

# Elastic Properties of Natural Rubber Tubes Produced by Dip-Coating

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**ABSTRACT:** The mechanical properties of rubber tubes produced by dip-coating technique and the influence of the fabrication process on their structural properties were evaluated. Cyclic tension versus deformation tests were performed to investigate the elastic properties of the samples and to understand the changes in rubber tubes behavior under repetitive stress. The effect of the wall thickness on the elastic response of the tubes was also studied. The mechanical properties of opened tubes were also investigated for transversal and longitudinal directions to evaluate the influence of the fabrication process on the alignment of the polymer chains. This investigation indicated that the fabri-

cated tubes are resistant and extremely elastic. They can be elongated up to 800% of its initial length before rupture, and thicker tubes are a bit more resistant to elongation than the thinner ones. In addition, the fabricated tubes have an anisotropic structure due to the fabrication process. Finally, natural rubber tubes may have a great potential to be used as vascular prosthesis, or in other applications that require a large range of resistance and elasticity. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 702–707, 2006

**Key words:** natural rubber; tubes; elastic properties; dip-coating

## INTRODUCTION

Natural rubber (NR) latex extracted from the *Hevea brasiliensis* is a polydispersed system containing about 40–45% weight of rubber molecules [*cis*-polyisoprene as seen in Fig. 1(a)], 4–5% weight of nonrubber constituents such as protein, lipids, carbohydrates, and sugar, and 50% of water.<sup>1</sup> NR is a naturally occurring form of isoprene and exhibits useful elastomeric behavior by introduction of intermolecular crosslink [i.e. vulcanization, as illustrated in Fig. 1(b)]. The elasticity of NR takes place by the sliding of the molecular chains past each other and it can be stopped by crosslinking the polymer. NR shows an elastomeric behavior: the polymer can be extended to many times its initial dimension and will spring back rapidly to take up its original shape. The properties of an elastomer are controlled by the nature and the amount of the crosslinked network.<sup>2,3</sup>

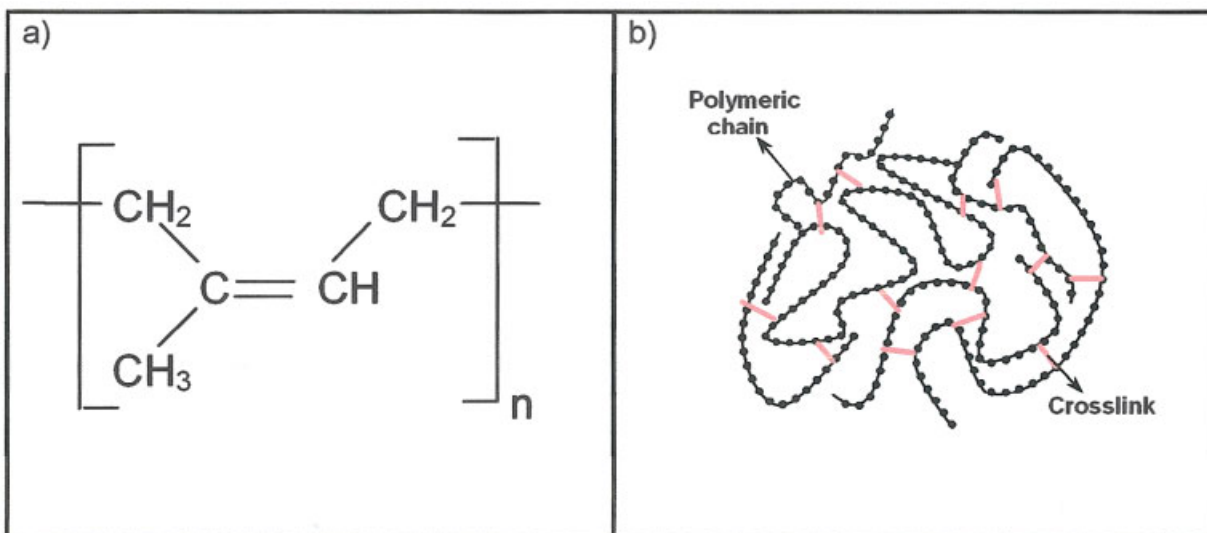
NR is an important raw material for a large range of industrial applications such as tires, automobile,

shoes, and aircrafts. In addition, it could be used as a biomaterial, as it has been investigated nowadays.<sup>4–7</sup> This material has all the requisites to be used in contact or inside the human body, being potentially biologically compatible. It was already demonstrated that it performs a biological action being a powerful stimulator of cicatrization.<sup>4–7</sup>

The fact that NR exhibits high resistance and elasticity and it is an easy-shaping material also increases its appeal for the fabrication of vascular prosthesis. In this context, there have been studies on the processing of NR trying to improve its biological application.<sup>4–10</sup> In view of the potential of this new biomaterial to be used in the construction of vascular grafts, the study of the fabrication techniques is very important. The main fabrication parameters must be related to the final physical properties of the produced grafts, as investigated elsewhere.<sup>11</sup> The influence of the main deposition parameters (dip-coating velocity, mold material, mold diameter, and number of coatings) and postdeposition drying process factors (temperature and time) on the production of NR tubes using dip-coating were investigated.<sup>11</sup> The optimized conditions are a dip coating velocity of 5 cm/min and a heating time of about 10 min for temperatures above 30°C. The dip coating withdrawal speed has a tremendous influence on the growth of the wall of the tubes, which is also influenced by the surface tension of the liquid

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**Figure 1** (a) *Cis*-isoprene monomer and (b) schematic diagram of the crosslinked polymer chain. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

bath. After the fabrication, the optimized heating process can be used to control the drying of the sample.

Many polymeric materials, such as polyethylene terephthalate (PET),<sup>12</sup> polyurethane (SPU),<sup>13,14</sup> and polytetrafluoroethylene (PTFE, ePTFE),<sup>15</sup> have been used in the development of vascular prosthesis, with good biocompatibility results. SPU has the highest flexibility among the existing synthetic rubbers and it has become a strong candidate for a graft substrate. The matching of the compliance between the prosthesis and the circulatory system is as important as the control of the prosthesis dimensions. Both must be controlled in the manufacturing process for the success of the tube-like implants.<sup>16</sup> The tubes must have regular and uniform walls, being available on a variety of sizes and diameters and they have to work in the vascular system as the original arteries to avoid thrombogenesis. All these variables depend on the fabrication method and also on the raw material properties, such as viscosity. To fabricate applicable prosthesis, it is necessary to understand how these variables are connected, and how they interfere on the physical characteristics of the final product. In this sense, the higher versatility and moldability of NR, compared to other industrial candidates, might increase its chances to present an improved mechanical performance when fitted into the vascular system.

After the study of the fabrication process,<sup>11,17</sup> the present work focuses on the mechanical characterization of the tubes. For that aim, we performed tension *versus* deformation cyclic tests to investigate the elastic properties of the studied prosthesis (and to understand the changes in rubber tubes behavior) under repetitive stress. The effect of the wall thickness on the elastic response of the tubes was also investigated.

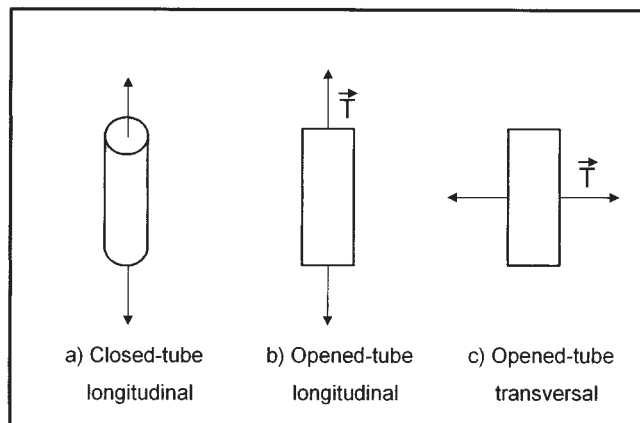
Finally, we also investigated the mechanical properties of opened tubes for transversal and longitudinal directions to evaluate the influence of the fabrication process on the structural properties of the tubes.

## EXPERIMENTAL

The original latex used in this work consists of a mixture of a noncontrolled variety of clones extracted from *Hevea brasiliensis*. After the extraction, the material is centrifuged and the pH is corrected to about 10, using an  $\text{NH}_4\text{OH}$  solution to avoid coagulation. A mixture of 4% sulfur and 2% polyvinyl methyl ether resin is also added to the latex, leading to a viscous and consistent material. The latex samples used to fabricate the tubes were characterized by a rheological test<sup>18,19</sup> (viscosity as function of the shear gradient) using a rotational viscometer Rheotest 2.

The tube fabrication process is based on the dip-coating technique, where cylindrical glass molds are vertically introduced into a latex bath at a constant speed of 5 cm/min. After immersion, the tubes were dried at 60°C for 30 min. Details regarding the latex extraction and tube fabrication can be viewed in our previous works.<sup>11,17</sup>

The tubes were stretched using an EMIC-MEM2000 system. The charge cell used in all the tests was 50 kgf. Cyclic tests at a speed of 20 mm/min were performed in samples with an original length of  $15.0 \pm 0.1$  mm and wall thickness of  $650 \pm 10$   $\mu\text{m}$ . The influence of wall thickness on the elastic behavior of the fabricated prosthesis was also investigated: we also present the results for wall thickness of  $100 \pm 10$  and  $300 \pm 10$   $\mu\text{m}$ , and we evaluated opened and closed samples. In addition, the elastic behavior was evaluated for different



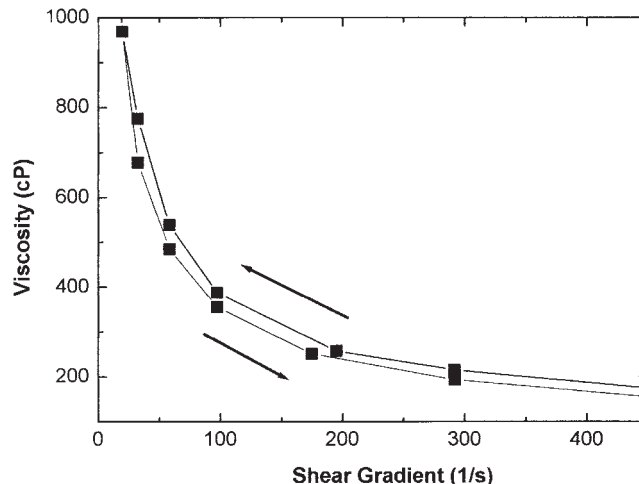
**Figure 2** Schematic diagram representing the directions for the tension versus deformation tests: (a) original closed tube, (b) opened tube that was stretched along the longitudinal, and (c) opened tube that was stretched along the transversal direction.

directions of the sample. For that, original tubes were cut along the longitudinal direction, becoming a membrane that we, from now on, refer as opened tube. Opened tubes with an original length of 15 mm were analyzed by the tension tests in transversal and longitudinal directions, i.e. the same sample was stretched in different directions to evaluate the elastic behavior of the fabricated tubes.

Figure 2 is a schematic diagram showing the different directions of the test. Figure 2(a) represents the closed tube along the  $z$ -axis (i.e. longitudinal direction) for the tension versus deformation test. Figure 2(b) shows the opened tube and the longitudinal direction of the test. Figure 2(c) indicates the opened sample and the transversal direction of the test. The velocity used for the test was 10 mm/min.

## RESULTS AND DISCUSSION

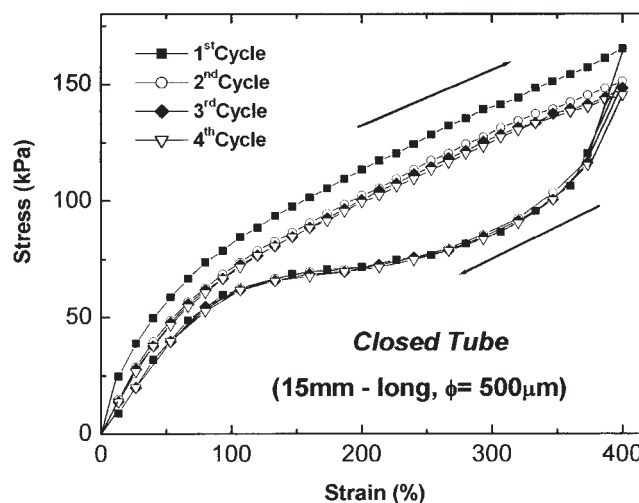
The viscosity of the latex used to fabricate the prosthesis was measured for an increasing shear gradient up to  $400 \text{ s}^{-1}$ , as presented in Figure 3. Above this value the viscosity was almost constant. Then, the viscosity was also measured for a decreasing shear gradient, as indicated by the arrows. The experiment was performed with the latex bath inserted between the two cylinders of a rotational viscosimeter, and it consists of a measure of the resistance imposed by the material to the spinning of the internal cylinder.<sup>18,19</sup> As can be seen in Figure 3 (i) the viscosity decreases nonlinearly with increasing shear gradient, and (ii) there is a hysteric behavior (as guided by the arrows), which might be an intrinsic property of the liquid or might be also evidencing a tixotropic behavior of the samples (in other words, the viscosity varies with time ref. 19).



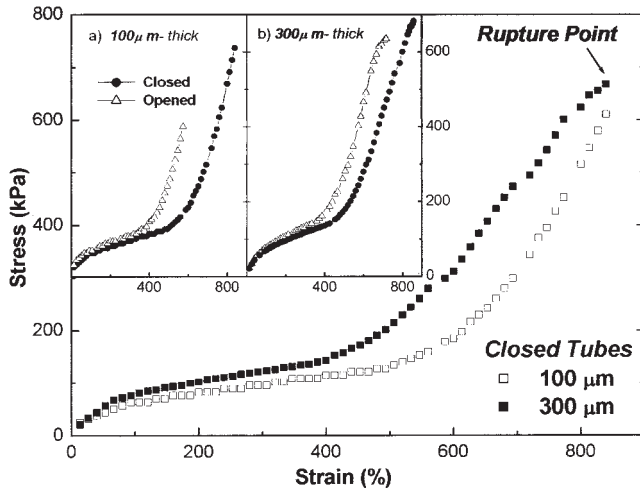
**Figure 3** Viscosity of the original latex bath as a function of the shear gradient.

The results obtained for cyclic stress tests of the rubber tubes are shown in Figure 4. We can see that the material presents significant elastic changes only for the first cycle (as squares in the figure). It suggests that, after the first deformation, the polymeric net stabilizes and can support the ingoing deformations without irreversible changes (up to the fourth cycle, as indicated by triangles in the figure).

The hysteric results observed in Figure 4 lead to the conclusion that the material has a strain memory, i.e. during the initial stretching, the polymer chains are forced to uncoil. When the process is reversed and the external force is removed, the net keeps a memory of the previous uncoiled stage. The area between the two curves is related to the energy dissipated within the cycle.



**Figure 4** Tension (stress) versus deformation (strain) cyclic tests for closed rubber tubes 15 mm long, with internal diameter of  $500 \mu\text{m}$  and thickness of  $650 \mu\text{m}$ .



**Figure 5** Elastic evaluation of closed rubber tubes with different wall thickness ( $\sigma \pm 10 \mu\text{m}$ ). The deformation was performed along the  $z$ -axis of the tube (i.e., longitudinal direction) up to the rupture point. The inset shows the comparison for opened and closed tubes for two thickness.

If the strain is further increased to higher values (above 400% for the case of Fig. 4), a new irreversible change could be expected. The strain can in fact be increased up to a value where the sample is ruptured, as presented in Figure 5. Tubes with a total length of about 15 mm were stressed along the  $z$ -axis (i.e., longitudinal direction) up to the rupture point. The 100- $\mu\text{m}$  thick tube (results are shown as white squares in Figure 5) cracks at an elongation of about 800%. The 300- $\mu\text{m}$  thick tube (results shown as black squares) also cracks at about 800%.

We can observe in Figure 5 that the samples present two distinct elastic behaviors, which are characterized by the slopes of the curves. The tube can be easily stretched up to an elongation of about 400%. Above this value, the material requires an increasing force to show the same relative deformation. It is well known that on deforming a rubber, the molecules tend to become aligned parallel to the stretching direction and as polymer molecules tend to become always packed side-by-side, this alignment reduces the entropy of the crystallization process. Generally, crystallization takes place slowly in NR at room temperature, but when a sample is stretched above about 300–400% of its elongation the degrees of crystallinity may increase over 30%.<sup>2,3</sup> This can explain the changes in the slope of the tension versus deformation curves shown in Figure 5.

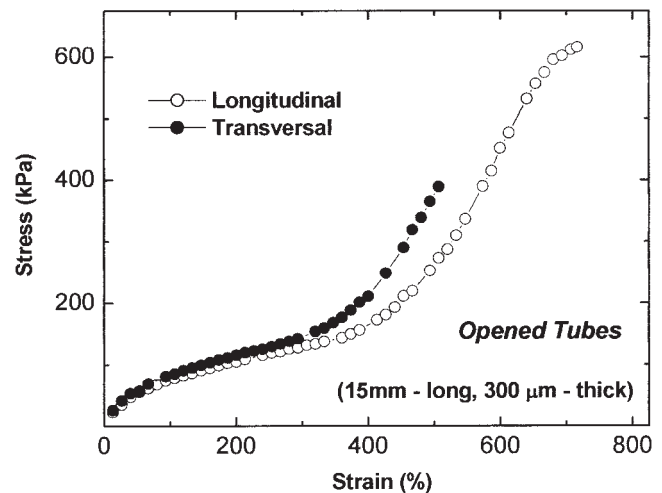
As shown in Figure 5, tubes with thicker wall (300  $\mu\text{m}$ ) are slightly more resistant to elongation than tubes with thinner wall (100  $\mu\text{m}$ ), as expected from a simple model that considers a system of parallel springs. The fact that the rupture of the tubes occurred at the same strain might be related to a cascade phenomena: given that some polymer chains start to

break, the net force is applied on a smaller amount of chains, each experiencing a higher effective load. For the studied range of thickness, each plane would behave independently.

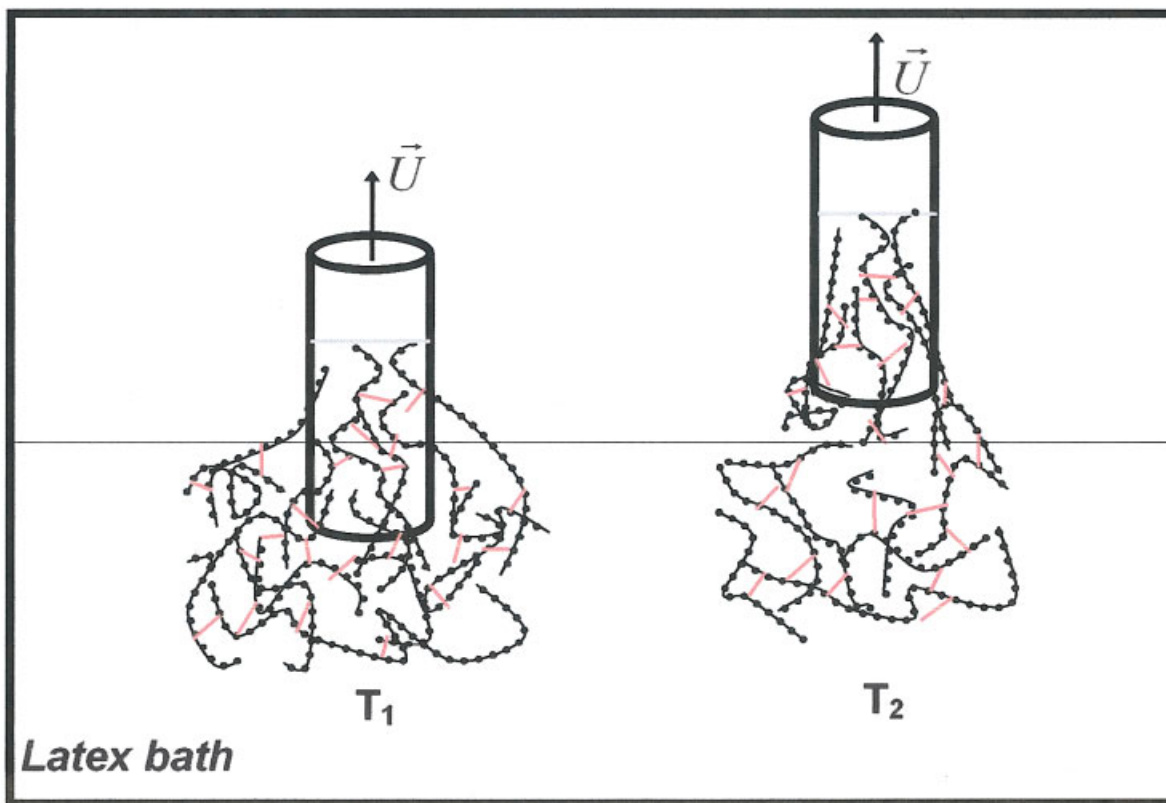
The inset of Figure 5 shows the results for the longitudinal stress tests for opened and closed tubes for varying wall thickness. For deformations up to 350%, both systems behave similarly. Nevertheless, for deformations above 350%, the comparison for opened and closed tubes reveals that the opened samples are more resistant to stretch than the closed ones. The thinner the sample, the larger the difference is. For opened tubes, the force is evenly applied along the polymer chains because the sample is flat. For closed tubes, the extreme part of the cylinder is pressed by the jaw of the set-up, which causes a bending of the extreme part of the tube. The nonflat shape can thus be easily elongated.

The results of tension versus deformation tests for longitudinal and transversal directions using a 300- $\mu\text{m}$  thick opened tube are shown in Figure 6. For deformations below 300% the behavior of the sample is the same, regardless of the chosen direction. On the other hand, for larger deformations there is an anisotropy: a larger resistance for the transversal direction is observed. For increasing wall thickness the effect is even more pronounced (not shown here).

The NR network is normally considered an amorphous polymer with no well-defined order in the structure [as represented in Fig. 1(b)]. A hypothesis for the anisotropic behavior observed in the rubber tubes might be the influence of the fabrication process (dip-coating) on the organization of the polymer chains, which could lead to a preferred orientation. A schematic diagram that suggests how the fabrication process could promote the orientation of the polymer chains and the induction of the material to an aniso-



**Figure 6** Tension versus deformation tests for the longitudinal and transversal directions for opened tubes.



**Figure 7** Schematic diagram for the behavior of the polymer chains during the dip-coating process. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

tropic behavior is presented in Figure 7. The fabrication process is based on the dip-coating technique: a cylindrical mold is vertically introduced into a latex bath at a constant speed  $U$ , and removed from the bath at the same speed. The withdrawal is represented in Figure 7 for two different times  $t_1$  and  $t_2$ . According to Probst, a fundamental key in coating process is to spread the liquid over a relatively large substrate by means of viscous forces while maintaining a thin layer of a uniform film at the substrate by the action of surface tension. The faster the substrate is withdrawn off the bath, the lesser the amount of liquid that is drained back to the bath and the thicker the layer adhered on the mold. This drainage process is related to the surface tension of the liquid bath. The latex adheres itself to the substrate during the withdrawal speed ( $U$ ), but it keeps also linked to the bath by the surface tension. The influence of the surface tension on the layer formation is smaller for faster withdrawal speed, and for extreme high speeds the latex practically does not suffer any drainage. Depending on a combination of an extreme withdrawal speed and the bath viscosity, an increasing accumulation of material can be obtained up to the substrate extension, even leading to a conic-like sample. This effect was previously theoretically verified in the literature.<sup>20–22</sup>

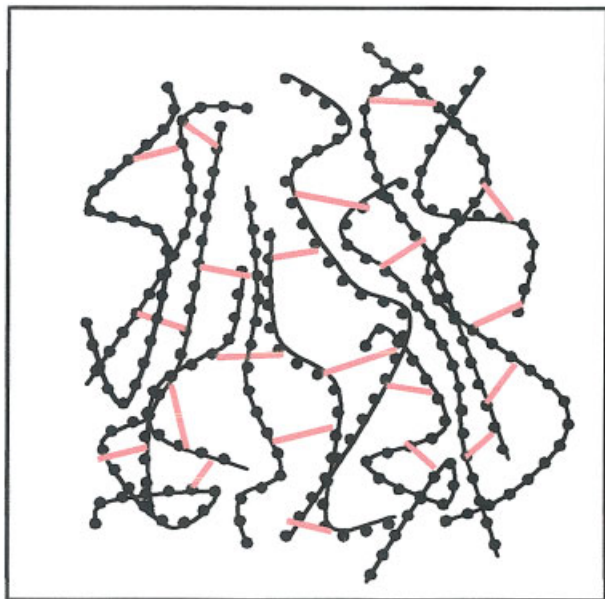
As the substrate is withdrawn from the bath, the polymer chains are adhered on the substrate by the

action of surface forces ( $t_1$ , Fig. 7). These polymer chains are also crosslinked with others on the latex bath. As the polymer chains are dragged by the substrate ( $t_2$ , Fig. 7), they tend to keep a preferential direction parallel to the withdrawal speed vector ( $U$ ). As a result, the rubber film will be deposited on the substrate with an anisotropic structure as presented at Figure 8.

The elastic properties along the longitudinal direction can be determined if a tensile stress is applied parallel to the direction of the polymer chains. On the other hand, if the sample is stretched by applying a stress at  $90^\circ$  to the direction of the polymer chains the elastic properties would be different when compared with those on longitudinal direction.<sup>23</sup> Given the fact that the polymer chain dislocation is easier in the longitudinal direction than in the direction of the crosslinks, the presented model can qualitatively explain the anisotropic behavior experimentally observed.

## CONCLUSIONS

After we have dominated the fabrication process of rubber tubes using the dip-coating technique,<sup>11,17</sup> the present contribution presents the results of their elastic characterization. This investigation indicated that the fabricated tubes are resistant and extremely elastic.



**Figure 8** Diagram of the molecular orientation of an anisotropic latex film produced by dip-coating technique. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

They can be elongated up to 800% of its initial length before rupture. The samples present important structural changes only in the first cycle of cyclic tension *versus* deformation test. It suggests that after the first deformation the polymeric net stabilizes and can support the ingoing deformations without irreversible changes. The variation of the elastic behavior was explained based on the coiling process of the polymeric chains in the material. The material presents two distinct elastic behaviors mainly because of the crystallization process that takes place in NR, at room temperature, when a sample is stretched above about 300–400%. Thicker tubes are a bit more resistant to elongation than thinner ones. In addition, the fabricated tubes have an anisotropic structure promoted by the influence of the fabrication process. Finally, on the basis of the results of this study, we can argue that NR tubes may have a great potential to be used as vascular prosthesis, or in other applications that require a large range of resistance and elasticity. In the sequence, further experiments will be conducted to determine the compliance<sup>24,25</sup> and stiffness<sup>26</sup> of the tubes to match their properties to those of arteries and veins.

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