Study of matrix inhomogeneity of natural rubber and synthetic polyisoprenes by a spin probe method

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Nitroxide spin probes have been used to investigate the matrix morphology of natural rubber (NR), deproteinized natural rubber (DPNR), synthetic polyisoprene (PI) and modified synthetic polyisoprene (PI-M). Composite electron spin resonance spectra with broad and narrow components appear in NR, DPNR and PI-M, above the glass transition temperature. The slow component is attributed to the spin probes in regions of higher density or gel phase, whereas the narrow component is identified with the nitroxides located in the sol phase. The intensity of the slow component depends both on the amount of gel phase and on the specific gel structure. The restricted spin probe motion above the glass transition is considered to be a measure of the participation of naturally occurring protein components or modifiers in the formation of gel and its structure. Several spin probes differing in size and shape are used in order to assess the free volume distribution.

(Keywords: spin probe; electron spin resonance; natural rubber; deproteinized natural rubber; synthetic polyisoprene; modified synthetic polyisoprene; matrix inhomogeneity; gel structure)

INTRODUCTION

There are numerous studies dealing with the differences in mechanical and rheological properties between natural rubber and synthetic polyisoprene with the same backbone chain structure. These differences are mainly attributed to the sol–gel composition, chain branching and to the molecular weight[1–3]. Although the molecular weight has considerable influence on the physical properties of natural rubber, the effect of gel is more dominant than that of molecular weight[4]. Therefore, the gel phase and its structure are very important in understanding the bulk properties of natural rubber.

It has been shown that the naturally occurring proteins in natural rubber interact with specific functional groups on the polyisoprene chain, thus contributing to the formation of a physically crosslinked fraction known as gel[5,6]. The gel fraction exhibits much higher strength and correspondingly lower relaxation rate than the sol fraction.

The separation technique of the two fractions is well established. However, it gives only the amount of gel/sol fraction which depends on the extraction solvent used. The electron spin resonance (e.s.r.) spin probe method is one of the techniques which can offer an insight into the rubber network morphology and gel structure. In some heterogeneous polymer systems the spin probe reflects a composite e.s.r. spectrum as a consequence of the unbound probe partitioned in the network of different local density or available free volume[7–10]. In the case of natural rubber the gel phase, especially so-called tight gel, refers to the slow motion component of the composite spectra above the glass transition temperature, while the motionally narrowed component is attributed to spin probes embedded in the sol phase[11].

The aim of this study is to investigate the influence of gel fraction and its structure on the heterogeneity of polyisoprene matrix. Attention is focused on the correlation between the protein component in natural rubber and the amount of slow component determined from the bimodal e.s.r. spectra. Furthermore, the difference between the gel of synthetic polyisoprene, with and without modifiers, and the gel of natural rubber will be analysed. The results should be relevant to the mechanical behaviour of natural rubber and synthetic polyisoprenes, respectively.

EXPERIMENTAL

Materials

Commercial samples of natural rubber (NR) (Malaysian origin), deproteinized natural rubber (DPNR) (Malaysian origin), synthetic polyisoprene (PI) (USSR origin) and modified synthetic polyisoprene (PI-M) (USSR origin) with 97–98% of *cis*-1,4 structures were investigated. PI modified with 4-nitrosodiphenylamine was purified by extraction in ethanol and a solvent mixture of acetone:chloroform:methanol (ratio 30:47:23) in order to remove low molecular products of the modifier and polyisoprene[12]. The gel fraction was isolated after 65 h extraction in n-hexane.

The spin probes I, II, III (Aldrich) and IV (Jozef Stefan Institute, Ljubljana) (*Figure 1*) were doped into the

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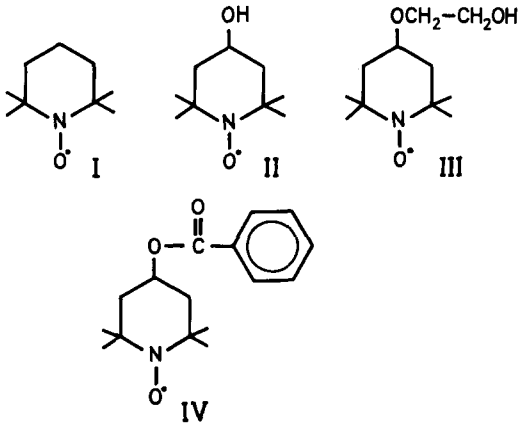

Figure 1 Chemical structure of the spin probes

polyisoprene matrix by swelling the polymer in benzene solution of the nitroxide at 308 K. After the solvent had slowly evaporated the samples were annealed in a vacuum at 313 K. The spin probe concentration was less than 0.1 mass %.

Methods

The e.s.r. spectra were recorded on a Varian E-109 spectrometer operating at 100 kHz modulation. The temperature was controlled by a variable temperature unit. The samples were kept at a temperature near the glass transition temperature, by means of a thermostat, for at least 30 min before recording the spectra. The complex spectra were analysed as a superposition of broad and narrow components. Experimental spectra were simulated with the single component spectra of natural rubber and its sol fraction, which had different line shapes and correlation times, τ_R. The τ_R of the narrow components was in the range 2×10^{-10} to 6.8×10^{-9} s, and of broad components $1.1 \times 10^{-8} < \tau_R < 2.5 \times 10^{-8}$ s. From this analysis the fraction of each component was determined with a deviation of less than 3%.

RESULTS AND DISCUSSION

The e.s.r. spectra of the spin probe II doped in the NR and PI differ in line shape at and above 250 K (*Figure 2*), a temperature referred to as T_{50G} (the temperature at which separation between the outermost maxima, $2A_{ZZ}$, becomes 5 mT). Below 250 K the e.s.r. line shapes are typical of probe molecules immobilized in a glassy polymer. However, above this temperature the e.s.r. spectra of NR appear to be a superposition of the two spectra. The narrow component originates from the spin probes located in the regions undergoing main chain segmental motions characteristic of a polymer above T_g. The broad component corresponds to the probes dispersed in regions with restricted segmental motions. The spin probes embedded in PI exhibit only a narrow line spectrum at and above 250 K. The origin of the bimodal e.s.r. spectra observed in NR has previously been explained as a partition of the probes in two different environments related to local matrix density[11].

A number of polymer segments in the gel regions are motionally restricted above T_{50G} due to the interchain interactions and chain entanglements. The influence of chain entanglements in 1,4-*cis*-polyisoprene has been demonstrated by pulsed n.m.r.[13]. Thus the spin probes located in domains whose segmental motions are under constraint will undergo slow tumbling. We may also assume, following the interpretation of e.s.r. spectra for some block copolymers[7], that the diffusion of nitroxide molecules between the motionally restricted and unrestricted domains is too slow to average out motional correlation times. As a result, the observed spectra would show two motionally non-interconverting spin probe species. If the gel phase of NR known as a tight gel is responsible for the restricted spin probe motion above T_g, it remains to be explained why the e.s.r. spectra of PI with $\approx 10\%$ gel fraction exhibits a relatively homogeneous matrix (*Figure 2b*). There is no evidence from the e.s.r. line shapes that the spin probes undergo a bimodal distribution of rotational correlation times above 250 K. For that reason the density of gel phase, or the shape and size of free volume in which the motion of spin probe takes place, should be considered. To examine the effects of the size of free volume we have used several spin probes differing in size and shape (*Table 1*).

The e.s.r. spectra of four different spin probes dispersed in NR and PI are displayed in *Figure 3*. The spin probes I, II and III in the NR matrix show a composite spectrum. The difference is, however, in the intensity of the broad component which increases with enlarged volume of a probe. On the other hand the large probe IV gives only a one-component spectrum resembling fast nitroxide motion. This spectrum indicates that the large probe does not penetrate into domains of higher density associated with the smaller free volume sizes. The free probe is expected, on thermodynamic grounds, to seek out regions in the bulk larger than the size of spin probe[14]. If we assume that the probe molecules are spherical we may quantitatively estimate the magnitude of free volume from the spin probe volume[15]. As the molecular

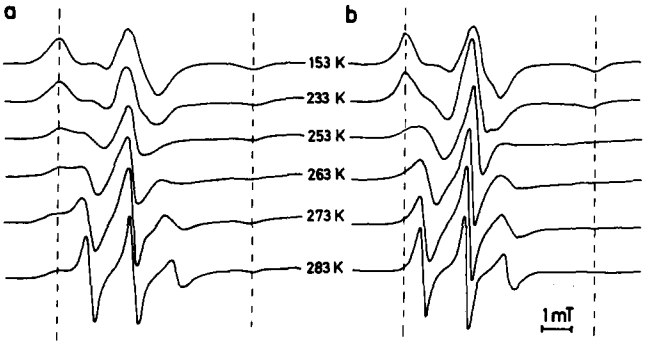

Figure 2 E.s.r. spectra of (a) NR and (b) PI doped with spin probe II as a function of temperature

Table 1 Molecular weights and volumes of spin probes

Probe	Molecular weight ($g\,mol^{-1}$)	Molecular volume ($10^{-30}\,m^3$)
I	156.25	169[a]
II	172.25	176[a]
III	216.30	222[b]
IV	276.36	276[a]

[a]Molecular volume from ref. 16
[b]Calculated using ref. 22

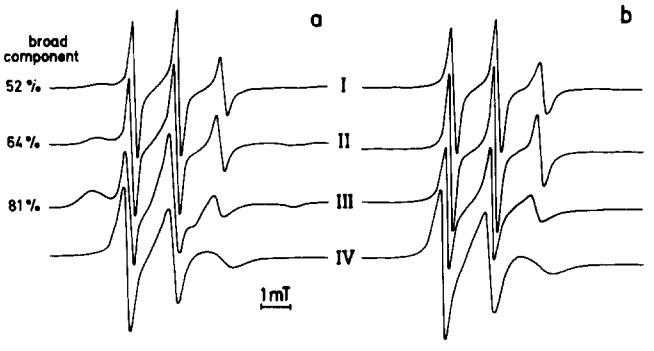

Figure 3 E.s.r. spectra of (a) NR and (b) PI doped with spin probes I, II, III and IV, measured at 293 K. Percentage of spin probes in the broad component is shown

Table 2 Temperature dependence of the e.s.r. broad component for natural rubber (NR) and the corresponding gel fraction (NR-gel) doped with probe II

	ESR broad component (%) at various temperatures (K)				
Sample	273	283	293	303	313
NR	71	65	64	40	12
NR-gel	86	83	79	74	48

volumes of probes I and II are 169×10^{-30} m^3 and 176×10^{-30} m^3, respectively, the free volume of denser regions where the probes are located is about the volume of probe II or smaller. Probe IV, with molecular volume of 276×10^{-30} m^3, will partition preferentially into the regions of lower density or local free volume larger than the probe volume.

The spin probes dispersed in the matrix of PI (*Figure 3b*), irrespective of the probe size or shape, show motionally narrowed spectra. A one-component spectrum for all four probe molecules can be explained in the following manner. The PI gel has lower density than the NR tight gel. This implies that the average hole dimensions in the PI gel are greater than those in NR gel. In this case even smaller probe molecules, located in the gel phase, would find themselves in a site of sufficient free volume to permit relatively rapid tumbling. Another possibility which should be considered is the lack of specific interchain interactions in the PI gel. This would cause unrestricted segmental motion of polyisoprene chains above T_{50G} and enhance substantial displacement of the local free volume which would increase rotation and diffusion of the spin probe and, consequently, the e.s.r. linewidth narrowing. As a result, the e.s.r. spectra of the four spin probes will be dominated by the motionally narrowed component. However, the rotational correlation time depends upon the size and shape of a probe at the same temperature[16]. For example, τ_R at 293 K for probes I, II, III and IV is 8×10^{-10}, 8×10^{-10}, 1.7×10^{-9} and 3.5×10^{-9} s, respectively.

As described earlier, the e.s.r. line shapes for the probes I, II and III doped in the matrix of NR show superimposed spectra. The intensity of the narrow component is increasing, at the expense of the broad component, with rise of temperature. However, the outermost peak-to-peak separation of the remaining broad component does not change. The enhancement of the narrow component with temperature is expected due to the increased free volume. It has already been mentioned that the segmental motions of the polyisoprene chains, being in the regions of relatively rigid chain associations[6], are still restricted at temperatures above T_g. As the temperature is raised above T_g and the segmental motions increase, a greater fraction of spin probes contributes to the fast component. The fraction of the slow component as a function of temperature between 273 and 313 K is evaluated by decomposing superimposed spectra of the natural rubber and the corresponding extracted gel phase doped with probe II (*Table 2*). The amount of the broad component in NR at 303 K is approximately similar to the percentage of gel phase determined by the extraction experiment. However, it should be noted that the fraction of the e.s.r. slow component will not only depend on the amount of gel phase and its structure, but also on the size and shape of a probe, temperature of measurements and partly on the doping procedure. Therefore the percentage of the broad component, when compared with that of the gel phase, should be considered as a relative measure.

The origin of bimodal spectra was previously ascribed to the presence of the gel phase in NR[11]. To further ascertain this assignment, the extracted sol and gel phases were spin probed and the typical e.s.r. spectra are shown in *Figure 4*. The sol phase (*Figure 4b*) exhibits a three-line spectrum characteristic of the fast spin probe motion, while the gel phase gives a composite spectrum (*Figure 4c*). A bimodal spectrum for the NR gel is expected, bearing in mind the inhomogeneous distribution of the regions of motionally restricted chains and an increase

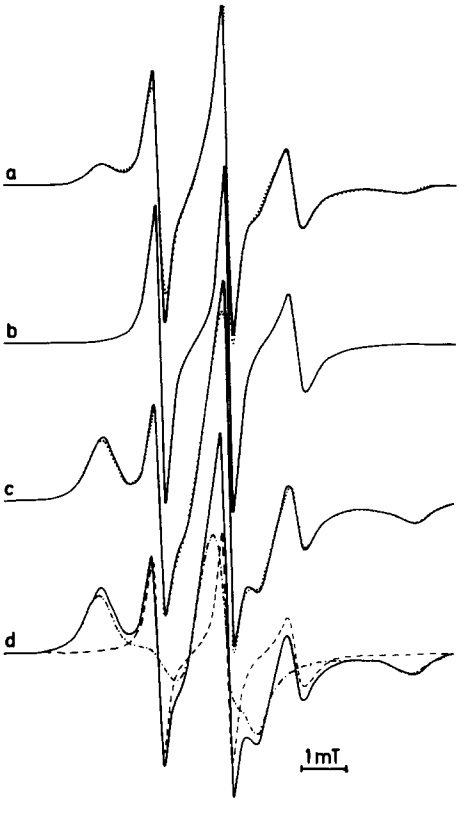

Figure 4 E.s.r. spectra of (a) NR, (b) NR-sol, and (c, d) NR-gel at 293 K doped with spin probe II. The dotted line corresponds to the simulated spectrum. Spectrum d displays the broad and narrow component as the best fit to an experimental spectrum

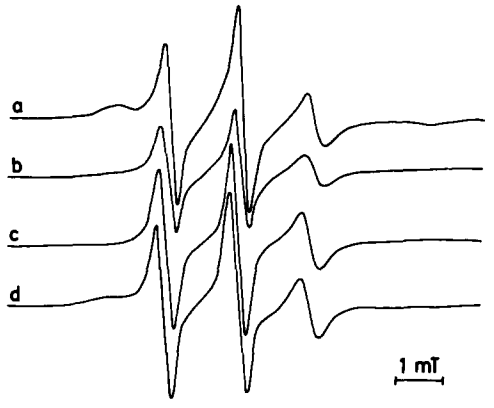

Figure 5 E.s.r. spectra of (a) NR, (b) DPNR, (c) PI and (d) PI-M at 283 K doped with spin probe II

of segmental motions above T_{50G}. Both isolated sol and gel phases of PI show only a motionally narrowed spectrum above T_{50G}.

It is known that the protein components contribute to the formation of gel and its structure in NR[5,17]. If the protein fraction is extracted from NR the constraints imposed by specific interchain interactions in the gel phase should be minimized. This would imply a faster increase of segmental motions in the gel above T_g and consequently a decrease of the e.s.r. slow component. This can be seen in *Figure 5b* on the spectrum of deproteinized rubber. A broad component shows the same tendency if the samples of NR are masticated prior to the incorporation of spin probes[11].

The presence of gel among other factors in NR, such as chain branching, entanglements, molecular mass and interaction between polar groups, contribute to the green strength, an important property in processing and applications[18,19]. The marked difference in the stress–strain curve between NR and PI is attributed to the green strength. There are several synthetic approaches to simulate the gel structure of NR in polyisoprenes in order to improve processability properties[20]. We have chosen PI modified by 4-nitrosodiphenylamine[21]. After the extraction of reaction by-products, the spin probed PI-M exhibits a composite e.s.r. spectrum similar to that of NR (*Figure 5d*). The modification of PI is expected to increase intermolecular interactions via amino groups[20]. The appearance of the broad component in the spectra of PI-M, is attributed to the increased inhomogeneity, which is similar to that of NR. Bearing in mind that both NR and PI have a high content of *cis*-1,4 sequences and that the gel and sol phases of NR differ in mechanical behaviour[6], the similarity of some physical properties between NR and PI-M are attributed partly to the presence of gel and its structure. For instance, the green strengths of NR, PI-M and PI are 2.55, 3.77 and 0.15 N mm^{-2}, respectively. Furthermore, additional interchain interactions in PI-M contribute to an increase of the cohesion strength which enables chain orientation and crystallization under stress[18].

The foregoing measurements have shown that the e.s.r. line shapes are sensitive not only to the partition of spin probes in the sol and gel phase, but also to the specific structure of the gel. It is known that protein components play a role in the formation of gel phase which is characterized by highly entangled and physically crosslinked polyisoprene chains. Protein components are not uniformly distributed in the rubber matrix. The concentration of nitrogen is 8 to 10 times higher in the extracted gel phase than in the sol phase.

The question arises as to whether the protein components expressed as a percentage of nitrogen in NR can be related to the fraction of the e.s.r. slow component. Experiments with several natural rubbers, with nitrogen contents of 0.50, 0.55 and 0.60%, have shown that the intensity of slow component increases with increased nitrogen concentration. The slow component varies from 50 to 93% at 273 K. This result supports our suggestion that the spin probe partition in NR depends on the amount and structure of the gel phase, which is related to the non-rubbery materials such as proteins.

ACKNOWLEDGEMENT

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