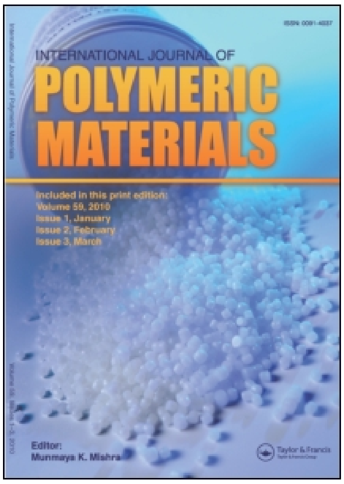

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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J. N. Aneli[a]; L. M. Khananashvili[a]
[a] Chemical Department, Tbilisi State University, Tbilisi, Republic of Georgia

To cite this Article Aneli, J. N. and Khananashvili, L. M.(1995) 'Diffusion of Stable Radicals and Electric Current in Polymeric Composites', International Journal of Polymeric Materials, 27: 3, 157 — 161

To link to this Article: DOI: 10.1080/00914039508009666

URL: http://dx.doi.org/10.1080/00914039508009666

Intern. J. Polymeric Mater., 1995, Vol. 27, pp. 157–161
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Diffusion of Stable Radicals and Electric Current in Polymeric Composites

J. N. ANELI and L. M. KHANANASHVILI

Chemical Department, Tbilisi State University 3, Chavchavadze Ave., Tbilisi 380028, Republic of Georgia

(Received March 9, 1994)

Influence of stable iminoxide radicals on the conductivity of several filled by carbon black polymers has been investigated. It has been shown that sorbtion—desorbtion of stable radicals correlates with the change of specific volume resistance ρ_v of these materials. This effect is due to capture of charges by radicals localized in the polymer matrix near conductive channels.

KEY WORDS Iminooxide radicals, carbon black filled polymers, conductivity.

Many studies devoted to diffusion of stable radicals in polymeric materials.[1-3] However, the radicals in these studies are primarily considered as molecular sensors providing information about the structure and dynamic of macromolecules.

It has been assumed[4] that charges are solvated by free radicals localized in polymeric matrix. It was, therefore, of interest to ascertain the influence of stable radicals on conductivity of polymeric composites containing conductive fillers during diffusion of these radicals.

Several conductive composites were used on the basis of polydymethilmethilvinilsiloxan elastomer SKTV and carbon black P803 and P257-E as a filler. The carbonate dimethilsiloxan block copolymer (CDS) with those fillers were also investigated. The contents of fillers in the composites were accordingly P803-100 mas.part and P257-E-50 mas.part.

The samples on the basis of SKTV were prepared by peroxide vulcanization, and samples on the basis of CDS by introduction of filler powder into mixtures of polymer-chloroform with subsequent drying in the thermostate at 60°C.

Introduction of stable radicals (2,2,6,6-tetramethil-4-carboximethilpiperidin-1-oxide) to the composites matrix was made by sorbtion of radicals during 30 min at 50°C. The radicals concentration was 10^{-3}–10^{-4} mol/l. The ESR spectra were recorded by standard spectrometer RE-1301 at different temperatures. Values of rotational diffusion coefficient has been determined using $D_r = 1/6\tau_c$, where τ_c = correlation time of rotating radicals (the atlas of ESR spectra of spin zondes and labels was used).[5] The transfer diffusion of stable radicals was determined by desorbtion of radicals from composite matrix. The samples were placed in the steam of thermostatical air during fixed time. At once after this procedure the ESR spectra were registrated. Values of transfer diffusion coefficients D_t were calculated by formulas:[5]

$$\frac{I_0 - I}{I_0} = \begin{cases} \frac{4}{d}\left(\frac{D_T t}{\pi}\right)^{1/2} & \text{if } \frac{I_0 - I}{I_0} < 0.5 \\ 1 - \frac{8}{\pi^2}\exp\left(\frac{\pi^2 D_T t}{d^2}\right) & \text{if } \frac{I_0 - I}{I_0} > 0.5 \end{cases}$$

where I_0 and I = intensivity of ESR signals accordingly before and after desorbtion of radicals during time t, d = film thickness.

Activation energies of diffusions were calculated using Arrhenius formula $D = D_0 \exp(-E/kT)$. The recording of ESR spectra and determination of ρ_v were carried out simultaneously.

The ESR spectra of nitroxide radicals sorbed in the investigated materials consist of three components, the symmetry of which depends on the type of polymer matrix. The spectrum for rubber has, on the basis of clean silicon elastomer SKTV (Figure 1a), a symmetric form. This spectrum corresponds to "rapid" nitroxide radicals, which are localized near segments having high mobility at room temperature. The ESR spectra of stable radicals localized in another polymeric material represent superposition of at least two simple spectra (Figure 1b–e), one of which corresponds

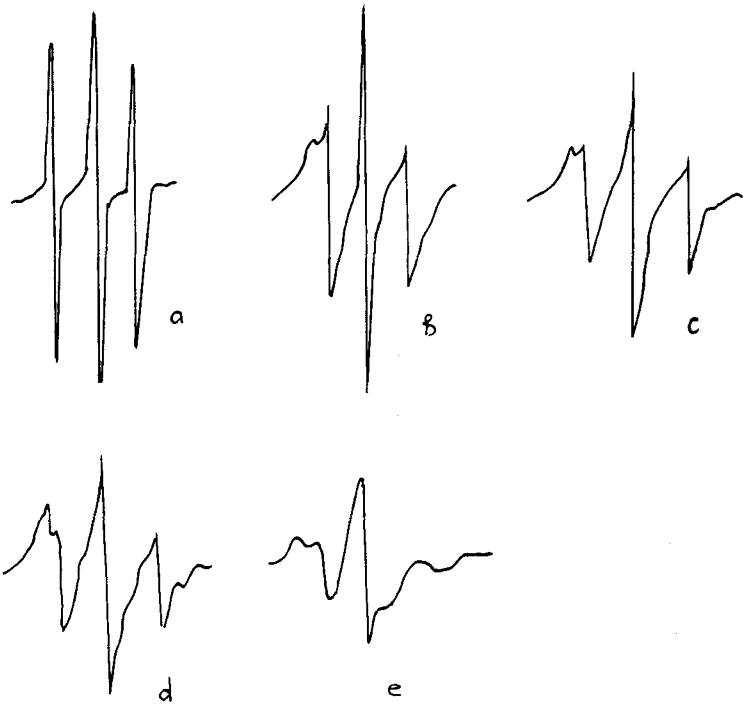

FIGURE 1 Specta of ESR of stable nitroxide radicals sorbed in SKTV(a), CDS(b), SKTV + P803 (100 mas. p.)(c), SKTV + P257-E (50 mas. p.)(d), CDS + P257-E (50 mas. p.)(e).

TABLE I

Diffusion parameters, concentrations of radicals before desorbtion and ρ_v polymeric materials

No.	Polymeric materials	D_r (rr),** sm/s	D_r (sr), sm/s	D_t (rr), sm/s	E_r (rr), kJ/mol	E_t (rr), kJ/mol	$R \times 10^{-4}$, mol/l	ρ_v, Ohm × m
1	SKTV	$1, 1 \times 10^{11}$	—	$2, 1 \times 10^{9}$	30, 3	114, 0	14, 2	—
2	CDS	$3, 8 \times 10^{9}$	$4, 5 \times 10^{8}$	$4, 4 \times 10^{7}$	19, 7	104, 5	9, 6	—
3	SKTV + P803(100)*	$4, 4 \times 10^{9}$	$4, 0 \times 10^{8}$	$5, 4 \times 10^{7}$	19, 2	105, 6	7, 8	12, 0
4	SKTV + P257-E(50)	$1, 8 \times 10^{9}$	$4, 8 \times 10^{8}$	$9, 6 \times 10^{6}$	12, 8	38, 4	5, 1	3, 1
5	CDS + P257E(50)	$1, 2 \times 10^{9}$	$2, 9 \times 10^{8}$	$6, 4 \times 10^{6}$	9, 0	31, 5	4, 4	2, 6

*Numbers in the brackets correspond to content of filler in mas. p.

**Letters in the brackets correspond to: (rr) = rapid rad and (sr) = slow rad. D_r and D_t were measured at room temperature.

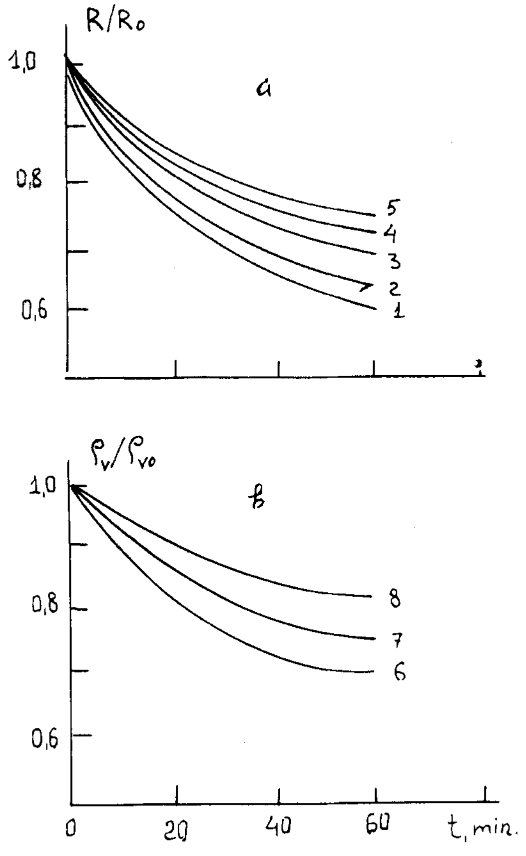

FIGURE 2 Depend of stable radicals concentration (a) and ρ_v (b) on desorbtion time at room temperature for SKTV(1), SKTV + P803(2), CDS(3), SKTV + P257-F(4,7), CDS + P257-E(5,8).

to "rapid" radicals and the other to "slow" radicals. It is known that velocity of rotation of radicals depends on segmental mobility of macromolecules.[6] In addition, macromolecules placed near the surfaces of filler particles form structures with higher density than those in regions that are far from filler particles.[7] Therefore, radicals localized in interface layers must be "slower," than those localized in polymer matrix beyond this layer. Since the density of the interface layer depends on interaction between polymer and filler, this interaciton should be reflected in diffusion parameters of radicals sorbed by the composites. For SKTV with fillers P803 and P257-E (Table I), this interaction is weaker with the first material than with the second.[8] Therefore, the coefficients for the first material are higher than for the second, because they depend on viscosity (density) of the localized region of macromolecular matrix (by formulas of Stokes-Einstein,[6] $D = kT/8\pi\zeta r^3$, $D = kT/6\pi\zeta r$, where ζ = viscosity of environment, r = middle diameter of radical).

The results in Table 1 show that the diffusion processes are fastest in polymers without fillers. Among composites, higher diffusion coefficients are found with materials based on SKTV and P803. Composites based on CDS and P257-E have very low penetration for radicals. This is attributed to both the influence of filler on composite structures, as well as the pecularity of molecular structure of CDS. In this polymer, stable radicals are localized among siloxane and carbonate blocks. The first of which diffusion processes proceed intensively, then the second.[9] The comparison of the number of sorbed radicals and ρ_v of these materials shows that the higher the ρ_v, the higher the degree of radical sorbtion.

The measurements of the radical concentration at desorbtion and their ρ_v show that the type of fillers and polymers affect the radical concentration changes and conductivity. The desorbtion of radicals proceeds faster from unfilled polymers SKTV and CDS more than from corresponding composites.

The identical character of curves for time dependence of radical concentration and ρ_v of polymer composites justified the assumption of solvation of charges by free radicals. Therefore, the current density increased in the samples when the stable radicals are desorbed from the polymeric matrix. The distortion of these curves as desorbtion time increases may indicate that the radical localization is inhomogeneous. Nonhomogenity of radical distribution and density of conductive channels in the polymeric matrix can lead to selectivity of interaction between radicals and charges. Particularly, the radicals localized in the deep traps desorbed with difficulty and do not take part in the processes of charge occupation by free radicals.

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