Viscoelastic Characterization of Uncured NR/Cel II Compositions

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ABSTRACT: In this work three types of equipments were used, namely, rubber process analyzer (RPA 2000), Mooney viscometer, and dynamic mechanical thermal analyzer, to characterize natural rubber mixtures containing different amounts of regenerated celulose (Cel II) as filler. The RPA 2000 is a new dynamic rheological tester that can analyze raw polymers and masterbatches as well as rubber compounds before, during, and after cure. The Mooney viscometer is probably the most widely used method for measuring shearing viscosity of unvulcanized rubbers or rubber compositions. DMTA is used to assess filler–rubber interactions. In the present investigation, RPA tests on unvulcanized natural rubber and regenerated cellulose (Cel II) mixtures were carried out using strain and frequency sweeps, and the Mooney viscosities were determined using the relaxation accessory and the small rotor. DMTA data were taken at a fixed frequency and temperature sweep. The filler content was increased up to 30 phr. Compositions were prepared by cocoagulation of natural latex and cellulose xanthate mixtures. The results showed a good dispersion of the filler in the rubber matrix and its large influence on rheological and dynamic properties of the resulting compositions. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 2125–2131, 2005

Key words: viscoelastic properties; rheology; composites

INTRODUCTION

Uncured and cured rubber are neither completely viscous nor elastic in nature, but rather viscoelastic in their properties. The understanding of this viscoelastic profile is very important in predicting processing behavior as well as the nature of the physical properties imparted to the final cured rubber product.[1]

The measurement of rubber viscoelastic properties with traditional dynamic mechanical rheological testers (DMRTs) has not been commonly done in the rubber industry. There are several reasons for this fact. Conventional DMRT rubber testing requires complex sample preparation, which needs a high degree of operator skill, not always available in the rubber industry. Most DMRTs do not confine the test sample under pressure that gives more repeatable and reproducible measurements of resistance to deformation.[2,3]

The rubber process analyzer (RPA) 2000 rubber process is a new dynamic mechanical rheological tester designed to measure the dynamic properties of raw polymers, uncured compounds, and final cured compounds.[2,4] The RPA strains a sample in shear by oscillating the lower die sinusoidally. Oscillation frequency can be set from 0.1 to 2000 cycles per minute (cpm). The magnitude of the lower die movement can be set by the angular oscillation of the lower die or by the required strain on a sample. The arc movement of the lower die can range from ± 0.05 to $\pm 90.00°$, which corresponds to strains from $\pm 0.7\%$ to $\pm 1256\%$. The available combinations of frequency and strain in the RPA are limited to a maximum shear rate of 30 s^{-1}. Table I lists some examples of allowable combinations.[4]

The upper die is attached to a torque transducer to eliminate noise from the lower die drive system and to measure the transmitted torque through the sample. This torque is called the complex torque or $S*$ and it is not in-phase with the applied strain due to the viscoelastic nature of rubber. The $S*$ signal is reduced by the RPA software into an elastic (S') component (in-phase with strain) and a viscous (S'') component (90° out-of-phase with strain) by applying a Fourier transform to the $S*$ signal. The Fourier transform also improves the signal-to-noise ratio of the test. Tan δ is calculated from (S''/S'). Torque values (S) are directly converted to the shear modulus (G) by multiplying by the appropriate die form factor and dividing by the strain. This procedure provides the storage modulus G' and the loss modulus G''. Also, dynamic viscosity calculations are performed since dynamic real viscosity, η', can be calculated by dividing loss modulus G'' by the applied frequency in radians per second.[5,6]

Strain range (%)	Frequency range (cpm)	Maximum shear rate (s^{-1})
± 0.7 to ± 1256	2 to 20	26.3
± 0.7 to ± 628	2 to 50	32.9
± 0.7 to ± 140	2 to 100	14.6
± 0.7 to ± 42	2 to 500	21.9
± 0.7 to ± 14	2 to 2000	29.2

The viscometer was introduced by Mooney (1934) and consists essentially of a knurled disc that rotates slowly and continuously in one direction in a closed cavity, which itself has a serrated or grooved surface.[7] This instrument displays the main disadvantage of rotational viscometers: to avoid a significant temperature rise in the test sample due to shear heating, or more precisely, viscous dissipation, the shear rate must be low. The very low shear rates and single-point measurement of the Mooney viscometer identify it as a quality-control instrument rather than a tool for development and problem solving. Even then, the correlation between Mooney viscosity, which is a torque measurement, and processing behavior should be established before proceeding to utilize it as a measure of material consistency.[8]

The Mooney viscosity gives some measure, within a class of rubbers, of the molecular size. Because of the very low shear rates involved, it gives little indication of the viscosities pertaining to higher shear rate processes such as injection molding.[7,9]

The Mooney viscosity results are reported in arbitrary Mooney units (1 MU = 0.083 Nm), which are based on torque as defined in ASTM[10] D 1646. Shearing is imposed by a disk rotating inside a shallow cylindrical cavity filled with the rubber under test. The rotor speed is usually 2 rpm and the shearing viscosity is generally obtained at 100°C. Two rotors are supplied, a larger (ML) (diameter 3.54 cm) one used for all viscosity determinations except those involving stocks with viscosities greater than 200-ML units, in which case the smaller (MS) (diameter 3.05 cm) rotor is used.[11] For a raw polymer, the choice of a correct viscosity level is important to ensure acceptable mixing and processing characteristics.[9]

However, a polymer conference held in Belgium in 1991 concluded that raw rubbers are not fully characterized in relation to processability by Mooney viscosity, since it is well known that two rubber mixtures can have very similar Mooney viscosity, and yet they would process very differently. RPA is able to quantify this performance difference. So, while Mooney viscosity can correlate with the average molecular weight, there are many other polymer characteristics related to rheological behavior that can be measured by RPA. Some of these include the following: (1) molecular weight distribution; (2) chain branching; (3) monomer ratios in copolymers (such as percentage bound styrene for SBR or percentage bound ACN for NBR); (4) oil and/or carbon black content in extended polymers (masterbatches); (5) microstructural differences in polymers (such as percentage vinyl, *cis* or *trans* structures); and (6) chemical modification of solution SBRs.[1,2,12]

The RPA equipment and Mooney viscometer require no special sample preparation and are easy to operate. In the case of RPA it is possible to apply a wide range of dynamic test conditions to a rubber sample, including very high strains and the Mooney viscometer allows the use of the relaxation accessory to measure the viscosity 30 s after stopping the rotor.

Applications of rubbers for use in tires, belts, and engine mounts involve fast repeating deformations, these being well known as the dynamic mechanical properties of the rubbers. The properties are dependent on both the chemical and the physical interactions between the fillers and the rubber matrix. One method that has been used to characterize rubber–filler interactions is dynamic mechanical thermal analysis (DMTA), particularly useful because of its nondestructive character and the capability of identifying the molecular mechanisms of polymer materials.[13]

DMTA data were used to assess filler–rubber interactions in terms of elastic modulus (E'), loss tangent (tan δ), and the variation of glass transition temperature (T_g). T_g is a very important parameter for elastomers because it correlates to the low temperature limit before the elastomers stiffen and lose their elastomeric properties.[14]

The properties of the rubber products are usually dependent not only on the types of the reinforcing fillers, such as carbon black and silica, but also on their structure and other characteristics, including particle size, surface area, and degree of dispersion in the rubber phase.[13]

Fillers, when added to polymer systems, are known to cause a considerable change in dynamic modulus, both viscous and elastics, and also in the loss factor, the ratio between these two parameters, which is related to the amount of energy dissipated during dynamic deformation.[15]

In this work, rubber composites were prepared by cocoagulation of mixtures composed of the latex from natural rubber and cellulose xanthate. These mixtures were prepared so that, after coagulation, filler content was varied from 0 to 30 phr. The results showed a good dispersion of the filler in the rubber matrix and its large influence on rheological and dynamic properties of the resulting compositions.

EXPERIMENTAL

The cocoagulation of the NR/Cel II mixes was carried out by adding, under stirring, natural latex/cellulose xanthate mixture to an equimolar acid solution of sulfuric acid and zinc sulfate. For processing controlling, the viscosity of the system was maintained constant in all compositions by keeping the same xanthate/water ratio. The natural latex was diluted in the proportion 2:1, and the final content of regenerated cellulose varied from 0 to 30 phr. After coagulation the fine rubber–cellulose particles were washed with distilled water to promote the removal of the residual acidity. The product was separated from the aqueous suspension by filtration, dried in an air-circulating oven at 50°C, and submitted to different tests.

Three types of equipment, RPA 2000, Mooney viscometer, and DMTA, were used characterize the mixtures.

Mooney viscosity and relaxation were determined according to ASTM[10] D 1646 in a Monsanto Model MV 2000 viscometer, using the small rotor, MS.

Rheological properties of the uncured compositions were measured on an Alpha Technologies rubber process analyzer. The measurements were taken according to ASTM[16] D 6204 using strain and frequency sweeps.

Dynamic mechanical thermal analysis were carried out according to ASTM[17] D 4065 in a Rheometric Scientific, Model MK III, DMTA analyzer, using mode of deformation geometry, single cantilever bending; heating rate, 2°C/min; frequency, 1 Hz; and temperature ranging from −80 to 0°C. For this test, samples were cut from $0.1 \times 15.0 \times 15.0$ cm plates molded in a Carver press at 120°C and 20,000 lb for 15 min.

RESULTS AND DISCUSSION

Figure 1 presents the results of Mooney viscosity and relaxation of the NR/Cel II compositions studied. In these tests the small rotor, MS, was used because, for compositions with filler content greater than 20 phr, the values measured with the large rotor exceeded the limits of the equipment. From Figure 1, it can be observed that, as expected, the Mooney viscosity ($MS_{(1+4)}$) increases with the filler incorporation. However, such increase might be related either to a perfect dispersion or to an elastomeric matrix–filler interaction. This statement is based on results observed with carbon black as well as silica, under some operational conditions such as an increase in time or temperature of mixing used, for instance, to get a better distribution and/or dispersion of the filler within the elastomer, in the search for more promising mechanical results.

The Mooney relaxation is defined[18] by Eq. (1),

$$MR = [M_{30}/ML_{(1+4)}] \times 100 \qquad (1)$$
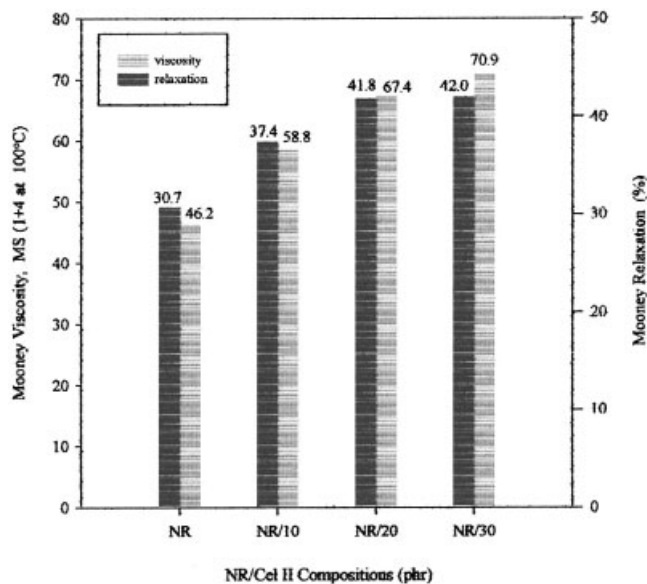
Figure 1 Mooney viscosity and relaxation of uncured NR/Cel II compositions.

where M_{30} is the viscosity measured 30 s after the rotor has been stopped, when $ML_{(1+4)}$ is then determined.

The percentage of relaxation, as a result of Mooney viscosities, shows that there is a limiting amount for the regenerated cellulose, around 20 phr. From this point on, by increasing the cellulose content, significative variations in Mooney relaxation are no longer detected, which can be a consequence of the higher values achieved for the Mooney viscosity and the very short period of time available for the measurement.

In RPA tests, strain and frequency sweeps were used to characterize the materials under investigation. The strain sweep was started at the lowest test strain and finished at the highest strain. This sequence reduces the breakdown of any polymer–filler interaction.[12]

Figure 2 shows the elastic torque versus frequency of the NR/Cel II compositions. An elastic torque increase is observed by adding regenerated cellulose, mainly at frequencies up to 100 cpm. At higher frequencies this increase becomes less significant.

The dependence of the viscous torque on the frequency was also evaluated and is shown in Figure 3. This parameter increases with the filler incorporation and is independent of the frequency in the entire range. Moreover, the viscous torque values are lower than those for elastic torque (Fig. 2).
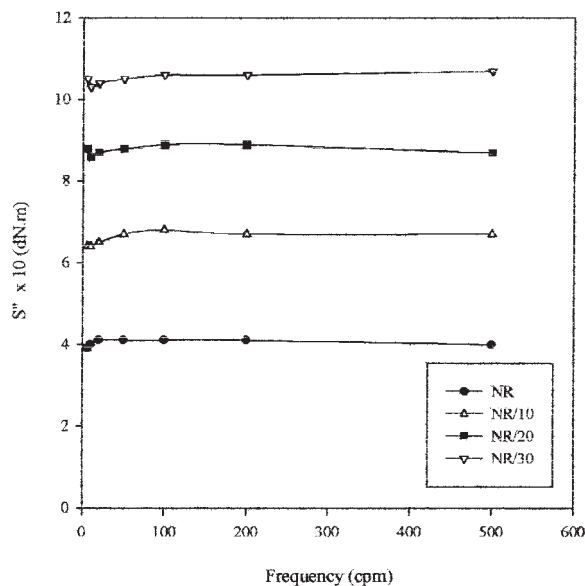
Figure 4 exhibits viscosity versus frequency and the influence of the regenerated cellulose due to the large viscosity increase is clearly seen. The curves show that viscosity varies inversely with the frequency and that for frequencies higher than 100 cpm no differences among the natural rubber compositions were detected.
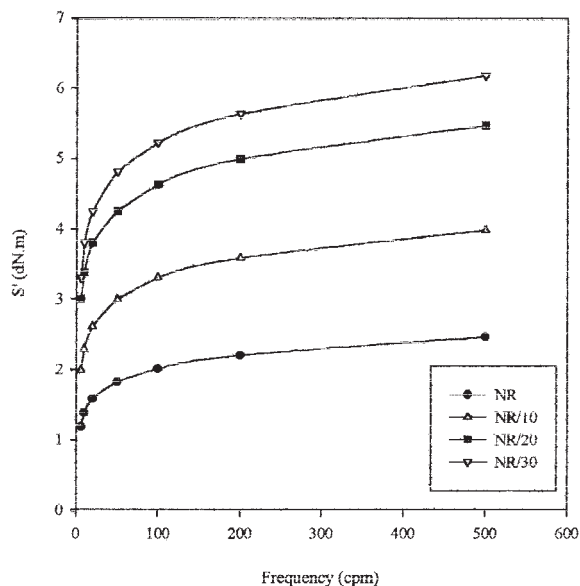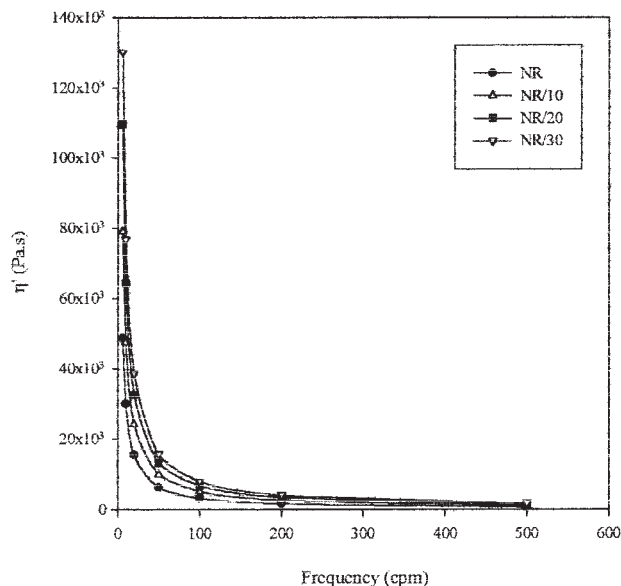
Figure 2 Elastic torque versus frequency of uncured NR/Cel II compositions at 100°C; 0.5°.

Figure 4 Real dynamic viscosity versus frequency of uncured NR/Cel II compositions at 100°C; 0.5°.

In Figures 2, 3, and 4 the large influence of regenerated cellulose on the rheological parameters of these compositions, indicative of a good filler dispersion in the elastomeric matrix, can be seen. It is interesting to note that the behavior for all NR/Cel II compositions is similar to that for natural rubber without filler, between 100 and 500 cpm.

Tan δ response at different frequencies is presented in Figure 5. As tan δ is defined as the ratio between S'' and S', increasing frequencies will lead to decreasing values of tan δ, with no significant differences in the range 100 to 500 cpm.

Unlike a literature report,[5] a good correlation was obtained by plotting elastic torque and Mooney viscosity for these natural rubber compositions (Fig. 6). A linear relationship between these two properties was obtained, with no frequency dependence and 0.98 as the calculated correlation coefficient, which may be an indication of filler distribution at a molecular level.

Figure 7 presents an excellent second-order correlation between S' and Mooney relaxation of the NR compositions, differently from data reported in the literature but corroborating the observation in the previous paragraph.

Figure 3 Viscous torque versus frequency of uncured NR/Cel II compositions at 100°C; 0.5°.
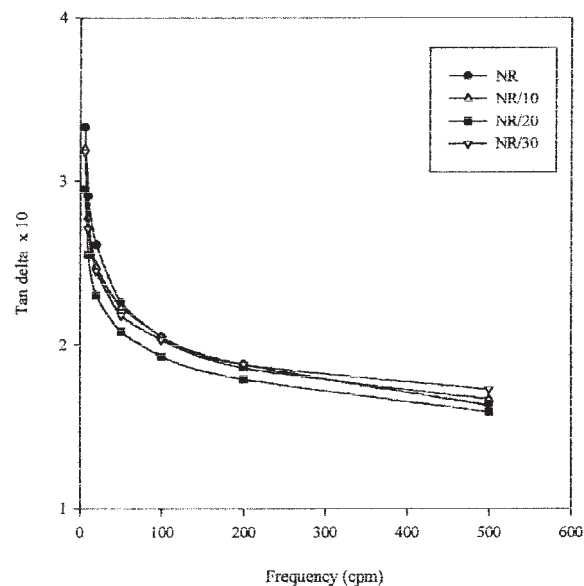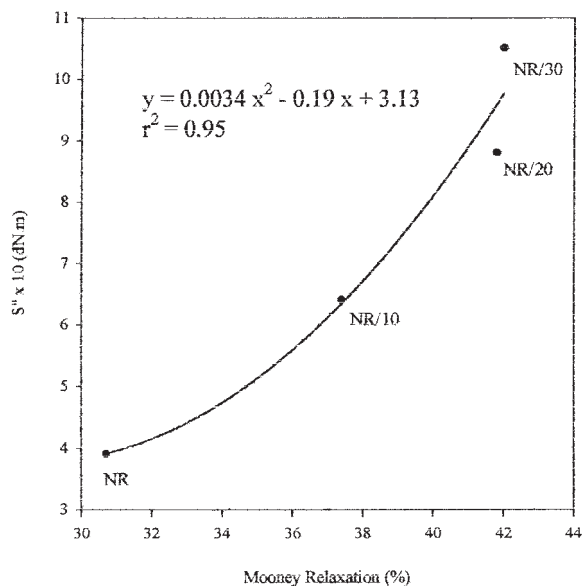

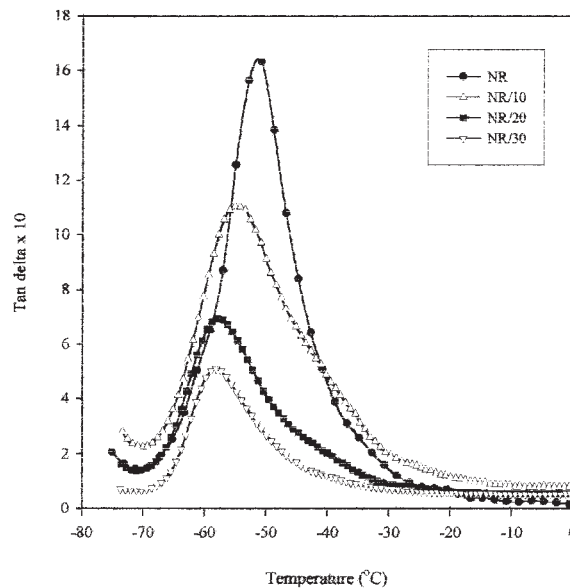**Figure 5** Tan delta versus frequency of uncured NR/Cel II compositions at 100°C; 0.5°.
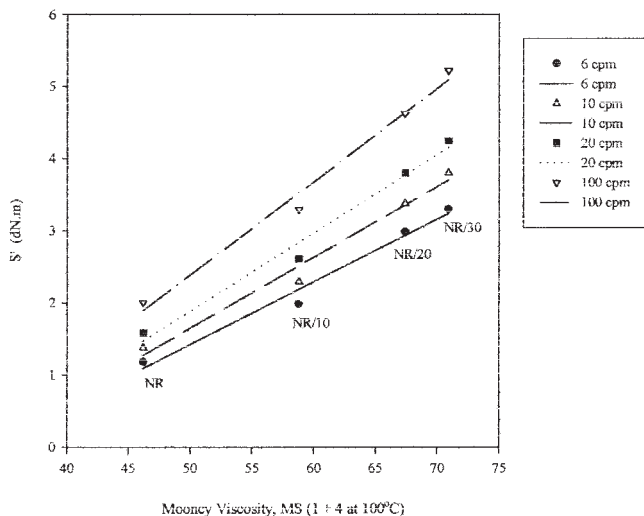
Figure 6 Elastic torque versus Mooney viscosity of uncured NR/Cel II compositions at 100°C; 0.5°.

DMTA data were also evaluated and are shown in Figures 8 and 9. Figure 8 presents the response of tan δ at different temperatures for the NR/Cel II compositions. The increasing incorporation of regenerated cellulose decreases the T_g of natural rubber, which indicates that, in this case, the rubber chains might be forced apart by the presence of this filler. This results in higher flexibility and, consequently, lower T_g. There is also a large increase in the elastic modulus of the filled compositions (Fig. 9), when compared to the unfilled natural rubber. In the glassy region this effect is small, considering all filled compositions, and becomes more pronounced upon entering the transition and rubbery regions.
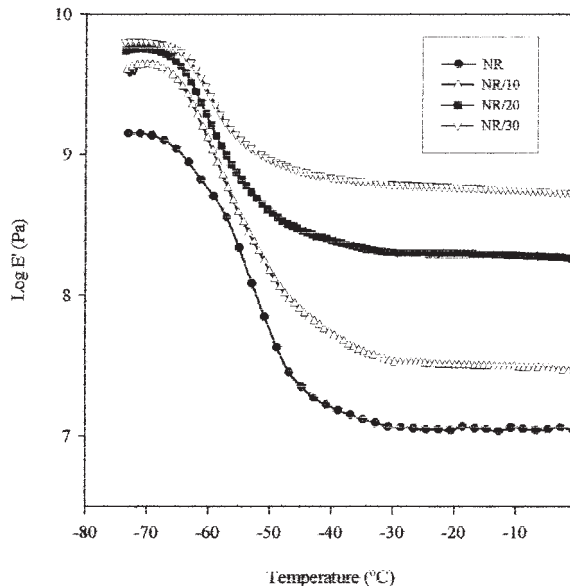


Figure 8 Tan delta versus temperature of uncured NR/Cel II compositions.

The value of tan δ_{max} and the shape of the tan δ curve,[13,19] respectively, lower and narrower, in the presence of regenerated cellulose (Fig. 8), as well as the considerable drop in $\Delta E'$ [20] (Fig. 9), also suggest a good dispersion of the filler throughout the elastomeric matrix, as discussed earlier.

It is interesting to observe that regenerated cellulose promoted an increase in the elastic modulus of the natural rubber compositions and a decrease in T_g, which indicates some sort of interaction between rubber and filler.

Figure 7 Viscous torque versus Mooney relaxation of uncured NR/Cel II compositions at 100°C; 0.5°; 6 cpm.

Figure 9 Elastic modulus versus temperature of uncured NR/Cel II compositions.
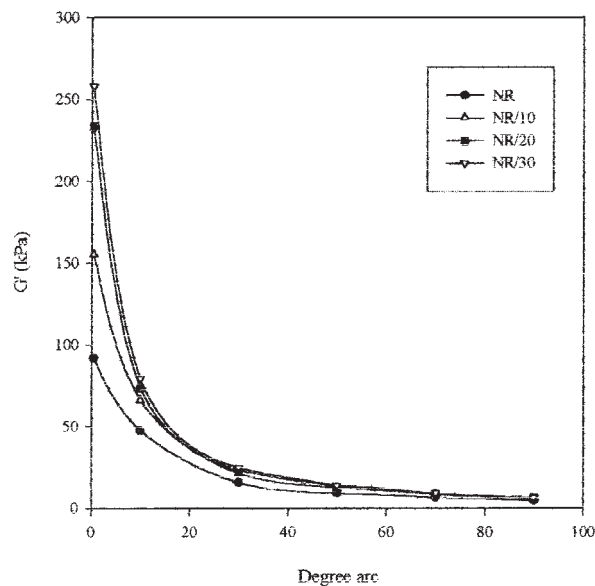
Figure 10 Storage shear modulus versus strain sweep of uncured NR/Cel II compositions at 100°C; 6 cpm.

Figure 11 Elastic torque versus strain sweep of uncured NR/Cel II compositions at 100°C; 6 cpm.
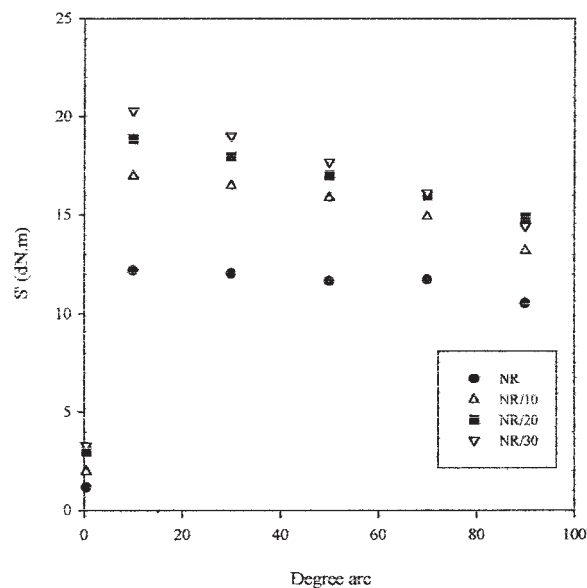
The strains available for testing in the RPA can be separated in two major groups: low and high strains, which commonly correspond to the linear and nonlinear viscoelastic regions, respectively.

Linear viscoelasticity occurs when the ratio of stress to strain is a function only of time and temperature. This ratio is not a function of the strain magnitude itself. Generally, this behavior is exhibited for a polymer below a particular strain level called the critical strain.[4]

Nonlinear viscoelasticity is observed when the ratio of stress to strain changes in a strain sweep, under constant conditions of temperature and frequency. Most industrial processing applications are in the nonlinear viscoleastic region for both raw rubber and compounded stocks. Therefore, rheological behavior investigations in the nonlinear region is a very important matter in predicting downstream processability in the industrial plant.[4]

Figure 10 shows G' response for a high strain sweep applied to these natural rubber compositions and Figure 11 presents the elastic torque response (S') for the same high strain test shown in Figure 10. By using S' instead of G', larger differences are seen at high strains. Typically, S' passes through a maximum with increasing strain. The torque response (S' or S'') was more suitable for studying rheological changes occuring at high strains in the nonlinear viscoelastic region. For the NR/Cel II compositions studied, all showed maximum S' at the same strain value (Fig. 11), differently from what is found in the literature.[4]

Figure 12 presents the S'' response from a high strain sweep applied to the investigated compositions. Viscous torque is higher than elastic torque (Fig. 11). In both cases, NR/Cel II compositions show similar behavior to natural rubber without cellulose.

Figures 10, 11, and 12 show that regenerated cellulose does have an effect on the processability of natural rubber since the profile of the rheological behavior is not modified. In all cases the values for the filled compounds are superior, which may be an indication that a good rubber–filler interaction has been obtained from the mixing technique used, that is, with the components in the liquid form rather than as solids, as traditionally done.
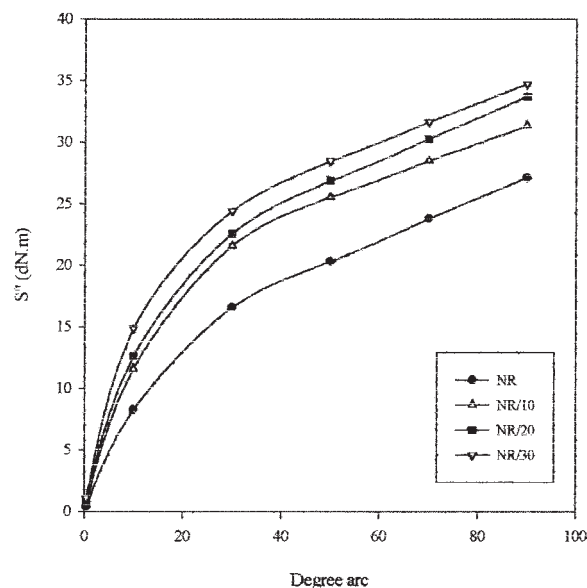
Figure 12 Viscous torque versus strain sweep of uncured NR/Cel II compositions at 100°C; 6 cpm.
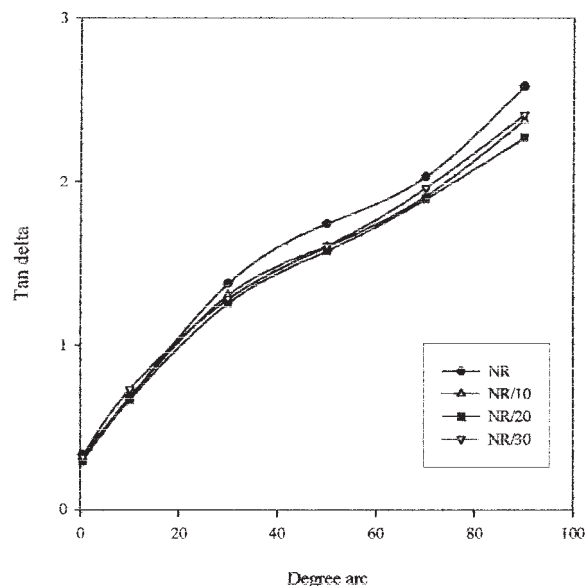
Figure 13 Tan δ versus strain sweep of uncured NR/Cel II compositions at 100°C; 6 cpm.

The response of tan δ to different strain conditions can be seen in Figure 13. The values of tan δ go up with increasing strains but there are no differences among the compositions studied. The slope of tan δ curves is constant up to 30° and then decreases from this point up to 70 ° arc. This change in the slope might be due to chain entanglements or possibly strain crystallization effects undergone by natural rubber. High strains are necessary to overcome chain entanglement effects (common with natural rubber). These effects are particularly noticeable with gum stocks, when no filler is incorporated. Once again, regenerated cellulose does not cause any change in the behavior of natural rubber.

CONCLUSIONS

The cocoagulation process used to prepare the uncured natural rubber and regenerated cellulose compositions promoted an excellent molecular dispersion of the filler in the elastomeric matrix, which could be seen from the rheological and dynamic results presented. In addition, regenerated cellulose has a large influence on the natural rubber viscoelastic properties, without changing the profile of its rheological behavior.

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