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ESR - Spin Probe Method in Studying Natural Rubber: an Effect of the Probe Incorporation Temperature

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Summary: Natural rubber (NR) latex containing 62 wt.% of solid phase was dried by evaporating the liquid phase at room temperature. 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl free radical, used as the spin probe, was incorporated into the NR matrix by swelling the samples in toluene probe solution at 4 °C, 24 °C and 37 °C. The probe incorporation temperatures were constant for each set of samples. When the solvent was slowly removed, all samples were annealed at 60 °C during 72 hours. Composite ESR spectra observed in the vicinity of T_{5mT} show a significant influence of the probe incorporation temperature on the spectral shape. More precisely, the amount of the broad component in a composite ESR spectrum increases with the increasing probe incorporation temperature. A simple model which describes the probe distribution inside the inhomogeneous NR matrix is proposed.

Keywords: ESR; natural rubber; probe-incorporation temperature; spin probe; swelling

Introduction

ESR spectroscopy has been extensively used in studying polymer systems during last decades.[1–4] Polymer systems usually do not possess paramagnetic centers and therefore cannot be directly studied by ESR spectroscopy. An introduction of such centers into the polymer matrix gives a possibility for the application of this method to the investigation of polymer materials. Most common paramagnetic centers that are used in studying polymers are free nitroxide radicals.[1–4] Nitroxide radicals can be introduced into a polymer either by mechanical incorporation of radicals into the polymer matrix or by chemical bonding of the radical on a polymer chain. The last method, known as spin labeling, usually requires longer experimental preparation and is rather limited due to the necessary functional groups of polymer chains and nitroxide radical that must react together resulting in a chemical bond. The simplest way to use the nitroxide radicals in studying polymer systems is to introduce them into the polymer matrix by diffusion. This method is known as spin probe method. The method implies that the polymer matrix and nitroxide radical must be soluble in the same solvent. In fact, the incorporation process of spin probe into a polymer matrix is regularly accomplished by swelling of polymer in the probe solution. This procedure is accompanied by diffusion of the probe molecules into the swollen polymer matrix and followed by slow solvent evaporation, which usually takes one or two days. During this time probe molecules immigrate from the solution to the polymer matrix and finally remain trapped in the free volume holes.

The main goal of this study is to investigate how the temperature of the probe incorporation process affects the shape of ESR spectra of a spin probe in the inhomogeneous polymer matrix. For that reason, we have chosen natural rubber as a typical inhomogeneous system.

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Experimental Part

Sample Preparation

The natural rubber (NR) latex with a solid content of 62 wt.%, was kindly supplied by the Rubber Research Institute of India. Original latex was diluted with 0.6 wt.% ammonia solution in order to get 30 wt.% of the total solid content. The diluted latex was then placed in the aluminium square vessel, dimensions of 10 cm × 10 cm × 1 cm. The samples were left at room temperature for several days to remove the liquid phase by evaporation and finally a transparent NR film having the thickness of about 1 mm was obtained. The NR film was then dried in vacuum at 40 °C during 72 hours, until a constant weight was achieved.

The free nitroxide radical 4-hydroxy-2,2,6,6,-tetramethylpiperidine-1-oxyl (TEMPOL) was used as a spin probe for ESR measurements. The probe molecules were incorporated into NR samples by swelling the samples in probe solution. Toluene, known as a good solvent for both, the nitroxide radical and NR, was used as the swelling agent. NR samples, cut in small parts, were put in the toluene solution of TEMPOL. Three different temperatures of the probe incorporation were chosen and kept constant during the process: 4 °C, 24 °C and 37 °C. The solvent was slowly removed from the solution by evaporation. In order to avoid the presence of residual solvent all samples were annealed under the same conditions - in vacuum at 60 °C during 72 hours. This time period was long enough to reach the constant sample weights in a function of the annealing time, indicating that the residual solvent was completely removed. The total amount of the spin probe of 0.15 wt.% was high enough to give a good signal to noise ratio.

ESR Measurements

ESR measurements were performed on Varian E-109 spectrometer equipped with a Bruker ER 041 XG microwave bridge and a Bruker ER 4111 VT temperature unit. Spectra were recorded at −10 °C. This temperature is in the vicinity of T_{5mT}, the temperature related to the glass transition temperature[5] (T_g), defined as:

$$T_{5mT} - T_g = 52[2.9f\{\ln(1/f) + 1\} - 1]$$

where f is the ratio of the activation volume of a probe to the activation volume of a polymer segment undergoing relaxation. The samples were kept at the temperature of measurement at least 10 minutes before the beginning of accumulation. EW (EPR-Ware) Scientific Software Service program (EPR Data Acquisition System Version 2.41A) was used for data accumulation and manipulation.

Interpretation of Bimodal ESR Spectra

Figure 1a shows the model ESR spectrum of a spin probe in a polymer matrix measured well above the glass transition temperature. The spectrum consists of three well defined narrow lines characteristic of the fast molecular motions. On the contrary, when the segmental motions are frozen ($T < T_g$), ESR spectrum indicates slow dynamics of the spin probe determined mostly by the size of free volume holes. A typical spectrum characteristic of the slow probe dynamics, which consists of three overlapping broad lines, is presented in Figure 1b. In a particular case of an inhomogeneous system, the ESR spectrum measured in the vicinity of T_{5mT}, shows a

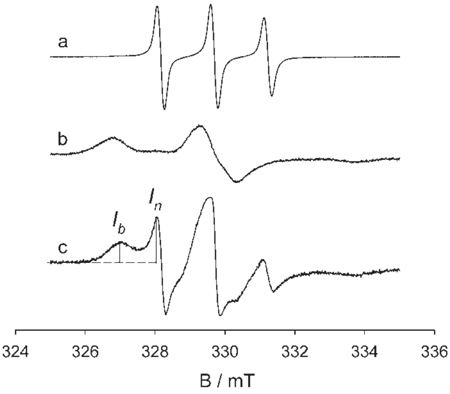

Figure 1.
Model ESR spectra of spin probe typical for the polymer: (a) well above T_g, (b) below T_g and (c) inhomogeneous system around T_{5mT}.

bimodal character. Such a composite spectrum consists of two components: the broad one being attributed to the slow motions and a narrow one that corresponds to the fast motions of the spin probe,[3] Figure 1c. The intensity ratio of the narrow and broad spectral line (I_n/I_b), as marked in Figure 1c, can be taken as a simple quantitative measure for the probe dynamics. The higher value of this ratio indicates a higher amount of the fast component present in a dynamically inhomogeneous system. The analysis of such composite spectra is often used in characterization of inhomogeneous systems, particularly elastomers, polymer blends, copolymers, block copolymers, interpenetrating networks and polymer-filler systems.[3,6–12]

Swelling Experiment

To compare the results of ESR measurements with the swelling experiment, NR samples were swollen in toluene at temperatures applied for the probe incorporation. The degree of swelling was determined gravimetrically by measuring the mass of dry samples (before starting the swelling process) and the mass of swollen samples. The swelling time was limited to 50 minutes, since the NR was uncrosslinked. For a longer swelling time the structure of the gel fraction, which allows swelling of NR, was destroyed at 37 °C. The degree of swelling (α) was calculated as a difference in the mass of swollen and dry sample over the mass of dry sample. An average value of three measurements was taken in calculating α. It should be noted that the fraction of the sol component remained in the solution was not estimated.

Results and Discussion

Figure 2 represents ESR spectra of the spin probe diffusing through the NR matrix, measured at −10 °C. These spectra consist of two components arising from nitroxide radicals in two motional domains.[3] It is evident that the same spin probe incorporated in the same material, using the same solvent, but at different probe incorporation temperatures gives different spectral shapes. Spectrum observed with the sample in which the spin probe was incorporated at 4 °C has a more pronounced narrow component in comparison with the other two spectra when the probe was incorporated at higher temperatures. Moreover, the amount of the narrow component, as measured by the intensity ratio, decreases regularly with increasing the probe incorporation temperature. For the probe incorporation temperature of 4 °C, 24 °C and 37 °C, the corresponding ratios were 1.61, 1.35 and 1.15, respectively, see Table 1.

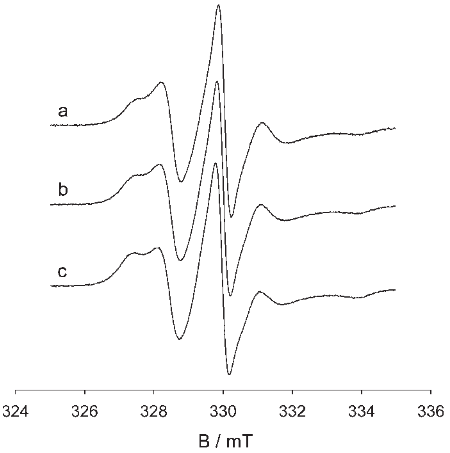

Figure 2.
ESR spectra of TEMPOL in NR measured at −10 °C. The probe incorporation temperature was: (a) 4 °C, (b) 24 °C and (c) 37 °C.

One could expect that the ESR spectra of spin probe should be the same when the temperature of the ESR measurement is kept constant, irrespective of the probe

Table 1.
The ratio of the narrow and broad ESR line intensities as a function of the probe incorporation temperature and temperature dependence of degree of swelling.

Temperature of probe incorporation and swelling/°C	I_n/I_b	Degree of swelling (α)
4	1.61	12.4
24	1.35	13.7
37	1.15	17.0

incorporation conditions. However, according to the results mentioned above, this is not the case. The spectra shown in Figure 2 clearly demonstrate that the probe incorporation temperature plays an important role in ESR spectroscopy of inhomogeneous polymer systems. In a special case of the composite spectra, characteristic of the temperature region of the phase transition, the amount of the broad and narrow component strongly depends on the temperature of probe incorporation. A higher amount of the narrow component for the lower value of the probe incorporation temperature is a consequence of higher probe mobility. Contrary, a lower amount of the narrow component, when the probe incorporation temperature is higher, indicates that the probe mobility is rather limited.

Such an interpretation of ESR results can be explained as follows:

At the lower value of the probe incorporation temperature the probe molecules enter in large free volume holes only and cannot penetrate into the high density regions of the NR matrix, Figure 3a. Therefore, in such case, they probe mostly the mobile parts of the matrix.

The degree of swelling (α) increases by increasing the temperature from 12.4 for 4 °C to 17.0 for 37 °C, Table 1. This allows the probe molecules to penetrate into the small holes, Figure 3b. Once the solvent is removed, the probe molecules remain trapped in these holes and consequently their motions are restricted.

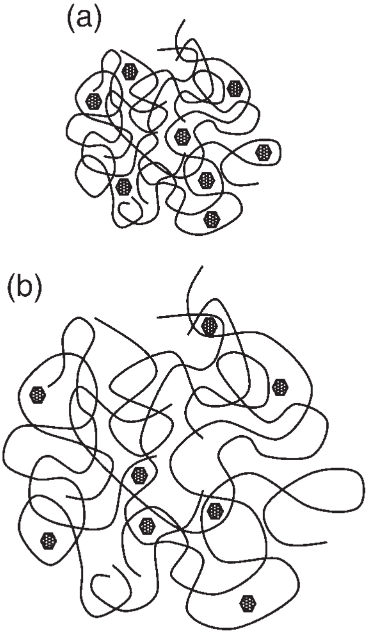

Figure 3.
Schematic representation of the probe incorporation process in NR at (a) 4 °C and (b) 37 °C.

Conclusion

On the basis of results of the present work it is clear that the probe incorporation temperature is an important factor when ESR spectroscopy - spin probe method is applied in studying inhomogeneous systems. Therefore, this temperature must be strictly controlled in order to avoid its unwished effect, which might lead to a possible wrong interpretation of ESR results.

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