

Mechanical and Dynamical Mechanical Properties of Chloroprene Rubber and Cellulose II Composites

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ABSTRACT: Vulcanized composites of chloroprene rubber (CR) with cellulose II (Cel II) as a filler were investigated. Cel II, obtained by the coagulation of cellulose xanthate, was incorporated in the rubber by the traditional method. The filler content varied from 0 to 30 phr. For comparison purposes, carbon black (CB)–CR composites were also studied. The CB amount varied from 0 to 45 phr. The mechanical and

dynamic mechanical properties were determined, and the CR composite containing 20 phr of Cel II showed the best set of properties. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2425–2430, 2004

Key words: composites; rubber; fillers; mechanical properties

INTRODUCTION

Chloroprene rubber (CR), the world's first commercial synthetic rubber, became available to the rubber industry in 1935 and rapidly established a firm position as an important raw material, first in the United States, its country of origin, and very soon throughout the world. After its commercial introduction, CR came to be known by the generic name *neoprene*, a term still generally used.^{1,2}

Properly compounded, CR resists sun, ozone, and weathering while remaining tough and durable. CR can stand cold environments up to -25°C and still performs well under a heat of 93°C , but specially formulated compositions permit service at temperatures as low as -55°C . In addition, the flame resistance of CR products can be enhanced by special compounding. Typical applications of this rubber include joint seals, bridge bearings, all-purpose hoses, conveyor belting, cable sheathing, automotive molded parts, and electrical connectors.^{2–5}

For adhesive applications, CR is prominent among elastomers because of its combination of polarity and crystallinity. The polarity gives a greater versatility in bonding a wide range of substrates, and the crystallinity gives improved strength. This latter property has made CR an attractive material for light applications.³ However, because CR has a high cost, the use of white fillers has become an alternative for the

achievement of CR articles with the desirable combination of feasible cost and properties. Cellulose is a white filler and a good choice for use in CR.

Recent research and development fields have focused on new materials based on cellulose as a filler. The growing willingness to develop new cellulosic compounds comes, of course, from the fact that cellulose, as the main constituent of the cell wall of woody plants, is renewable. However, from the polymer chemist's point of view, the unique structure of the polymer is combined with such promising properties as⁶

- Hydrophilicity
- Biocompatibility
- Stereoregularity
- Multichirality
- Reactive hydroxyl groups (polyfunctionality)
- Last, but not least, the ability to form superstructures (e.g., helix formation, cholesteric mesophases, Langmuir–Blodgett layers)

In the rubber field, treated cellulosic fibers were developed under the commercial name Santoweb. These available commercial fibers follow: (1) Santoweb D contains a methylene acceptor as additive and needs a bonding agent (a methylene donor) for use in natural rubber, styrene–butadiene rubber, butadiene rubber, and CR; (2) Santoweb DX is same as Santoweb D and is for use in rubbers but without a bonding agent; (3) Santoweb H contains a methylene acceptor as additive and needs a bonding agent (a methylene donor) for use in ethylene–propylene–diene methylene and isobutylene–isoprene rubber elastomers; and (4) Santoweb W is for use in poly(vi-

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TABLE I
Characterization of the Rubber and the Fillers

Material	Supplier	Characteristic
CR	Du Pont do Brazil S/A	Type W $M_w = 435,400$; $M_w/M_n = 4.4$ Mooney viscosity ^a = 46-ML (1 + 4) at 100°C 1,4- <i>trans</i> ; 1,4- <i>cis</i> ; 1,2; 3,4 (% w/w) = 89.3, 8.4, 0.6, and 1.6, respectively
Cel II	Vicunha Têxtil S/A	Surface area = 0.16 m ² /g
CB	Copebrás Indústria e Comércio S.A.	Type N762 Surface area = 30 m ² /g

M_w = weight-average molecular weight; M_n = number-average molecular weight.

^a ASTM D 1646. 46-M is the Mooney viscosity number, L indicates the use of the large rotor, 1 is the time in minutes that the specimen was permitted to warm in the machine before the motor was started, 4 is the time in minutes after the motor was started at which the reading was taken, and 100°C was the temperature of the test.

nyl chloride), acrylonitrile-butadiene rubber, and nonblack rubber compounds; it contains no bonding agent. With the exception of Santoweb W, all of the fibers need discoloration.⁷

Cellulose I and cellulose II (Cel II) have identical chemical compositions but different degrees of crys-

tallinity, 0.485 and 0.312%, respectively.⁸ In previous articles,⁹⁻¹¹ Cel II has been reported to impart good reinforcing behavior to several elastomers. In those studies, the incorporation of the filler in the rubber was performed with an elastomeric latex with cellulose xanthate.

In this work, Cel II (also called *regenerated cellulose*), obtained in powder form by the coagulation of an aqueous solution of sodium cellulose xanthate, was used. This last product is part of rayon viscose industrial production.¹² Different from Santoweb, this type of cellulose is yellowish, transparent, and superficially untreated. Cel II was incorporated in CR on a two-roll mill, and the filler content varied from 0 to 30 phr. The aim of this work was to study the influence of Cel II on the mechanical and dynamic mechanical properties of the CR matrix. For comparison purposes, carbon black (CB)-CR composites were also investigated. The CB amount varied from 0 to 45 phr.

EXPERIMENTAL

The raw rubber was characterized by Mooney viscosity, molecular weight, polydispersity, and microstructure. Mooney viscosity was determined according to ASTM D 1646 in a Monsanto MV 2000 viscometer (St. Louis, MO). The molecular weight and polydispersity were determined by size exclusion chromatography in

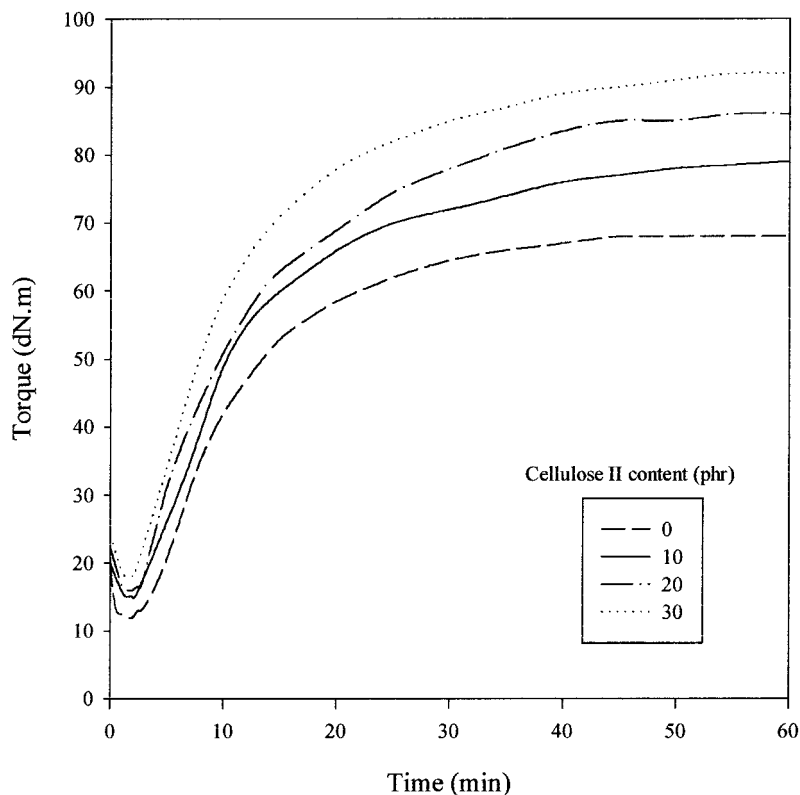


Figure 1 Rheometric curves of CR-Cel II composites.

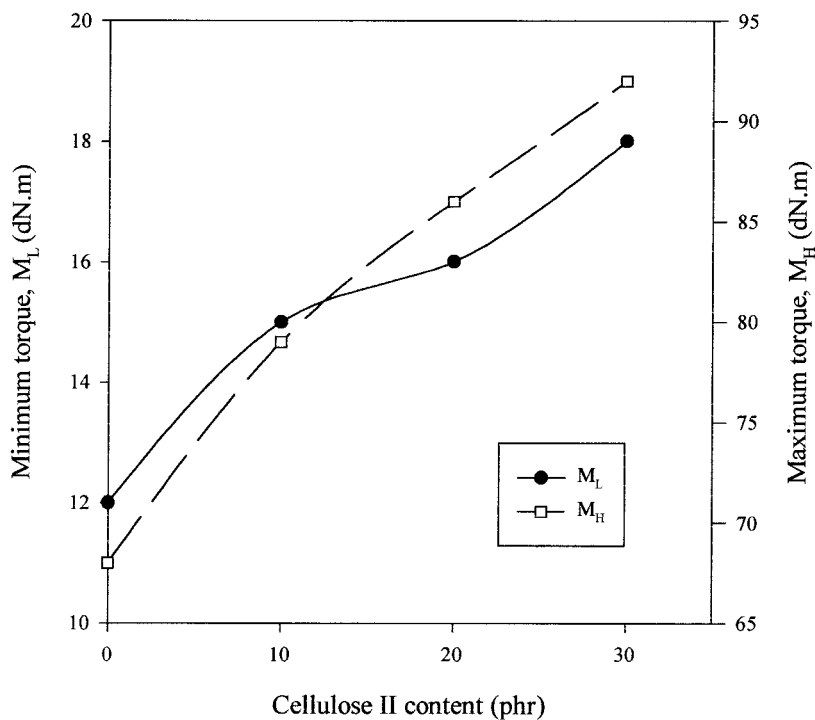


Figure 2 M_L and M_H values of CR-Cel II composites.

a Waters 600E gel permeation chromatograph (Milford, MA) with tetrahydrofuran as the solvent. The calibration curve was taken with monodisperse polystyrene standards. The microstructure of CR was de-

termined by $^1\text{H-NMR}$ at room temperature with a Varian INOVA-300 (7.1T) NMR spectrometer (Palo Alto, CA) operating at 300 MHz for ^1H . The sample was dispersed in *o*-dichlorobenzene (1%) at 80°C. A

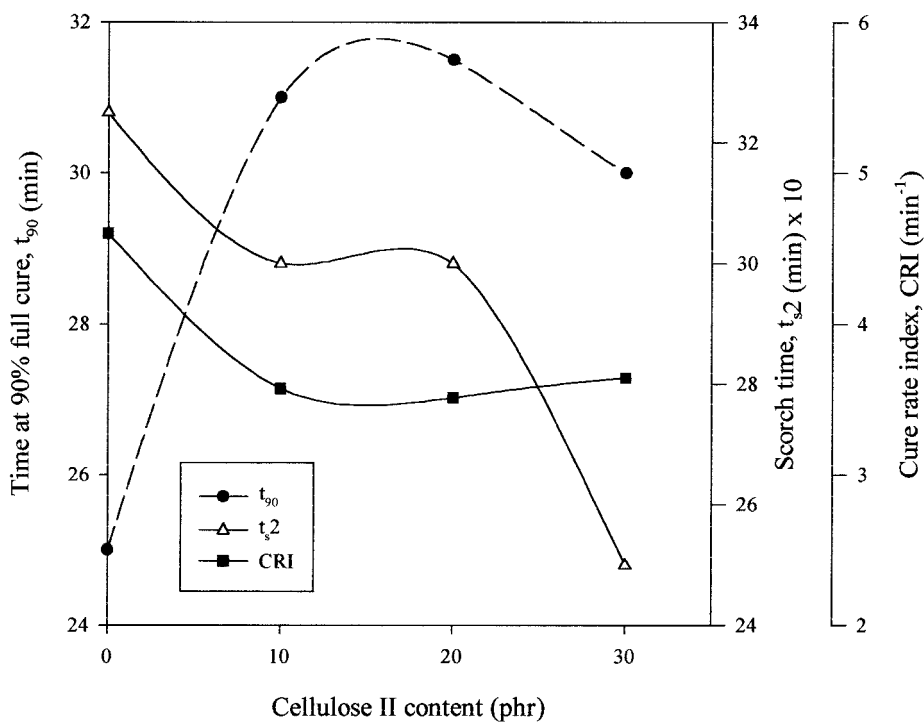


Figure 3 Cure parameters of CR-Cel II composites.

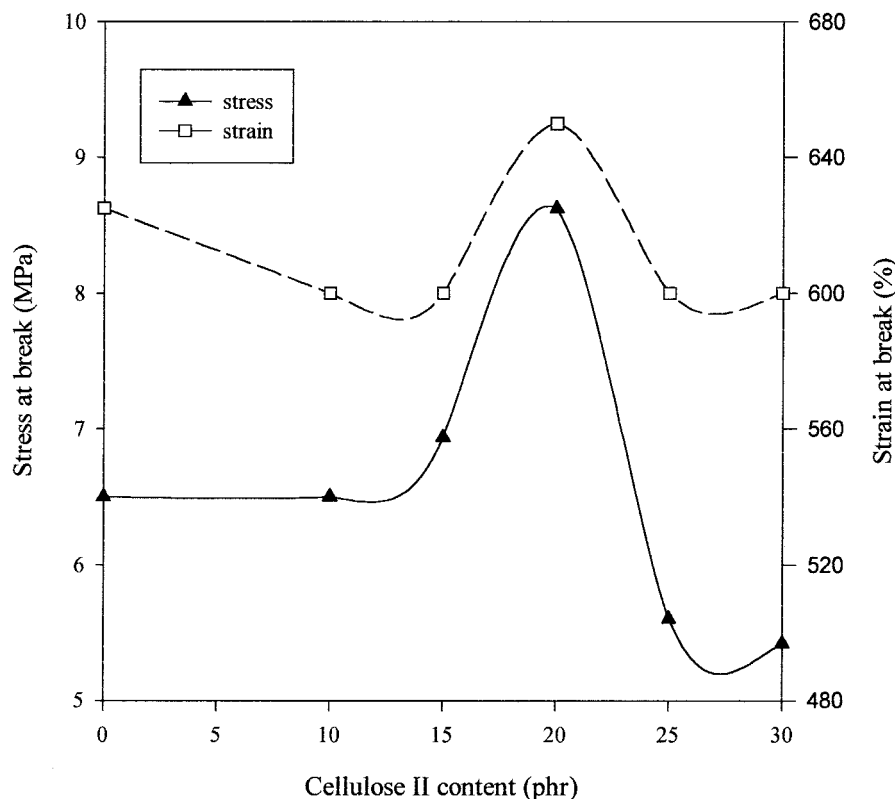


Figure 4 Tensile strength values of CR-Cel II composites.

pulse width of 30° (5 μ s) with acquisition time of 3.3 s was applied, and 256 transients were accumulated. A spectral width of 4.5 kHz was used for data acquisition. Deuterobenzene was the suitable medium used. Cel II and CB were evaluated by the Brunauer-Emmett-Teller surface area. The results are shown in Table I.

CR-Cel II composites were prepared according to ASTM D 3182, and the formulation used followed ASTM D 3190. Cel II was obtained from cellulose xanthate with sulfuric acid (15% w/w) as the coagulating solution. After coagulation, Cel II was washed with water to promote the removal of residual acidity. The product was separated from the aqueous suspension by filtration and then dried in an air-circulating oven at 50°C. Before it was mixed with CR, Cel II was

dried at 50°C for 24 h. The mixtures were prepared in a Berstorff two-roll mill (Hannover, Germany) at 50°C with a friction ratio of 1 : 1.25.

The cure parameters were determined according to ASTM D 2084 on an oscillating disk rheometer (model 100S, Monsanto), operating at 150°C and with a 3° arc. Vulcanization was carried out at 150°C with cure times (t_{90} 's) established previously in the rheometer in an electrically heated hydraulic press. From the resulting vulcanized sheets, samples for the mechanical tests were cut.

Tensile and tear strength tests were carried out on an Instron universal machine (model 1101) (Canton, MA) according to ASTM D 412 and D 624, respectively, at room temperature and a crosshead speed of 500 mm/min. Hardness data was determined according to ASTM D 2240.

TABLE II
Mechanical Properties of the CR/CB Composites

CB content (phr)	Stress at break (MPa)	Strain at break (%)	Tear strength (kN/m)
0	6.5	625	24
10	10.1	525	35
20	13.4	450	41
30	17.1	400	46
40	19.6	350	42
45	18.3	300	44

TABLE III
Mechanical Properties of CR/Cel II Composites

Cel II content (phr)	Tear			
	Hardness (Shore A)	strength (kN/m)	Compression set (%)	Abrasion loss (g/1000 cycles)
0	42.5	24	10.53	0.15
10	48	28.9	10.18	0.25
20	53	26.3	10.09	0.65
30	61	21.5	8.26	1.06

Other mechanical properties, compression set and abrasion resistance, were also determined according to ASTM D 395 and D 1044, respectively.

Dynamic mechanical thermal analyses (DMTAs) were carried out according to ASTM D 4065 in a Rheometric Scientific model MK III dynamic mechanical thermal analyzer (New Castle, DE) with a mode of deformation geometry, single cantilever bending, a heating rate of 2°C/min, a frequency of 1 Hz, and the temperature ranging from -80 to 20°C.

RESULTS AND DISCUSSION

Figure 1 presents the rheometer curves for the CR-Cel II composites under investigation. The presence of Cel II increased the minimum torque (M_L), maximum torque (M_H), and t_{90} and decreased the scorch time (t_{s2}). The effects of the cellulosic filler on these parameters are better shown in Figures 2 and 3.

As shown in Figure 2, the behaviors of the torque parameters, either M_L or M_H , were similar; that is, they increased as the level of Cel II increased, and the effect was more pronounced for M_H . Because M_L represented the effective viscosity of the unvulcanized blends, the results indicated that the incorporation of Cel II did not facilitate the processing of CR.

Figure 3 presents the cure parameters of CR-Cel II composites. The t_{s2} for all of the CR-filled composites decreased as the Cel II content increased compared to unfilled CR. The decrease in t_{s2} values was related to the basic character of Cel II, which was responsible for

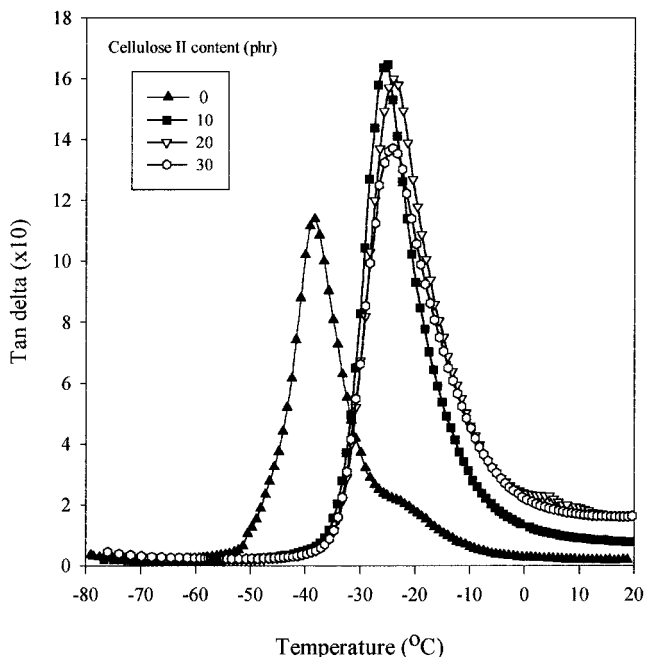


Figure 5 Tan δ versus temperature for CR-Cel II composites.

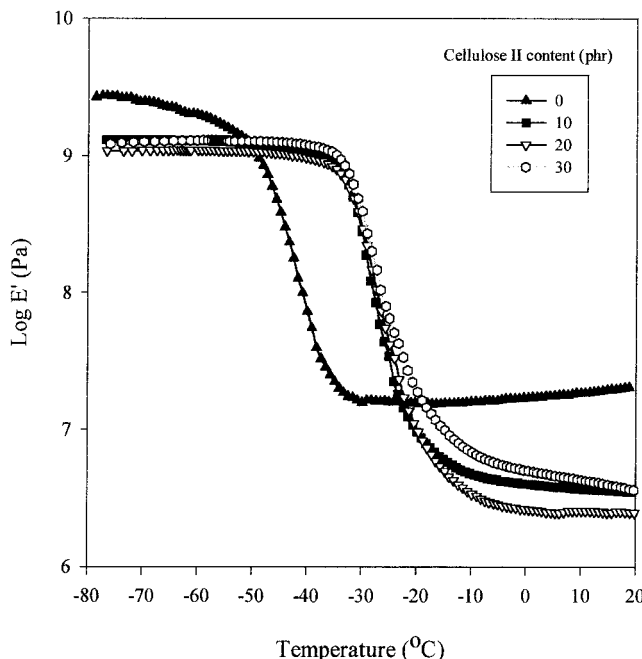


Figure 6 E' versus temperature for CR-Cel II composites.

the shorter times that the filled composites needed to begin the cure reaction.

As also shown in Figure 3, the values of cure rate index (CRI) for all of the filled composites were lower than that for the unfilled one. The CRI is a parameter proportional to the average slope of the cure rate in the step region ($100/t_{90} - t_{s2}$). The negative effect of the filler content on the vulcanization may have been due to the poor rubber-filler interaction, which caused a decrease in the reactivity, leading to higher optimum t_{90} 's when Cel II was present as compared to unfilled CR.

Figure 4 shows the tensile strength results of the CR composites studied. It is interesting to note the similar behavior of both properties, stress and strain at break. Both properties were at a maximum for the composite containing 20 phr of Cel II and then decreased to values from this point that were lower than those for the unfilled rubber, with this being more pronounced for the stress at break. From these results, 20 phr was considered the optimum level of Cel II to achieve the best tensile properties when in CR. It was also interesting to observe that the incorporation of Cel II, except for at a level of 20 phr, kept the strain at break constant, independent of the amount.

Different results were found for CR composites with CB, as shown in Table II. The best reinforcement was given by the composite with 40 phr of CB. When we compared the maximum values of stress at break for the composite with CB and Cel II, we observed that the black filler was superior to Cel II, which could be explained by the large difference between the surface

areas of the fillers and also by the well-known CB–CR interaction. Nevertheless CR–Cel II composites presented some advantages such as (1) a light color, (2) a constant level of strain at break, and (3) a low cost compared to pure CR.

Mechanical properties of the CR–Cel II composites are shown in Table III. The crescent incorporation of Cel II in CR caused an increase in hardness as expected, which was indicative of a higher stiffness in the filled CR composites, which was confirmed by the increase in M_H values (Fig. 2). The compression set decreased as Cel II content increased due to the lower flexibility of the polymeric chains in the filled composites caused by the addition of the filler. Abrasion resistance was not favored by the presence of Cel II when compared to the unfilled CR, probably because of the large particles of Cel II, which were removed from the surface when the material was subjected to wear during the test. The tear strength was at a maximum for the composite containing 10 phr of Cel II. Interestingly, the dependence of both tensile strength and tear strength on the filler content followed different patterns for Cel II and CB (Tables II and III), which is in agreement with the literature.¹³

Tan δ and the elastic modulus (E'), obtained from DMTA, are shown in Figures 5 and 6, respectively. As shown in Figure 5, CR had two relaxations at -40 and -20°C , which were related to the glass-transition temperature (T_g) and crystallization temperature, respectively. All CR–Cel II composites presented a T_g shifted to higher temperatures around -20°C . The presence of cellulosic filler restrained the mobility of the rubber chains, as was expected. The tan δ values of CR–Cel II composites (Fig. 5) were higher than that for the unfilled CR, which was related to the lowest E' values of the filled composites (Fig. 6). The effect of the Cel II was very significant in the E' of the filled composites, mainly in the transition region and the rubbery plateau. The E' values of the filled composites suggested a noneffective dispersion of the filler in the elastomeric matrix and low crosslinking densities for these composites.

The DMTA results corroborated the mechanical properties of the CR–Cel II composites studied.

CONCLUSIONS

CR and Cel II composites were evaluated, and the composite containing 20 phr of filler achieved the best set of properties. Cel II was a new filler and showed good mechanical properties, although they were lower than those of CB. Nevertheless, Cel II presented some advantages, such as a low cost and the attainment of yellowish composites, and can be thought of as a good alternative for the production of reinforced CR composites.

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