JOURNAL OF MATERIALS SCIENCE **38** (2003) 2415–2422

Mechanical and fractographic behavior of natural rubber-cellulose II composites

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Composites of natural rubber (NR) and cellulose II (Cel II) were prepared by co-coagulation of natural latex and cellulose xanthate mixtures. The influence of increasing amounts of Cel II, varying from 0 to 30 phr, on the mechanical properties was investigated. The topography of the fracture surfaces of tensile, tear and abrasion specimens after testing was observed by scanning electron microscopy (SEM). The fracture surface morphology was correlated with the mechanical properties. As the cellulose II content increases, the materials showed a gradual change in the mechanical properties and in the fracture mechanisms. The composite with 15 phr of Cel II was found to give the best tensile and tear performances. The failure surfaces and the fracture mechanisms of unfilled and filled natural rubber composites depended on the nature of the test-tensile, tear or abrasion. The SEM evaluation of the tensile fracture surfaces was the best observation method to show the effect of cellulose II on the elastomeric matrix.

1. Introduction

Reinforcement of polymers has received a lot of attention due to considerable processing advantages and better performance. In the case of elastomers reinforcement is normally achieved by blending fillers, being carbon black and silica the most important ones. Rubber composites have been studied since the early days of the rubber industry, in the search for reduced cost and specific properties, which are dependent not only upon the matrix properties but also on the filler characteristics [1–3].

In the special case of cellulose acting as filler, the reinforcing efficiency is related to the nature of cellulose itself, in particular to its crystallinity, which in turns is dictated by its molecular weight [4]. Cellulose II is obtained from xanthate industrial process, as described earlier [5, 6].

There are two basic modes of failure in macromolecular materials: brittle and ductile. The mechanical behavior of polymeric materials can be explained based on the failure mode and the nature of the fracture surface. Fractography, a direct observation of the fracture surfaces, provides information about morphology of the fracture surfaces and fracture mechanisms [7].

In this work, composites of natural rubber and cellulose II were prepared by co-coagulation of natural latex and cellulose xanthate mixtures. The influence of increasing amounts of cellulose II, varying from 0 to 30 phr, on the mechanical properties was studied. The fracture mechanisms of the composites subjected to different modes of failure such as tensile, tear and abrasion, were investigated by scanning electron microscopy (SEM). Attempts were taken to correlate the fracture surface morphology with the mechanical properties.

2. Experimental

Natural rubber latex (type 1; total solids, 61.6%; dry rubber, 60.1%) and cellulose xanthate (cellulose, 8.0%; total sulfur, 2.1%; NaOH, 4.9%; $\bar{M}_w = 750{,}896$; $\bar{M}_w/\bar{M}_n = 1.7$) were the raw materials. NR/Cel II composites were prepared by co-coagulation process, as described elsewhere [8]. Mixing was carried out in a Berstorff two-roll mill at 55°C and the formulation followed ASTM D 3184 [9a]. The vulcanization at optimum cure times was carried out at 140°C and 3 MPa in an electrically heated hydraulic press.

Tensile and tear tests were performed at room temperature in a model 1101 Instron universal testing machine with a cross-head speed of 500 mm/min, using specimens punched out from the moulded vulcanized sheets. Tensile testing followed ASTM D 412 [9b], using dumb-bell specimens. The tear strength was measured with an unnotched 90° angle test specimen according to ASTM D 624 [9c]. After the tests, both fragments of the specimens were collected for fracture analysis.

The abrasion test was carried out in a model 503 Taber Abrasion Tester according to ASTM D 1044 [9d]. A H 22 grade aluminum oxide abrasive produced by Taber Industries was used. For the SEM analysis two samples for each abraded specimen, one located 180° in relation to the other, were cut.

A JSM 5800LV model JEOL scanning electron microscope was used for fractographic analysis. The study of the failure mechanisms was carried out by direct observation of the topography of fracture surfaces of the tensile, tear and abrasion test specimens. The samples were sputter-coated with gold in a vacuum chamber before examination.

3. Results and discussion

3.1. Mechanical properties

The tensile and tear properties are presented in Fig. 1. From the results of tensile strength, it can be observed that, compared to the unfilled natural rubber, the highest value of the stress at break is achieved by the composite containing 15 phr of cellulose II, while the strain at break decreases more accentuately for filler contents above 15 phr. The tear strength results show that the maximum value for this property was achieved with 15 or 20 phr of the filler. For filler contents of 10 and 30 phr the values are identical and smaller than that for the unfilled NR. The limit content of cellulose II

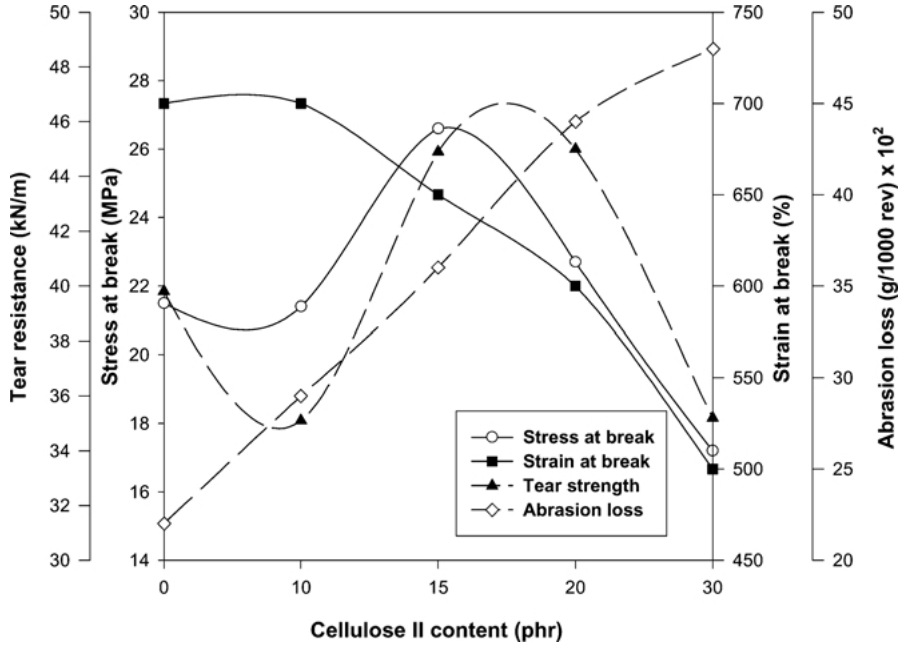


Figure 1 Mechanical properties of unfilled natural rubber and NR/Cel II composites.

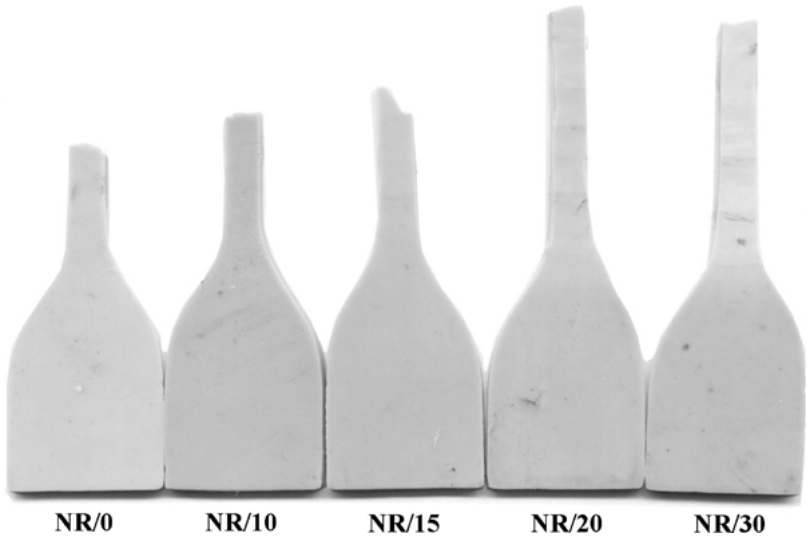
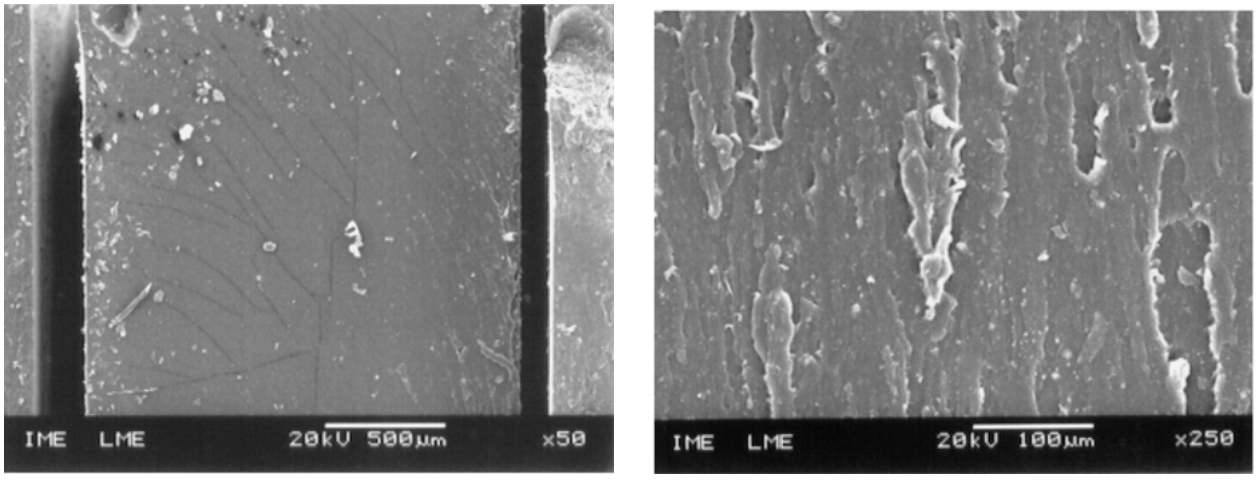


Figure 2 Macroscopic view of the tensile specimens of unfilled natural rubber and NR/Cel II composites, after testing.

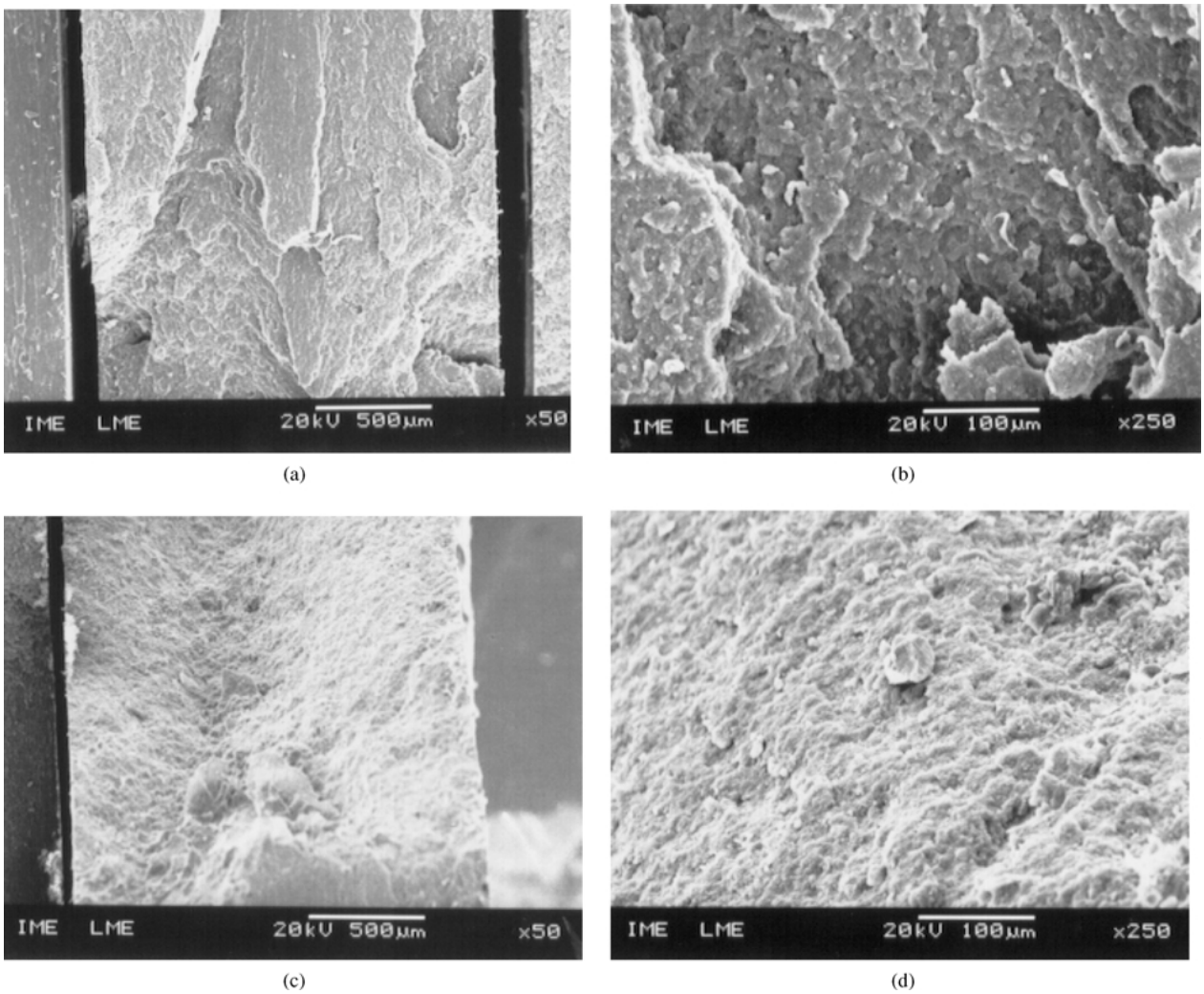


(a) (b)

Figure 3 SEM photomicrographs of tensile fracture surfaces of unfilled natural rubber: (a) general view and (b) a detail of the central area.

for good tensile and tear characteristics is in the 15 to 20 phr range.

Fig. 1 also shows that abrasion loss increases with the incorporation of cellulose II indicating a reduction in wear resistance. According to the literature [10], additional crosslinks (physical) apparently introduced into the matrix by reinforcing fillers are different from chemical crosslinks, which consist of sulfur bridges or covalent carbon-carbon bonds. Abrasion resistance is increased by reinforcing fillers and reduced by chemical crosslinks. It can therefore be concluded that the "crosslinks" introduced by reinforcing fillers



(a) (b)

(c) (d)

Figure 4 SEM photomicrographs of tensile fracture surfaces of NR/Cel II composites: (a) 10 phr cellulose II composite, (b) a detail of (a), (c) 15 phr cellulose II composite, and (d) a detail of (c).

are of a mobile nature, allowing more creep and involving frictional energy dissipation [10]. Then, the results of abrasion loss obtained suggest chemical crosslinks, such as sulfur bridges, whose formation was somehow favoured by the presence of cellulose II because this filler does not chemically compete with the vulcanization system.

3.2. Scanning electron microscopy

3.2.1. Tensile test

Fig. 2 presents a general macroscopic view of the tested tensile specimens showing clearly changes in the behavior of the tensile fracture. All specimens, except for the 15 phr of filler, present a normal fracture, while the one containing 15 phr shows a shear fracture. For the samples with the highest levels (20 and 30 phr) of cellulose II some stress whitening phenomenon is observed in the region between the bench-marks in the lengthwise direction, which reflects the ability of the material to undergo some plastic deformation.

Figs 3 to 5 present SEM photomicrographs of the fracture surfaces of the unfilled and filled composites after tensile tests. In none of them, a distinct phase separation is observed. However, the samples show significative modifications in the topographic aspects of the failure surfaces and in the fracture mechanisms. By adding cellulose II, the fracture topography changes from a completely smooth fracture, of a rubbery nature, to a rough surface with a typical plastic nature. This change indicates the occurrence of a transition in the tensile fracture mechanism. The unfilled NR specimens presents a typical tensile fracture with a network of surface cracks (Fig. 3a), as expected. Observations at higher magnification (Fig. 3b) show flat fracture surfaces with ragged zones, indicating that NR failed through a typical elastomeric fracture mechanism. As cellulose II content increases the samples lose their rubbery nature and begin to show characteristics related to a plastic fracture mechanism. However, the failure mechanisms for each composite are quite different. For the samples with 10 phr (Fig. 4a and b) the fracture surface is relatively smooth with tear ridges and plastic deformation areas, characterizing a partially ductile behavior. This behavior is very close to that of the unfilled NR. The presence of flat regions limited by rivers suggests that an intercellular type of fracture has occurred. Samples containing 15 phr of cellulose II (Fig. 4c and d) exhibit a failure by shear yielding with local plastic deformation and dimples, which characterize a typical ductile fracture mechanism. The composites with 20 and 30 phr present fracture surfaces with similar

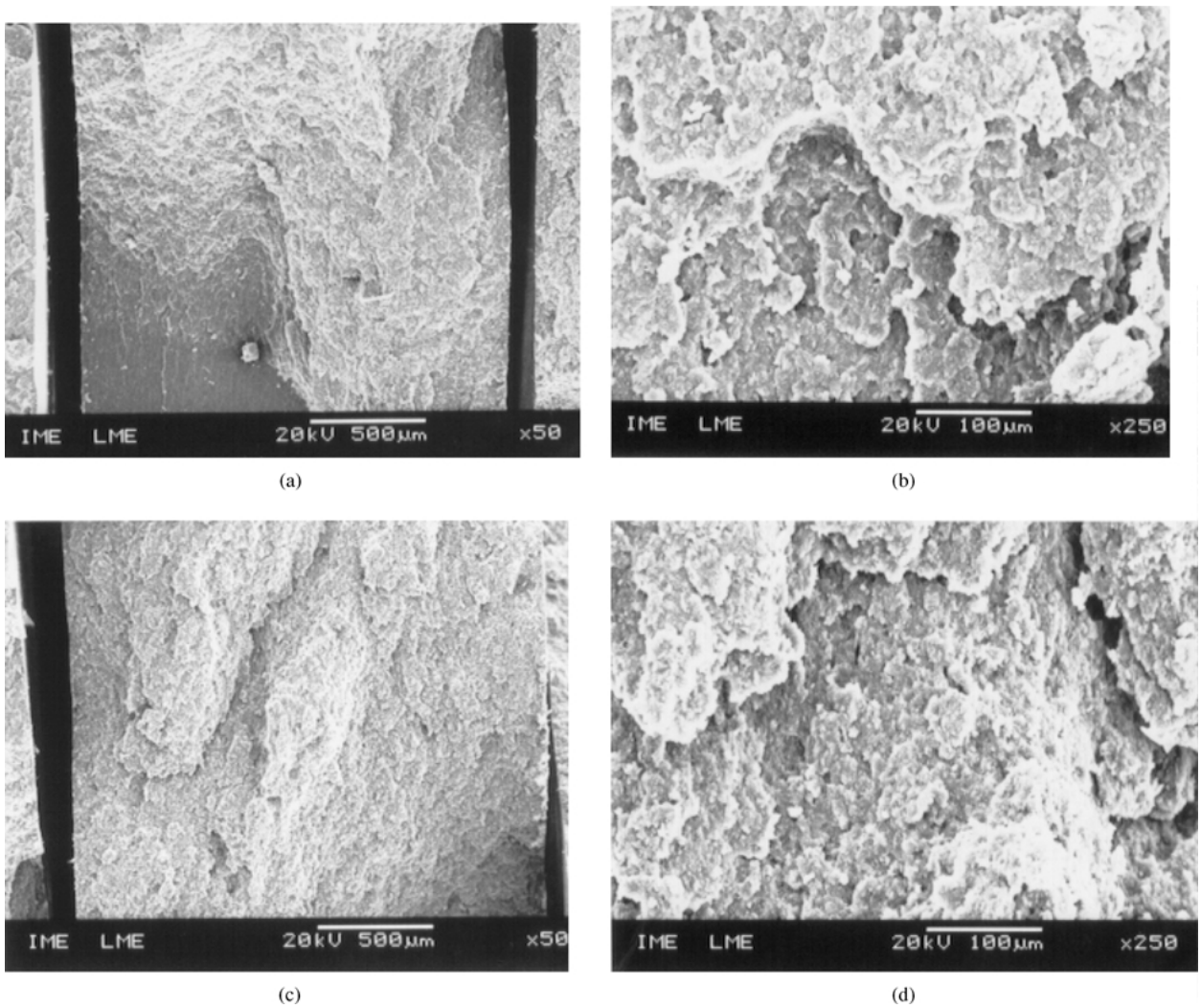


Figure 5 SEM photomicrographs of tensile fracture surfaces of NR/Cel II composites: (a) 20 phr cellulose II composite, (b) a detail of (a), (c) 30 phr cellulose II composite, and (d) a detail of (c).

microscopic features (Fig. 5), with rough surface, ridges and holes, characteristic of a plastic fracture mechanism as indicated by the macrocospic whitening region.

3.2.2. Tear test

Figs 6 to 8 present SEM photomicrographs of the fracture surfaces of composites after tear tests. As cellulose II content increases, the tearing features change from a relatively smooth tearing in the unfilled material to a discontinuous stick-slip process in the 15 phr filled material. The fractography of the unfilled NR shows a smooth fracture surface with a main slip line, a characteristic aspect of a typical brittle fracture (Fig. 6a and b). The 10 phr samples show flat fracture surfaces with branched and broken shear zones (Fig. 6c) and

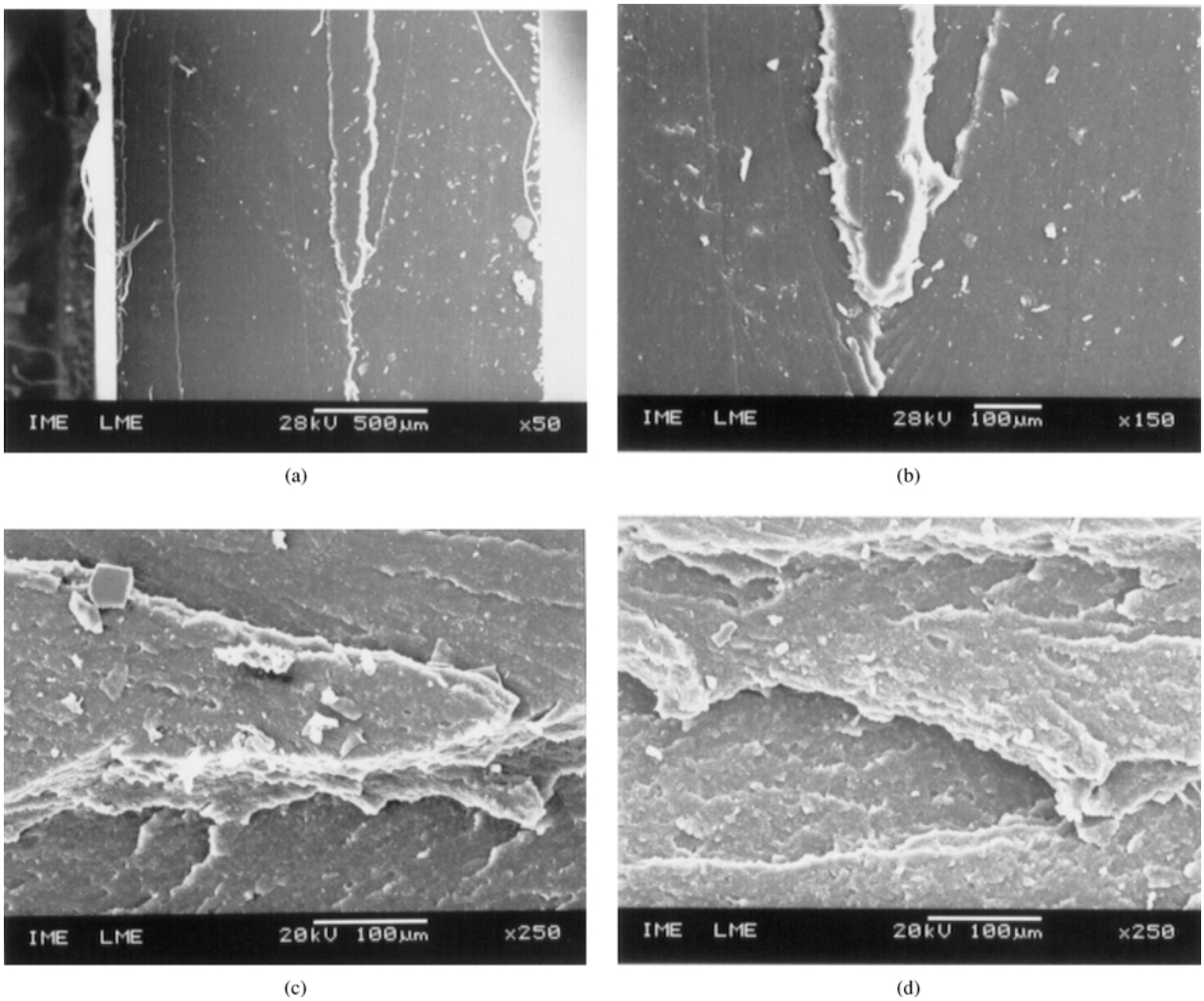


Figure 6 SEM photomicrographs of tear fracture surfaces of unfilled natural rubber and NR/Cel II composites: (a) unfilled natural rubber, (b) a detail of (a), (c) 10 phr cellulose II composite, and (d) a detail of (c).

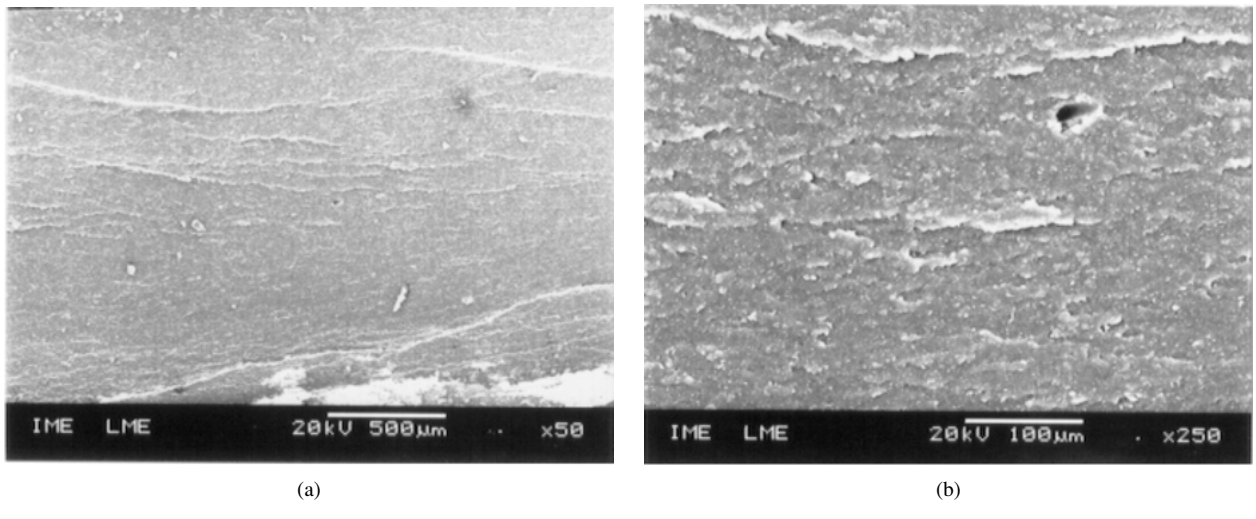


Figure 7 SEM photomicrographs of tear fracture surfaces of 15 phr cellulose II composite: (a) general view and (b) a detail of (a).

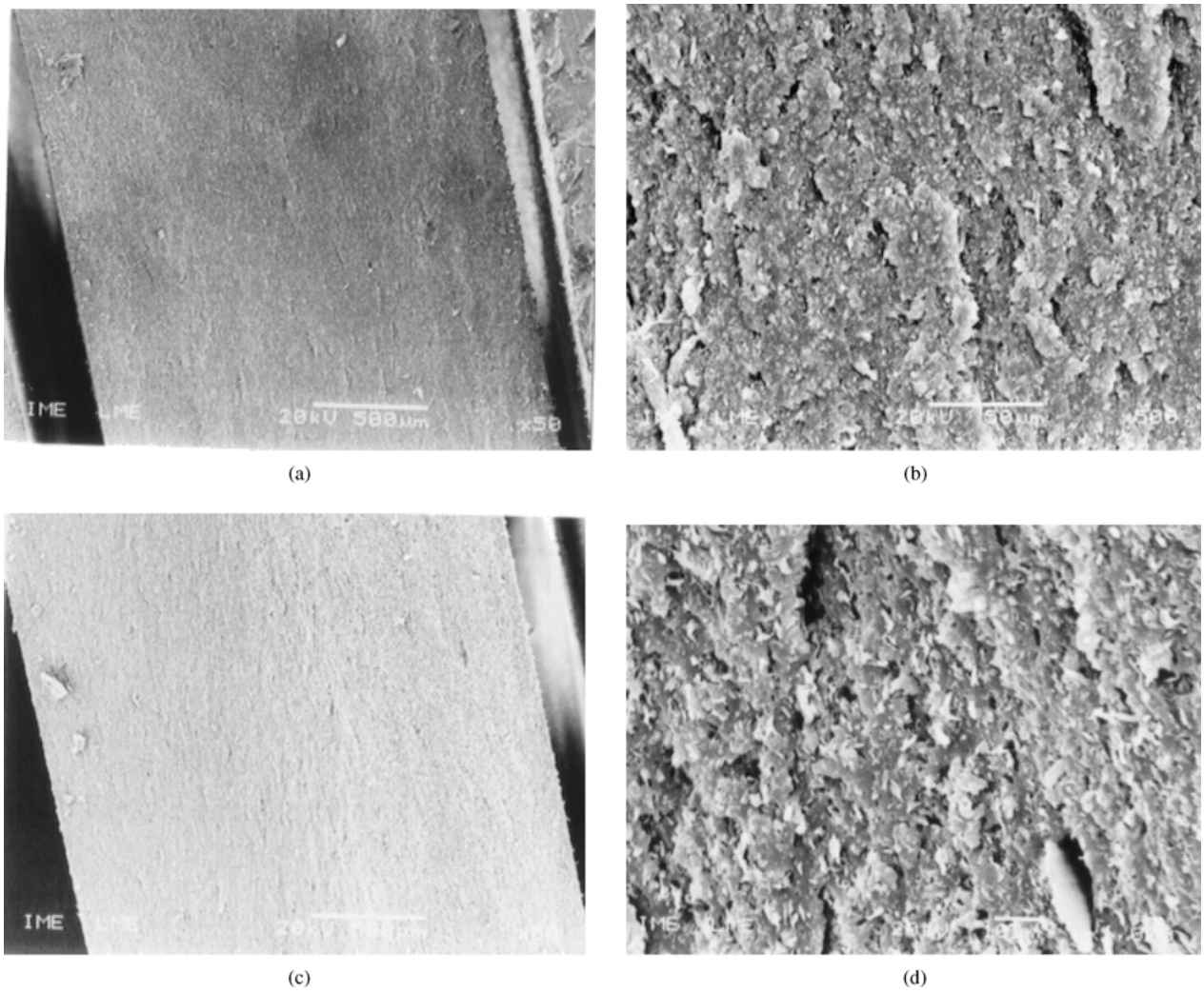
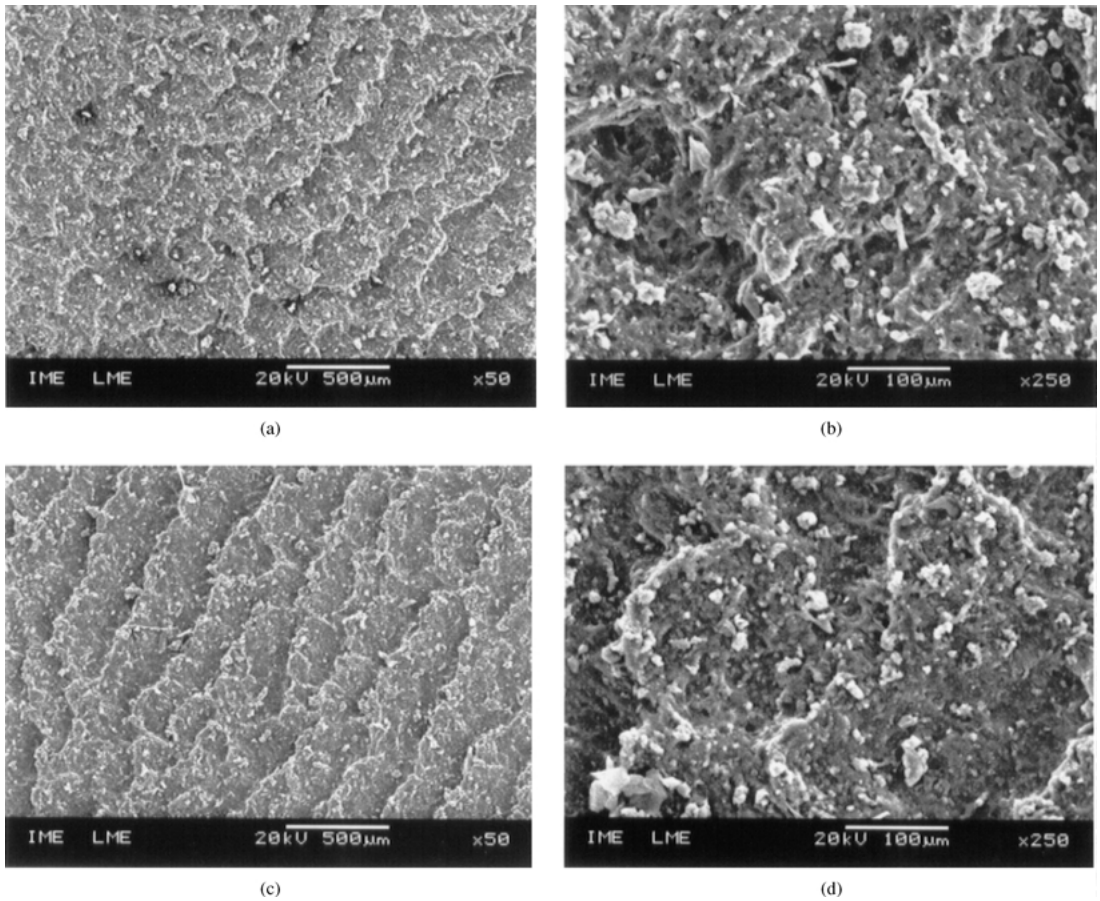


Figure 8 SEM photomicrographs of tear fracture surfaces of NR/Cel II composites: (a) 20 phr cellulose II composite, (b) a detail of (a), (c) 30 phr cellulose II composite, and (d) a detail of (c).

regions with a more rough fracture surface with a layered structure (Fig. 6d), indicating failure by a fracture mechanism similar to that for the unfilled composite, where the stress dissipation is minimized. Samples containing 15 phr of cellulose II exhibit a fracture surface with a larger number of tear lines propagating by the stick-slip process, which requires high energy for propagation (Fig. 7). The branching of the tear lines indicates a tear deviation and accounts for the highest tear resistance of the 15 phr sample. The increase in the cellulose II content changes the fracture mode remarkably as seen in the SEM fractographs of 20 and 30 phr samples. The fracture surfaces are rough and do not show any tear lines (Fig. 8a and c). The high tear resistance of 20 phr samples can be correlated to the roughness of the surface and to the appearance of a large number of short rounded areas distributed at random (Fig. 8b). The fracture surfaces of the 30 phr samples present large number of agglomerates (Fig. 8d). A low level of rubber-cellulose II interaction causes the agglomerates to come out of the matrix, which act as stress raisers and provide an easy path for propagating the tear, thereby reducing the overall strength of the vulcanizate.

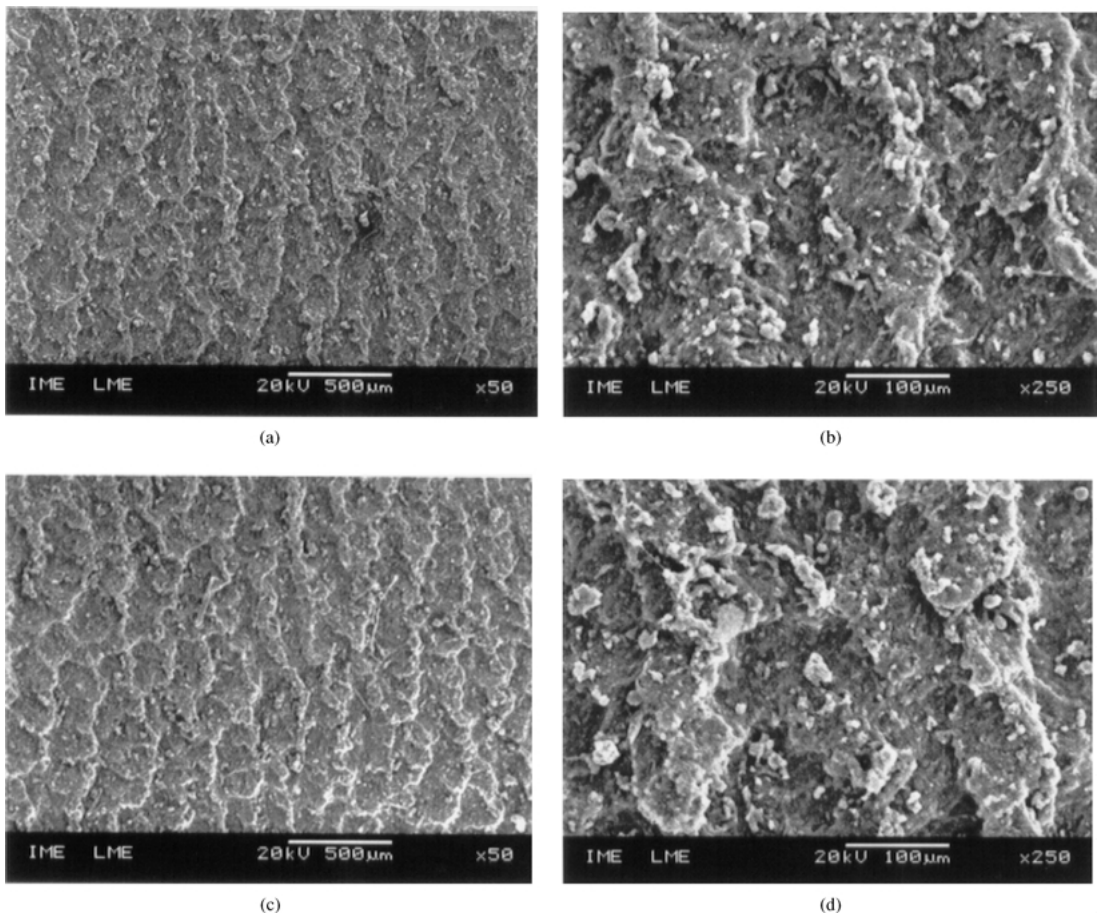
3.2.3. Abrasion test

SEM photomicrographs of the abraded surfaces composites are shown in Figs 9 to 11. The abrasion mechanism is clearly different in the samples with a high content of cellulose II. In general the abrasion pattern is more prominent. The features of the abraded samples change, from a relatively coarse and discontinuous surface in the unfilled material, to more smooth surfaces with chipped off particles in the filled composites. Unfilled NR shows a coarse abrasion pattern with ribs and cavities on the surface (Fig. 9a and b), a characteristic aspect of NR abraded surfaces. The ribs are large and wide apart and the regions in-between show an approximately rounded aspect. The composite containing 10 phr of cellulose II exhibits an abrasion mechanism similar to that of the unfilled sample (Fig. 9c). Observations at higher magnification show the occurrence of ridges in the ribs, fewer holes and some pull-out particles from the surfaces (Fig. 9d). In the samples with 15 and 20 phr cellulose II the ribs are closer to each other and approximately aligned at right angles to the direction of abrasion; the rounded texture observed in the unfilled and 10 phr specimens is lost (Fig. 10a and b). At higher magnification more pronounced ridges



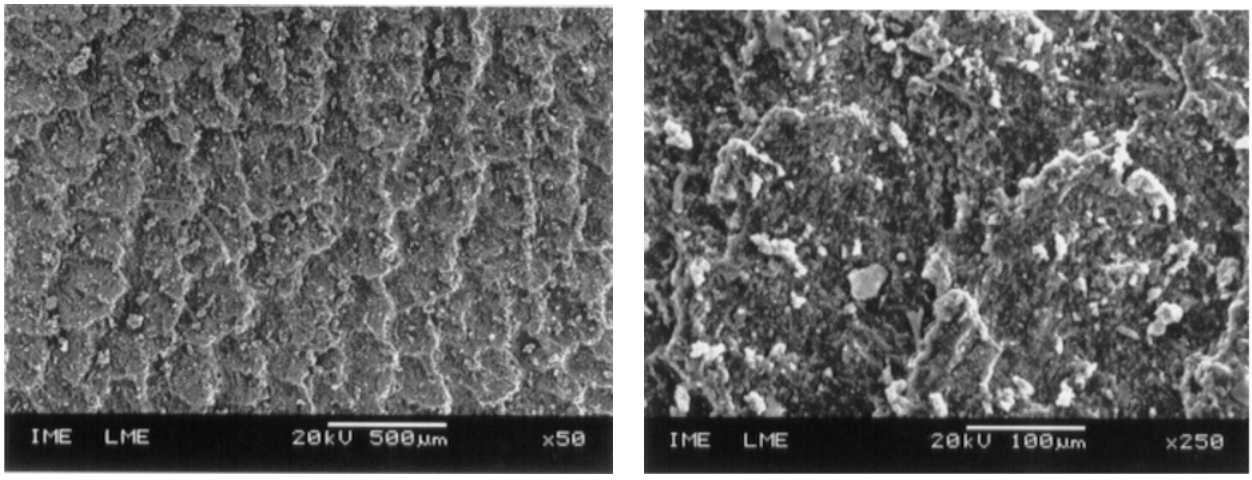
(a) (b) (c) (d)

Figure 9 SEM photomicrographs of abraded surfaces of unfilled natural rubber and NR/Cel II composites: (a) unfilled natural rubber, (b) a detail of (a), (c) 10 phr cellulose II composite, and (d) a detail of (c).



(a) (b) (c) (d)

Figure 10 SEM photomicrographs of abraded surfaces of NR/Cel II composites: (a) 15 phr cellulose II composite, (b) a detail of (a), (c) 20 phr cellulose II composite, and (d) a detail of (c).



(a) (b)

Figure 11 SEM photomicrographs of abraded surfaces of SEM microphotographs of tear fracture surfaces of 30 phr cellulose II composite: (a) general view and (b) a detail of (a).

and pull-out particles are observed (Fig. 10c and d). At lower magnification (Fig. 11a) the abraded surface of the composite with 30 phr cellulose II shows a pattern similar to that produced in the 15 and 20 phr samples, but at higher magnification (Fig. 11b) smoother surfaces between the ribs are seen. The damage caused by abrasion is mainly due to some pull-out material from the surface, probably the filler component. Hence, the increase of cellulose II content produces higher weight loss and a consequent decrease of the wear resistance of this series of composites.

SEM features are in agreement with the mechanical results and support the observed changes in the properties of the NR/Cel II composites.

4. Conclusions

Cellulose II reinforces natural rubber composites, indicative of a good rubber-filler interaction. The best tensile and tear performances were given by 15 phr of cellulose II.

The fracture surfaces after different mechanical tests conditions were evaluated by SEM. The failure surfaces and the fracture mechanisms depended on the nature of the test. Tensile fracture shows the occurrence of two different fracture mechanisms, normal and shear fracture, while tear fracture is characterized by flow lines. The abrasion tests generate a ribbed structure on the surface but, for high cellulose contents, the mechanism of failure is mainly due to the pull-out of the filler component. The SEM evaluation of the tensile fracture surfaces was very efficient to show the effect of cellulose II in the elastomeric matrix.

Acknowledgements

The authors thank the Brazilian funding agency, Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), for providing the financial support and Fibra S. A. for supplying cellulose xanthate.

References

1. J. R. WHITE and E. L. THOMAS, *Rubber Chem. Technol.* **57** (1984) 457.
2. G. L. WILKES and J. WEN, "Concise Polymeric Materials Encyclopedia" (CRC Press, London, 1999) p. 972.
3. C. ALBANO *et al.*, *Polym. Deg. Stab.* **73** (2001) 225.
4. R. C. R. NUNES and L. L. Y. VISCONTE, in "Natural Polymers and Agrofibers Composites," edited by E. Frollini, A. L. Leão and L. H. C. Mattoso (Brazil, 2000) p. 135.
5. R. L. MITCHELL and G. C. DAUL, "Kirk-Othmer Encyclopedia of Chemical Technology" (John Wiley & Sons, New York, 1968) p. 168.
6. *Idem.*, "Encyclopedia of Polymer Science and Technology" (John Wiley & Sons, New York, 1969) p. 810.
7. W. G. PERKINS, *Polym. Eng. Sci.* **39** (1999) 2445.
8. A. F. MARTINS, L. L. Y. VISCONTE and R. C. R. NUNES, *Kautsch. Gummi Kunstst.* **55** (2002) 637.
9. American Society for Testing and Materials. (a) ASTM D 3184-95; (b) ASTM D 412-98a; (c) ASTM D 624-98; (d) ASTM standard D 1044-94.
10. B. B. BOONSTRA, "Rubber Technology and Manufacture" (Newnes-Butterworths, London, 1975) p. 227.

Received 18 June 2002
and accepted 16 January 2003