

Influence of Nonrubber Constituents on Tack of Natural Rubber. I. At Very Short Times of Contact (Pendulum Test)

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ABSTRACT: The effect of nonrubber constituents such as proteins and lipids on tack of natural rubber (NR) was studied. Tack or adhesion at short contact time was determined for contact between crosslinked rubbers and glass plates. Various types of natural rubber, with or without nonrubber constituents, were prepared. Synthetic polyisoprene was used as a reference because of its chemical similarity. In this work, the impact pendulum test was carried out to study very short contact times t_c of the order of milliseconds. The results show an increase of tack energy with t_c for all the rubbers. This is attributed to an increase in true contact area with time and to a modification of the interfacial energy. Furthermore, the natural rubber without lipids and also polyisoprene exhibited the highest tack values while whole natural rubber remained always the less tacky. These results cannot be explained by differences in either the bulk viscoelastic properties of the crosslinked materials or their overall surface energy. The presence of a thin layer of varying composition at the surface of the rubbers appears to be the essential factor that affects the tack properties of the crosslinked materials. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1486–1494, 2000

Key words: natural rubber; nonrubber constituents; network; adhesion; tack

INTRODUCTION

Tack is the ability of two materials to resist separation after bringing their surfaces into contact for a short time under light pressure.^{1–3} Tack of polymers depends on different fundamental mechanisms. First, the development of intimate contact between the polymer and the substrate (wetting of the substrate by the polymer) is necessary: this is related to the deformability of the polymer. Adsorption of polymeric chains can then occur. Interdiffusion can also be involved when the second material is a polymer or is grafted with chains compatible with the

polymer. At very short times of contact, this diffusion phenomenon is limited to chains with sufficient mobility (short chains) and to chain ends. During the separation of the materials in contact, the viscoelastic properties will contribute to the measured energy through dissipation phenomena.

Tack is essential for different applications of polymers and elastomers. In the rubber industry (e.g., tires), very high speed processes necessitate immediate good contact of the elastomer with the substrate. In the area of adhesives and especially pressure-sensitive adhesives, good adhesion after short times of contact and under low pressure is required. The formulation of such adhesives is still based on empirical law. A full understanding of the mechanisms governing adhesion at short time would be of great interest. Some recent fun-

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damental and experimental studies⁴⁻⁸ have addressed this subject.

In this work, the tack of lightly crosslinked natural rubber and especially the influence of its nonrubber constituents will be studied. Natural rubber (NR) contains in addition to the rubber chains, about 3–5 wt % of proteins, fatty acids, lipids and some inorganic constituents. It is well known that these compounds can affect the mechanical properties of NR.⁹ Tack properties should also probably be modified. In this study, different samples were prepared with or without nonrubber compounds of different nature. Synthetic polyisoprene (PI) was used as a reference due to its chemical similarity with NR. The Lüpke pendulum^{10,11} was developed for the tack measurements. The results obtained were analyzed in terms of viscoelastic behavior of the different elastomers and the potential chemical modification of their surface during crosslinking.

EXPERIMENTAL

Sample Preparation

Elastomer

The elastomers used are synthetic polyisoprene (Natsyn 2200, Goodyear Tire and Rubber Company) and NR. The latex was supplied from Thailand with 60% dry rubber content. The procedure used to prepare several types of sample is described below.

Whole Natural Rubber (WNR). This rubber was prepared by casting the latex on glass plates, and then drying for one day at room temperature and then for 12 h at 50°C in an oven.

Deproteinized Natural Rubber (DPNR). DPNR was produced by treatment of the latex with a proteolytic enzyme (KP-3939, Kao Co.) to digest the nitrogeneous material, in the presence of sodium dodecylsulphate (SDS) at 37°C for 24 h, followed by centrifugation. The cream rubber was dispersed in SDS and centrifuged. It was then cast on a glass plate and further dried as in the case of WNR.

Acetone Extracted Natural Rubber (ANR). The solid WNR rubber was extracted in a Soxhlet apparatus with boiling acetone for 24 h and dried at 50°C for 12 h.

Table I Molecular Mass Between Crosslinks M_c and Sol Fraction f_s of Samples After Crosslinking with DCP

Sample	DCP (phr)	M_c (g/mol)	f_s
Natsyn 2200	1.00	30,600	0.06
WNR	0.75	32,700	0.06
DPNR	1.10	33,600	0.08
ANR	1.00	35,300	0.07
PNR	1.25	35,600	0.07

Purified Natural Rubber (PNR). The DPNR was extracted with acetone and dried at the same condition as ANR.

Mixing and Molding

The raw rubbers were mixed with dicumyl peroxide (DCP) and 1 phr antioxidant (N-isopropyl-N'-phenyl-p-phenylene diamine, IPPD) by milling on a two-roll mill. In order to prepare the network with approximately the same degree of crosslinking, the amount of added DCP was varied (Table I). The samples were cured at 150°C for 2 h in a form of 1 mm thick sheet molded between two sheets of protective films (Mylar) to avoid contamination of the surface.

Glass Plates

Transparent fused silica glass (Suprasil) was purchased from Heraeus. It consists of extremely pure synthetically produced silica (SiO₂) with only 0.001% impurities. The content of OH is about 1200 ppm ($\mu\text{g/g}$).

The glass plates were cleaned in an ultrasonic bath with toluene, acetone, and methanol for about 10 min in each solvent to remove organic contamination, and then for 2–3 min in mild conditions: 1% aqueous solution of sodium hydroxide, to avoid serious attack of the glass. They were rinsed with double-distilled deionized water and dried under nitrogen flow. This cleaning method leaves a perfect surface covered with water. For all the experiments, the glass plates were carefully cleaned by the same process.

Characterization

Bulk Properties of the Elastomers

Crosslinking Density. The molar mass between crosslinks (M_c) and sol fraction (f_s) were evalu-

Table II Surface Energies of the Elastomers and Substrate

Sample	γ^d (mJ/m ²) ^a ±2	γ^p (mJ/m ²) ^a ±2
PI (Natsyn 2200)	27	3
WNR	29	3
DPNR	30	4
ANR	28	4
PNR	29	4
Glass	22	46

^a γ^d : Dispersive component; γ^p : polar component.

ated by swelling method using Flory–Rehner's equation.¹² In order to obtain similar bulk properties of the materials, we chose to prepare networks with approximately the same crosslinking degree by varying the amount of DCP in the mixture. The M_c and sol fractions obtained for the different samples are presented in Table I.

As previously observed,¹³ the presence and nature of the nonrubber constituents can significantly affect the crosslinking behavior of NR: for instance, the PNR requires more peroxide than the other rubbers to achieve the same degree of crosslinking.

Viscoelastic Properties. The viscoelastic properties of the crosslinked rubbers were determined by means of dynamical viscoelasticity measurement (Metravib Viscoanalyser VA815). Based on Williams–Landel–Ferry (WLF) analysis,¹⁴ the time-temperature superposition principle was used to construct the master curve of the complex dynamic modulus (E^*) as a function of reduced frequency at a reference temperature of 298 K, i.e., about 70 K above the glass transition temperature of the elastomer. This temperature was chosen because tack measurements were done at room temperature.

Surface Analysis

Surface Energy. The surface energy of the different crosslinked elastomers and glass plates were evaluated by means of contact angle measurements of drops of liquids of known properties (α -bromonaphtalene, water), allowing us to determine the dispersive (γ^d) and polar (γ^p) components of the surface energy (Table II). The low polarity of the rubbers surface is indicated by the low value of γ^p . Furthermore, no significant dif-

ferences can be observed between the surface energies of the different rubbers, which means that the presence of nonrubber constituents has no significant effect on this parameter.

The γ^p value of the glass plate is higher than that of rubber and its surface energy is very close to that of water ($\gamma_s = 72$ mJ/m²): the clean glass can thus be considered as a surface totally covered by a thin layer of water.

Chemical Surface Composition. The chemical compositions of the rubber surfaces were determined by means of infrared attenuated total reflectance spectroscopy (IR-ATR) (Brucker IFS66 spectrometer). Two crystals were used to analyze the composition of each material at different depths: KRS-5 (thallium bromide/thallium iodide) and Ge. With the germanium crystal, the depth of the analyzed subsurface layer is only one-third that of KRS-5 crystal, i.e., respectively 0.17 and 0.55 μm at 3800 cm^{-1} .

Tack Measurements

Lüpke Pendulum

The contact between two surfaces at short time was obtained by the Lüpke pendulum (Fig. 1) first used for tack measurement by Gent and Kim.^{10,11} It consists of a pendulum holding the sample. An electromagnet is used to hold and release the pendulum at fixed positions to obtain the required impact velocity. At the other side, the test piece is mounted on a rigid plate supported by a spring. A stop piece is added to prevent further extension of the spring from its neutral position when the two contacted surfaces are separated, particularly with the soft spring.

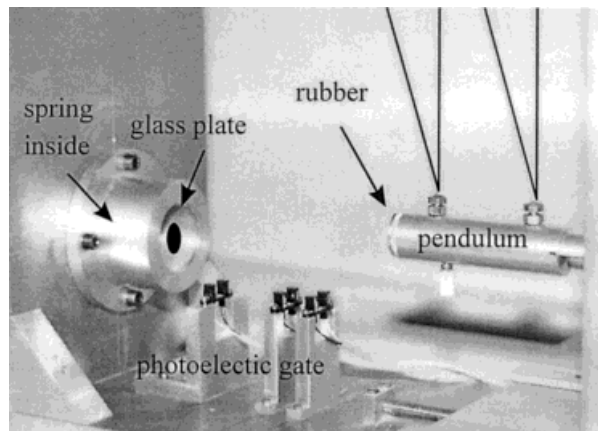


Figure 1 Pendulum test for short contact times.

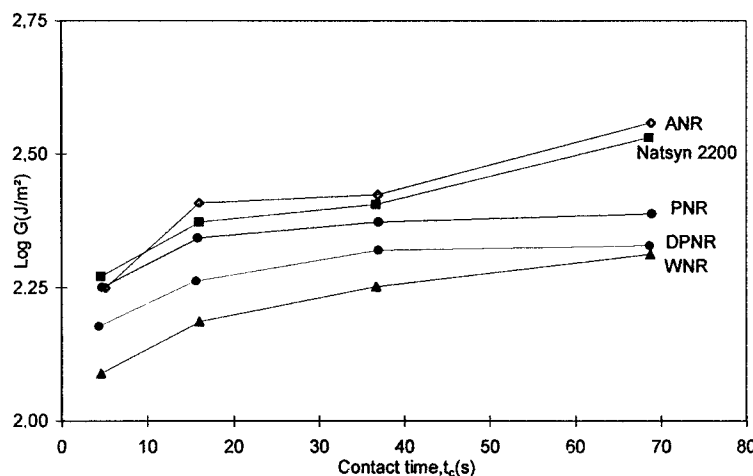


Figure 2 Evolution of the real energy of adhesion G_r , as a function of contact time (t_c) for the different elastomers. Pendulum test; impact rate $V_i = 0.5 \text{ m s}^{-1}$.

By varying the spring stiffness, the contact time could be changed from about 3 to 70 ms with the pendulum of 500 g. The impact speed can be varied between 40 and 80 cm/s. The contact time of the pendulum was measured directly by using a photoelectric gate. Another photoelectric gate is used to measure the impact and rebound velocities.

Experimental Procedure

The tack measurement was carried out using a testpiece of cured rubber of 10 mm diameter and 1 mm thickness. The rubber sample and the glass plate (25 mm diameter) were fixed respectively on the pendulum and on the rigid wall. The protective film at the surface of the elastomer was removed just before the first impact, and then the same sample was dusted with mica powder to prevent adhesion. The rebound velocities of the pendulum for clean and dusted surfaces were recorded. The measurement with the mica powder was necessary to minimize the interfacial adhesion and thus estimate the energy dissipated (hysteretic losses) in the bulk and in the experimental setup. The values obtained were subtracted from the adhesion measurements to obtain the energy dissipating solely in overcoming surface adhesion.¹¹

Calculation of Tack Energy (G)¹⁰

In this method, the tack value is evaluated as the energy per unit area required to separate two surfaces after contact. It is obtained from the

difference of energy measured for the clean surface and dusted surface by using eq. (1)¹⁰:

$$G = m(V_p^2 - V_c^2)/2A \quad (1)$$

where G is the tack energy per unit of interfacial area, m is the mass of the pendulum, V_p is the rebound velocity for a powdered sample, V_c is the rebound velocity for a clean sample, and A is the sample surface area.

The rebound velocity depends on two properties: the viscoelastic property of the bulk rubber and the interfacial adhesion. Since the dust surface has no more tack, V_p is higher than V_c . For powdered surface, the rebound energy with different springs was about 90% of the impact energy, indicating that energy losses due to dissipation in the support and the spring were small. In the system without spring, the rebound energy was found to be only 60% of the energy input for all the rubbers. We suggest that most of the dissipated energy is lost in the bulk rubber. Furthermore, the contact time decreased as the impact speed increased. This observation is in accordance with the viscoelastic behavior expected for the rubbers.¹⁰

RESULTS AND DISCUSSION

The measured values of tack energy between the different rubbers and the glass plate are shown in Figure 2 for contact times ranging from 3 to 70 ms. These results will be discussed in two parts.

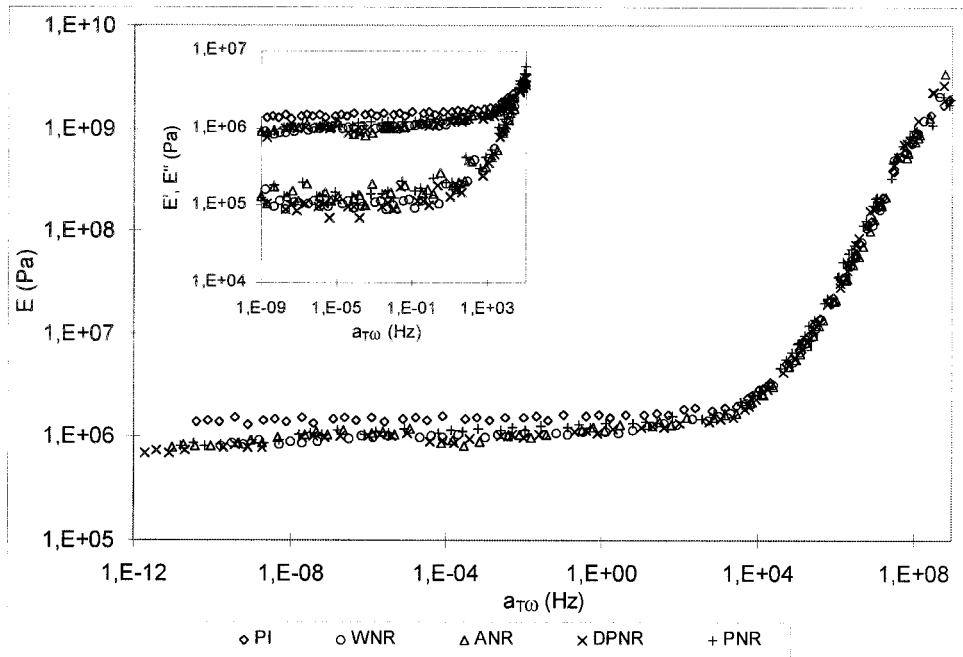


Figure 3 Dynamic bulk viscoelastic properties of the different elastomers. E^* : Complex modulus; E' : storage modulus; E'' : loss modulus; $a_T\omega$: reduced frequency.

First, the influence of the nonrubber constituents on the tack properties of the different elastomers will be analyzed. Second, the evolution of tack as a function of contact time will be examined.

Influence of the Nature of the Elastomers

For a given contact time, the tack energy of NR containing different amounts of nonrubber compounds differs from one another. It is clear that nonrubber constituents strongly affect the tack properties of NR. The whole natural rubber has the lowest tack and the tack energy of ANR or NR without lipids is close to that of synthetic polyisoprene. From WNR to ANR, the tack energy increases by more than 40%. Therefore, we can conclude that the presence of the acetone extractable materials in WNR, consisting of fatty acids, ester, sterols, and resins, is certainly responsible for the lower tack properties observed for this material and DPNR. To explain these differences, some hypotheses will be examined in turn.

Viscoelastic Properties

First, the bulk properties, and more specifically, the viscoelastic properties of the materials, can govern tack properties in two ways:

- During bond formation: the achievement of good contact requires deformation of the materials and the kinetics of this contact formation depends on the compliance (flow ability) of the elastomer, which is related to the dynamic storage modulus¹⁵ E' .
- During debonding: the energy dissipated upon deformation during this step is related to the loss modulus^{15,16} E'' .

Thus, the tack energy depends on both E' and E'' , which are directly related to the complex dynamic modulus E^* . To a first approximation, the dynamic bulk modulus and the tack energy obtained for the different rubbers will be compared.

Figure 3 presents the master curves of the dynamic bulk modulus obtained via time–temperature superposition. In the low range of reduced frequency, in the rubber plateau zone, the modulus of polyisoprene is higher than the moduli of all NR samples. At higher frequencies, in the glass transition zone, no significant difference could be observed.

In order to compare the tack measurements and the viscoelastic behavior of the elastomers, one has to convert the rate of separation V_p into deformation frequency \dot{V}_p of the elastomer.

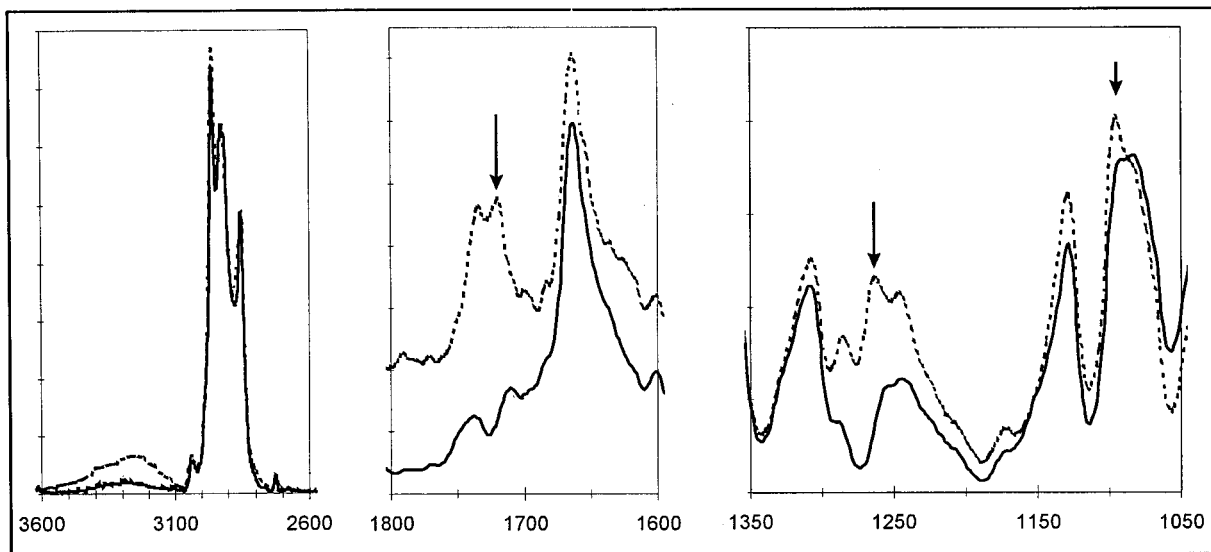


Figure 4 ATR spectra of WNR + 0.75 phr peroxide + 1 phr antioxidant before and after curing by peroxide. Before curing: —; After curing at 150°C for 2 h: - - - - -.

The following relationship has been proposed for transformation¹⁷: $\dot{V}_p = V_p/h$, where h is the thickness of the deformed materials. However, this transformation is based on the hypothesis that the materials are perfectly elastic (Hooke's law), which is not the case here. The elastomers are viscoelastic materials. A better transformation¹⁶ can be the conversion of reduced frequency ($a_T\omega$) into reduced effective rate (a_TV_{eff}): $V_{\text{eff}} = (\omega/\sqrt{2})\varepsilon_0$, with ω the angular frequency and ε_0 the deformation amplitude used in the viscoelastic measurement.

As room temperature was chosen as the reference temperature for the WLF representation of the dynamic modulus, tack and viscoelastic measurements can be directly compared.

The value of the separation rate in tack measurement is $V_{\text{eff}} = 50 \times 10^{-2} \text{ m s}^{-1}$, which corresponds to a frequency of about $1.4 \times 10^4 \text{ Hz}$. This value lies at the start of the glass transition zone of the different elastomers where the viscoelastic properties are equivalent. However, even if this value is overestimated, the best tack properties of polyisoprene cannot be explained by its bulk viscoelastic properties: the dynamic storage modulus E' of PI is the highest at low frequencies, which corresponds to a lower deformation ability and its dynamic loss modulus E'' is equal to those of NR samples (inserts in Fig. 3) which means that the bulk viscoelastic dissipation is equivalent.

Thus, differences between the bulk viscoelastic behavior of the elastomers cannot explain their

different tack properties. Differences in the surface properties of the elastomers might be the factor responsible.

Surface Properties

Due to the different chemical composition of the NR samples studied, some differences in their surface properties are expected, which might explain their different tack behavior.

However, the surface energies measured for all elastomers are of comparable magnitudes (Table II). It seems, therefore, that the different tack properties cannot be due to the reversible energy of adhesion between the elastomers and the glass plate. However, the contact angle method used to determine the surface energy and especially its polar component is certainly not sensitive enough in this case. Thus, no definite conclusion can be drawn from these results.

A more precise analysis of the surface of the elastomer is needed. The chemical compositions of the surface of the elastomers were then determined by means of IR-ATR.

The spectra for WNR before and after crosslinking are shown in Figure 4 (Ge crystal). It appears clearly that there was a modification of the materials due to crosslinking which is indicated by a change in spectra in the 3700–3100 cm^{-1} range. The higher intensity of the peaks in this region before crosslinking is characteristics of the formation of new hydroxyl and amine

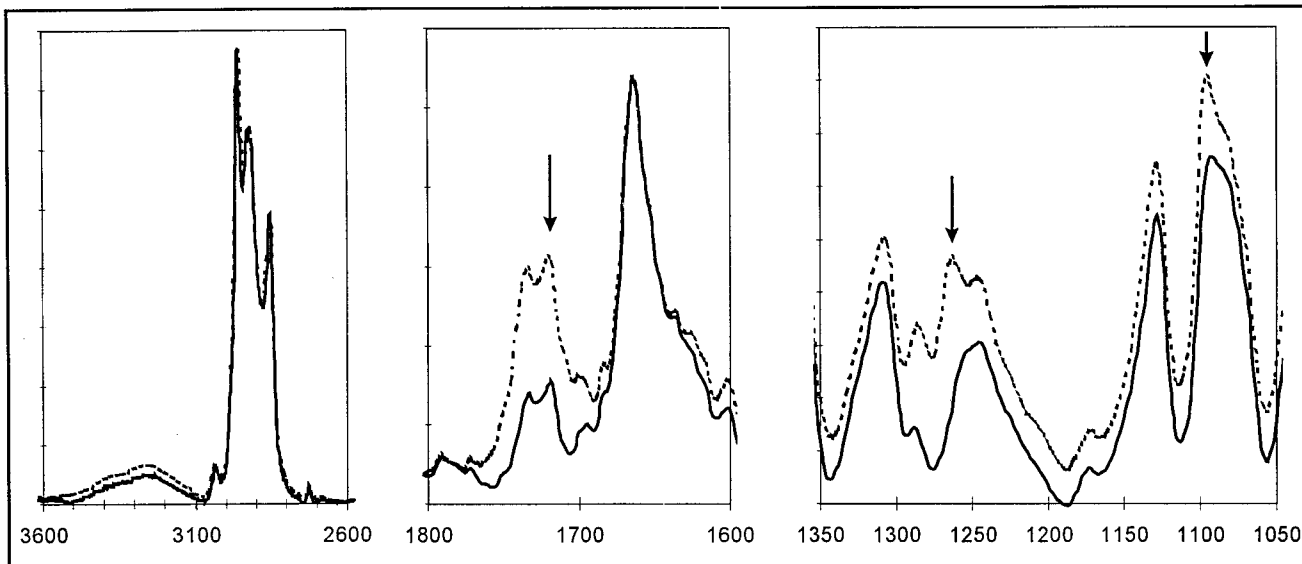


Figure 5 ATR spectra of cured rubbers containing the same quantity of proteins. ANR: —; WNR: - - - - -.

groups. The intensities of some other bands (1095 , 1260 , 1720 cm^{-1}) also increased. These bands are characteristics of the oxidation of compounds present in the rubbers (elastomer chains or nonrubber constituents).¹⁸⁻²¹

An increase of the intensity of the broad band around 3300 cm^{-1} could also be observed for all the other rubbers samples. From the examination of the spectra of crosslinked WNR and ANR (Fig. 5), one can see that the bands at 1095 , 1260 , and 1720 cm^{-1} are more important in the case of WNR, which means that it is much more oxidized than ANR. The same observation could be made when comparing the spectra of DPNR and PNR. Thus, it seems that the presence of acetone extractable constituents induces a greater modification of the elastomer surface. Studies by other workers showed that this is most likely due to the presence of lipids, which can be preferentially oxidized.^{18,21}

The chemical composition of the surface was analyzed at various depths to check if the modification induced by the crosslinking step occurred also in the bulk of the materials. The broad band at about 3400 cm^{-1} observed on the spectrum of PI with a Ge crystal is no longer present when the KRS5 crystal was used (Fig. 6). For all the other NR samples, the same results were obtained. The modifications of the elastomer surfaces by oxidation were thus limited to thin surface layers of the materials. The thickness of this layer was estimated to be about 1 μm .

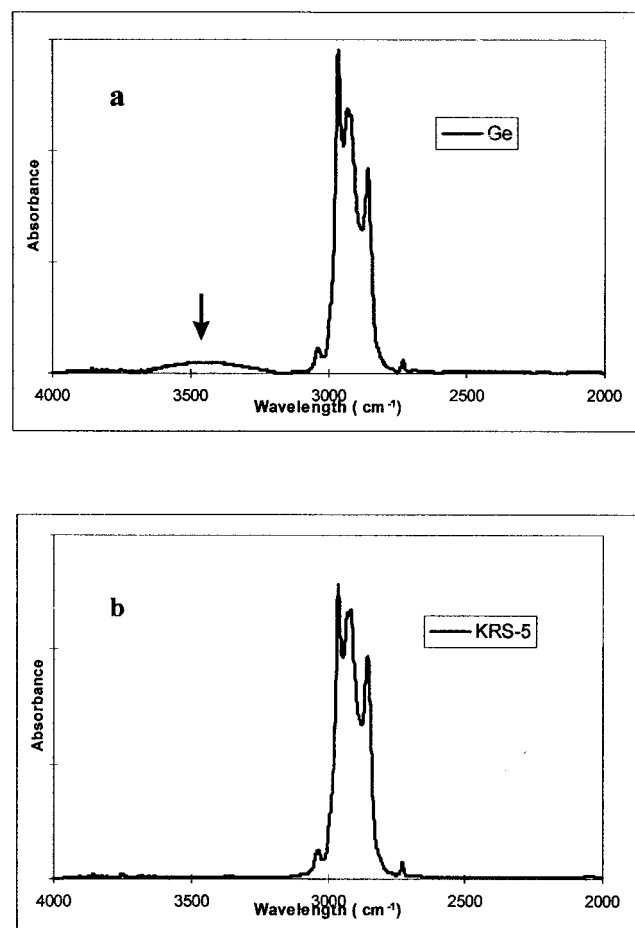


Figure 6 IR ATR spectra of crosslinked polyisoprene with different crystal. (a) Ge and (b) KRS-5.

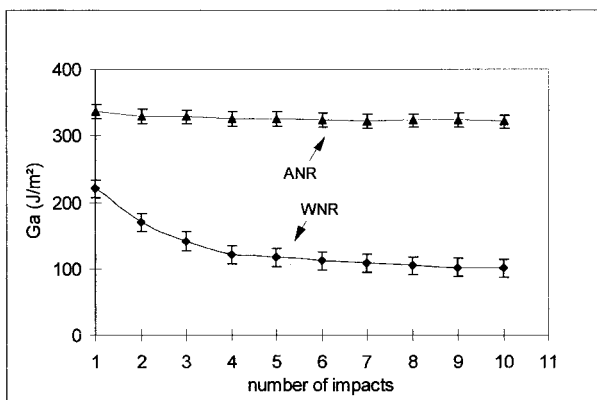


Figure 7 Evolution of the real energy of adhesion G_r , as a function of number of impact for WNR and ANR. Pendulum test; impact rate $V_i = 0.5 \text{ m s}^{-1}$.

These IR analyses show that more polar components were present at the surface of WNR and DPNR. This should be in favor of higher tack properties for these two elastomers. However, the opposite behavior was clearly observed (Fig. 2). Therefore, the chemical nature of the species present at the surface cannot explain the tack differences between the elastomers studied.

It is well known that oxidation induces a modification of the mechanical properties of the rubbers.^{18,19} Thus, the mechanical behavior of the modified surface layer should be different from the bulk of the elastomers and vary with the oxidation level. A decrease of the tack is then expected from ANR to WNR and from PNR to DPNR, in agreement with the data shown in Figure 2.

In addition to these localized mechanical property differences, oxidation of the surface of the elastomers produces low molar mass components and can lead, under drastic conditions, to the formation a weak boundary layer.¹⁸⁻²¹ When contact is done with the glass plate, the low molar components can be adsorbed at the glass surface and decrease the energy required to separate the two materials. In the case of the more oxidized WNR and DPNR, the amounts of low molar mass components accumulated at the surface should be much more important and induce a decrease of the tack properties. To check this hypothesis, the tack energy was determined as a function of the number of impact (Fig. 7) for WNR and ANR, which differ only by the presence or absence of lipids. In the case of WNR, drastic decreases of the tack energy were observed up to the fourth impact. Subsequent impacts produced rather un-

changed impact energy. The results obtained show that transfer of matter occurred from the elastomer to the glass. On the contrary, the tack energy of ANR was almost independent of the number of impact. These behaviors showed that the lower tack properties can also be due to a mechanism of transfer of some species present at the elastomer surface to the glass surface. This transfer is higher when the surface is more oxidized.

In conclusion, the influence of nonrubber constituents on the tack properties of crosslinked NR mainly occurs through chemical modification of the surface. The presence of lipids induces a more pronounced oxidation of the surface. A thin layer with varying composition and properties is formed at the surface of the elastomers. This layer can affect the tack properties in two ways: (1) its mechanical properties, which are different from one elastomer to the other; (2) the amount of components transferred during contact with the glass plate.

Influence of Contact Time

Tack energy increased with contact time for all samples (Fig. 2). In the case of DPNR and PNR, the increase slows down after about 40 ms. During these short durations of contact, the time dependence of adhesion between the elastomer and the glass can be attributed to the development of complete contact. So, it is possible that the contact area for the two rubbers, DPNR and PNR, has a tendency to become constant after 40 ms contact time. However, another explanation can also be made. First, the different chemical composition of the extreme surface of the elastomers can be responsible for their different tack behavior as a function of time. In this case, the different viscoelastic properties⁴ of the upper surface is an important parameter. A modification of the interfacial energy during the contact can also occur due to orientation of polar groups present at the surface. In the case of WNR, which exhibited the most oxidized surface, transfer of matter during the contact with the glass plate was already observed. The almost constant value of tack energy observed after 40 ms can also be due to a constant transfer of matter.

CONCLUSION

1. The influence of nonrubber constituents on the tack properties of lightly crosslinked

natural rubber in contact with glass was studied by means of a pendulum test. For this purpose, different types of NR totally or partially extracted were prepared.

2. The acetone extractable components appear to decrease drastically the tack properties of NR.
3. The bulk viscoelastic properties of all the rubber samples studied, which determine the bulk dissipation and the compliance (i.e., the wetting ability) of the materials, are almost identical. The same is true for the surface energies. Therefore, these two properties cannot be responsible then for the observed differences in tack energy.
4. The chemical modification of the surface occurring during the crosslinking step appears to influence the tack properties: this modification is larger when the elastomer (WNR, DPNR) contains acetone extractable components.
5. Some characteristics of thin layer at the NR surface appears to affect tack by
 - (a) its mechanical properties, and
 - (b) a transfer mechanism of some components from the thin layer to the glass.
6. Work is now in progress to determine which parameter (viscoelastic properties of this thin layer or transfer mechanisms) is the most important.

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