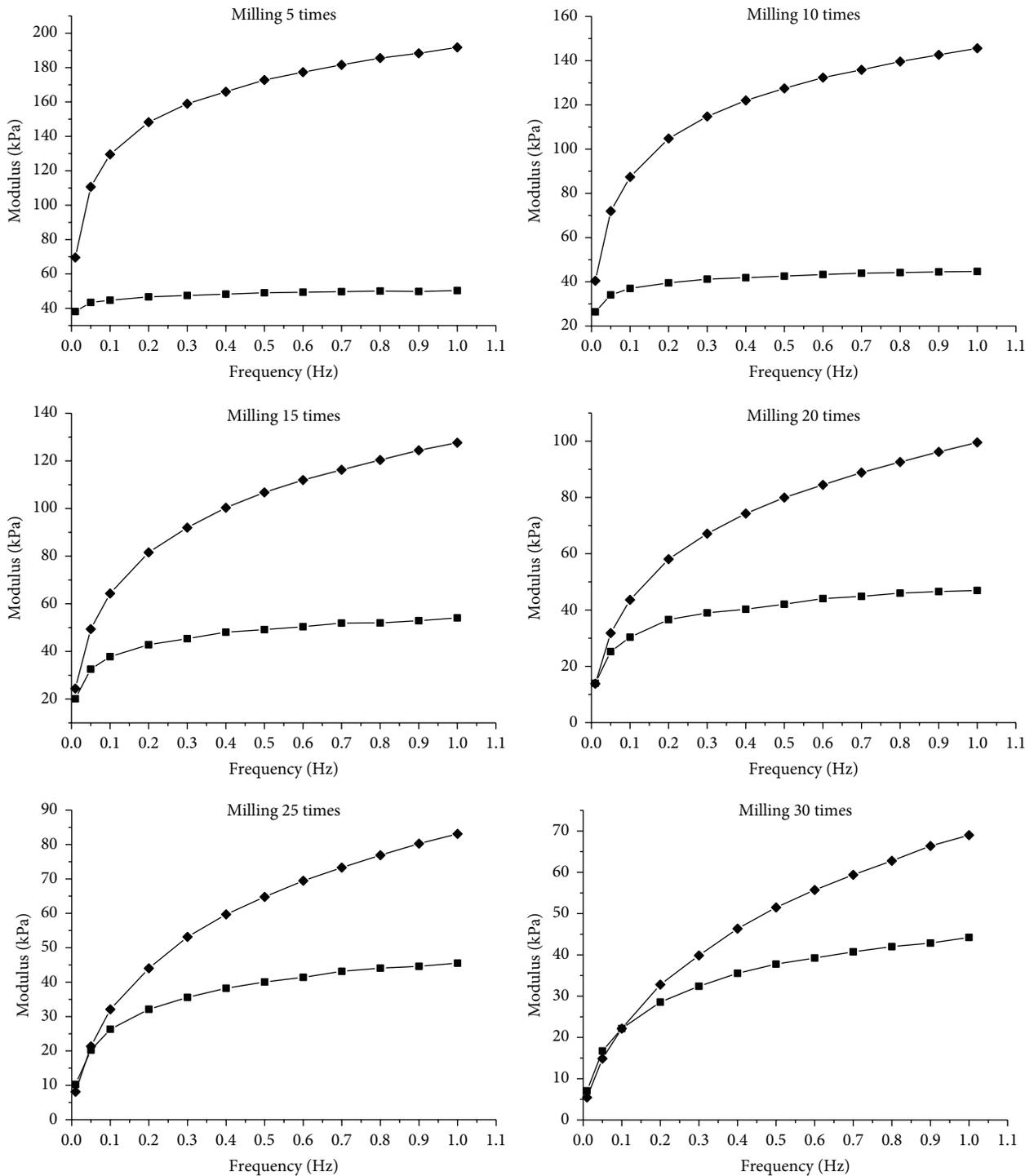


FIGURE 5: Curves of elastic modulus (G') and viscosity modulus (G'') response of frequency sweep (G' : \blacklozenge ; G'' : \blacksquare).

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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