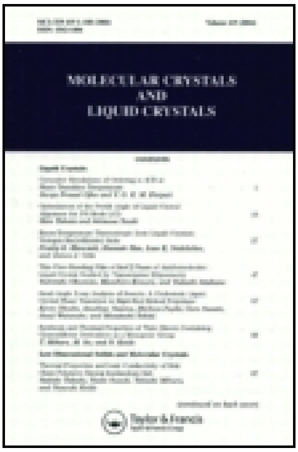

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Electrical Conductivity of Polymer Composites During Mechanical Relaxation

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The effect of mechanical relaxation on the relaxation behaviour of electrically conductive polymer composites was investigated. Experiments showed that filler content significantly affects the relaxation characteristics of the material due mainly to the effect of the filler type on the relaxation processes. Rubbers with active carbon blacks show ranges of slow and fast relaxation much more clearly than those with low-active carbon blacks, even at increased concentrations. With active carbon blacks, the increase in the filler-filler and polymer-filler interactions is balanced by the high content of low-active carbon blacks, because in both cases the elasticity modulus of the material and the internal friction during relaxation processes increase.

Keywords Electrical conductivity; filler concentration; polymer composites; relaxation time; resistance; stretching

Introduction

Mechanical stresses caused by the deformation of composite materials affect both the molecular and supermolecular structures of polymers [1–3]. Structural changes occurring in composites produced by various types of mechanical deformation (stretching, compression, shear, etc.) affect the structure of an electrically conducting system. As a consequence, they affect the substructure and the filler particles bound to it [4–6]. It is evident that in the case of conducting polymer composites, mechanical deformation influences the electrical conductivity of the materials.

Results and Discussion

It is well known that forces formed in the polymer matrix counteract external influences right at the outset of deformation. The elucidation of the relaxation effects on electrical conductivity is complicated during the deformation of electrically conductive polymer composites (ECPCs) due to several overlapping factors.

Tests were done to study the electrically conducting properties of polymer composites during mechanical relaxation. The same composites were studied at high deformation [7].

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The electrically conducting rubbers were polydimethyl-methyl-vinylsiloxane (industrial-type SKTV). Thinly dispersed carbon black of type P357E was used as the conducting filler and dimethyl-aminomethyl-triethoxisilane as the hardening material. The rubber ingredients were mixed in laboratory mills for 10–15 min at room temperature. Cross-links were formed at room temperature after 25–30 min.

The following experiment was carried out to determine the electrical volumetric specific resistance, ρ, during relaxation of the mechanical tension, σ. A thin sheet (2 mm) of electrically conducting rubber was stretched on a stretching machine at a specific deformation, ε. The change in ρ was recorded by an automatic recorder as soon as the stretching was stopped. The scale of the automatic recorder was graduated in ohms on time τ, and a synchronous recording was made of the time dependence of σ at a fixed deformation. The relaxation characteristics were recorded for the same samples at the end of the stretching-contraction cycle.

As Fig. 1a shows, the values of ρ increase during relaxation of tension σ. Here ρ increased at a higher rate in rubbers, which deformed at relatively high rates. An increase in the stretching rate also induced an accelerated increase of ρ in these materials. The kinetics of the reduction in mechanical tension σ were in complete agreement with the nature of the change in ρ. This means that the faster the mechanical relaxation of the sample, the greater the rate of sample deformation (Fig. 1b). The increase in ρ with time during relaxation of σ can be explained by the effect of the disordering of the elastomer molecular system that occurs after the deformation has stopped. In this case, the internal mechanical tensions are reduced by the transition of a highly regulated system to a lower regulated state at this stage of deformation. Disordering of macromolecules in the system induces destruction of the conducting circuit, i.e. an increase in ρ of the material. Since the increase in the deformation rate causes an increase in the intensity of the structural transformation in the

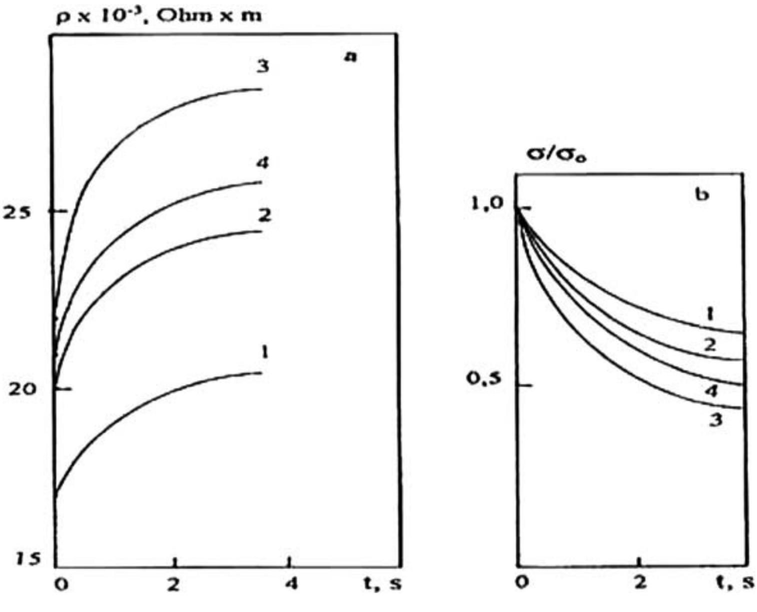

Figure 1. Time dependences of ρ (a) and σ (b) during relaxation of mechanical tension after stretching the rubber, based on SCTV elastomer with P357E carbon black (350 mass parts), by 50% (1, 4), 100% (2) and 150% (3). The rate of elongation is 2.5 (1–3) and 5.0 mm/s (4) respectively.

material, it is evident that significant deformation will occur in an electrically conducting system that interacts with the polymer matrix.

The time dependences of ρ during relaxation of the rubbers are successfully described by the expression:

$$\rho = \rho_\infty - (\rho_\infty - \rho_0)\,\mathrm{e}^{-t/\tau} \tag{1}$$

where ρ_0 and ρ_∞ are border values of ρ during relaxation under fixed stretching deformation; and τ is the relaxation time.

Eq. (1) is the solution of the differential equation, similar to that deduced for the kinetics of mechanical polymer relaxation [1]. According to Eq. (1), the kinetics of relaxation are described by the Maxwell model [2]. Applying the logarithm from Eq. (1), we get:

$$\ln\frac{\rho - \rho_\infty}{\rho_0 - \rho_\infty} = -\frac{\mathrm{t}}{\tau} \tag{2}$$

Thus if Eq. (1) is correctly applied to the relaxation kinetics, the dependence should fit into a straight line in the coordinates of Eq. (2).

As shown by Fig. 2, the time dependences are straightened by Eq. (2). This allows the model of connected strings and damper (the Maxwell model) to be used for describing the kinetics of the change of ρ during relaxation of the mechanical tension of electrically conducting rubber.

The relaxation times, τ, for composites of SCTV elastomer with P357E carbon black were determined by tangents of straight lines (Fig. 2). Comparison of the mechanical relaxation characteristics with similar characteristics obtained for electrical conductivity of the same materials leads to the conclusion that the mechanical and electrical conductivity

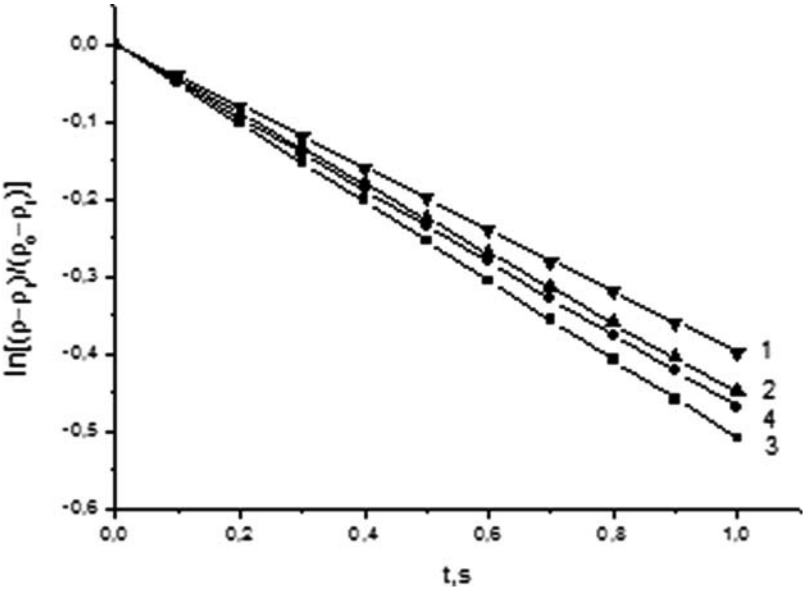

Figure 2. Dependence of ρ of the samples based on SCTV elastomer with P357E carbon black (50 mass parts) on time during relaxation in coordinates of Eq. (1). Numbering of the curves coincides with those presented in Fig. 1.

Table 1. Relaxation characteristics of stretched ECPC based on SCTV elastomer*

Filler, mass parts	Deformation %	Deformation rate mm/s	Relaxation time τ s
P357E (50)	50	2.5	1.00
	50	5.0	0.88
	100	2.5	0.91
	150	2.5	0.84
P357E (60)	30	2.5	0.60
	60	2.5	0.44
P803 (50)	100	2.5	3.84
P803 (60)	100	2.5	2.28

*Elastomers were obtained by the additive vulcanisation technique.

relaxations correlate well. Moreover, by means of electrical conductivity it is possible to obtain new relaxation phenomena in solid polymers which is not possible with other methods.

The data shown in Table 1 confirm that the increase in the deformation of polymers leads to an increase in the relaxation rate of both ρ and σ. This effect is strengthened when the filler concentration in the composite is increased. For example, at comparable rates of deformation ρ, rubber containing 60 mass parts of active carbon black relaxes at a higher rate than the same rubber containing 50 mass parts of the same carbon black. The effect of interphase growth is observed here. This growth causes a conditional increase in the equilibrium modulus of the system. In composites containing less-active carbon black (P803), relaxation times are much greater than in rubbers containing active carbon blacks. This indicates a relatively low adhesive interaction between the polymer and the filler in rubbers with P803 carbon black. However, weak absorption forces also increase during deformation (the tension increases).

Investigation of the relaxation processes at the end of the deformation cycle (stretching-contraction) after complete discharge of the samples showed that the relaxation phenomena are more complex than the facts described above indicate. Firstly, the complexity is expressed in the functional ρ-t dependence, starting from the completed end of the cycle (Fig. 3). Wuth respect to the curves in Fig. 3, it should be mentioned that they actually represent a superposition of at least two relaxation processes. One of these processes relates to the most linear parts of the curves, and the second relates to the most curvilinear parts with limit overwhelming at $t \to \infty$ (see Fig. 3, curves 2 and 3). Both parts of the curves are a sign that the conducting system regulates the macromolecular part of the composite. However, the rate of relaxation and time to reach equilibrium values of ρ at the end of the relaxation period depend significantly on the filler concentration. For the composite containing 40 mass parts of carbon black, the process proceeds at a slow rate, but its equilibrium state occurs quite rapidly, whereas in rubbers with 50 and 60 mass parts of P357E, higher rates are observed at the initial stage of relaxation with a decelerated growth curve in the later stages of the kinetics. Another characteristic of these dependences is that the difference between the minimum and maximum values of ρ during the whole relaxation interval also depends strictly on the degree of filling.

From the analysis of the dependences shown in Fig. 3, it is possible to conclude the following. It can be assumed that two physical processes occur during relaxation of the systems, taking into account the ideas of Bartenev [1] on the formation of a complex

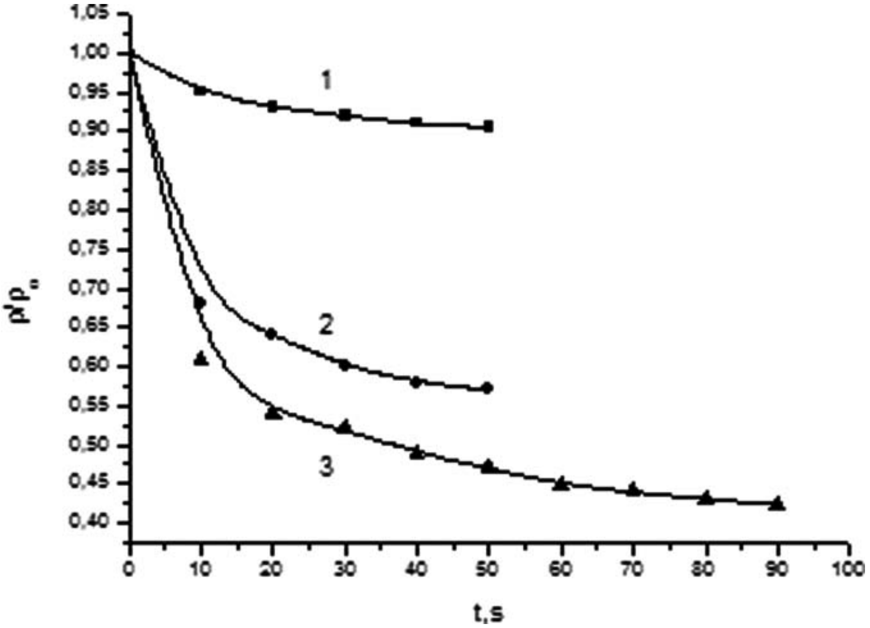

Figure 3. Dependence of ρ on delay on completion of contraction (relaxation without loading) for rubbers based on SCTV elastomer containing 40 (1), 50 (2) and 60 (3) mass parts of P357E carbon black respectively. At the moment of discharge $\rho_0 = \rho$.

heterogeneous system after injection of active carbon blacks into a polymer that is characterised by non-linear viscoelasticity (processes of this type are non-linear relaxation at low deformation and non-linear viscoelasticity at high deformation; see the thixotropic effect by Mallins-Patrikeev [6] in particular). The first process is close to the elastic range of deformation (Hooke's range) of a macromolecular system. It is known that this process proceeds quickly in both branches of the deformation cycle and is defined by the elastic properties of the composite matrix. Elastic forces rapidly drive the system into equilibrium after release of the external influence. However, it is often difficult to separate this process in polymers. The electrically conducting system of a composite material associated with adsorption forces can clearly respond to the smallest structural changes in topology of structural polymer units (globules, for example), which are absolutely controlled by them. In the present case, the conducting system of the polymer matrix acts as a relay-contact scheme which translates information about the state of the surrounding (polymer) medium into the "language" of electrical conductivity. Thus the abrupt decrease of ρ values shown in Fig. 3 corresponds to the reduction of the conducting channels that exist in close connection with the macromolecules of elastomer, the elastic properties of which are often promoted by the bonds mentioned.

The second process is the reduction of the initial system (before deformation) with the participation of filler particles split from the macromolecules during deformation (stretching) of the polymer system, or no participation in adsorption of the macromolecules during deformation (carbon black agglomerates, for example). It is known that these particles decelerate regulation in the macromolecular system, and intensify the internal friction and non-linear effects at the high deformations connected with it. That is why their presence in the composite always prolongs the relaxation processes. Apparently this is the reason for

Table 2. Relaxation characteristics of electrically conducting rubbers based on SCTV elastomer at the end of deformation cycles*

No.	Filler Mass parts	Sample prehistory: Maximal deformation in the cycle, %	Sample prehistory: Deformation rate, %	Relaxation time, s: Fast	Relaxation time, s: Slow
1.	P357E (40)	150	2.5	1.2×10^{-2}	7
2.	P357 (50)	150	2.5	4.0	21
3.	P357E (60)	60	2.5	6.7×10^{-2}	28
4.	P803 (60)	200	2.5	—	6
5.	P803 (120)	150	2.5	2.2×10^{-2}	11
6.	P357 (40)	150	2.5	10.6×10^{-2}	48
7.	P803 (60)	150	2.5	5.1×10^{-2}	24
8.	P803 (60) + SCTN (20)**	200	2.5	2.8×10^{-2}	16

*Composites 1–5 were obtained by the additive vulcanisation technique; composites 6–8 were obtained by the peroxide vulcanisation technique.

**SCTN – low-molecular elastomer (M.n. about 25,000).

the deceleration of the re-establishment of the primary conducting system of the composite material. Therefore, taking this into account, it becomes clear that the delay in the complete reduction of the equilibrium structure in high-filled polymer matrices is greater than in low-filled polymers. At first glance, this seems to be paradoxical. It should be remembered that according to the exponential dependence of ρ on the concentration of the active filler, reduction of the structure is much greater for a composite with 50 mass parts of carbon black than for a composite with 60 mass parts of the same carbon black.

The ρ–τ dependences shown in Fig. 3 reflect morphological changes in a heterogeneous system. Analysis of these curves showed that the exponential parts are successfully described by Eq. (1), the only difference being that ρ_∞ is substituted by ρ_m at the end of relaxation, and ρ_0 by ρ_1, which corresponds to the value of ρ at the crossing of the exponential curve by the straight line.

Relaxation times were determined using Eq. (1) for the various composites tested. The numerical values obtained are shown in Table 2.

Analysis of the data from Table 2 shows that:

1. Filler content significantly affects the relaxation characteristics of the material. For example, the rubber containing 40 mass parts of P357E carbon black has a fast relaxation rate of about five times lower and a slow relaxation rate of four times lower than the relaxation rates of similar rubber with 60 mass parts of the same filler. The rubber containing 60 mass parts of P803 carbon black has no fast relaxation range at all, but the same rubber displays relaxation ranges at a filler concentration of 120 mass parts of P803. The main reason for these differences is the increase in the modulus of elasticity of the rubber with the increase in filler concentration. On the one hand, this leads to an increase in the surface square of the interphase, and, on the other hand, to the occurrence of broken polymer filler bonds, which promote the increase of internal friction and deceleration of the relaxation process in the macromolecular system. That is why, although the increase in the modulus of elasticity is the reason for the increase in the rate conditionally referred

to as “fast relaxation”, the mechanical tensions caused by accumulation of the filler particles, detached from the polymer globules, lead to a noticeable increase in the slow relaxation time.

2. The effect of the filler type on the relaxation processes is also significant. Rubbers with active carbon blacks (P357E) display ranges of slow and fast relaxations much more clearly than those with low concentrations of active carbon blacks (P803), even at increased concentrations. Firstly, the effect of the filler type is determined by the formation of an interphase layer and is similar to the effect of the filler content. In the case of active carbon blacks, the increase in the filler-filler and polymer-filler interactions is balanced by the high content of low-active carbon blacks, because in both cases the modulus of the material and internal friction during the relaxation processes increase.
3. A comparison of the characteristics of the rubber produced by two different vulcanisation techniques shows that the rate and time of relaxation depends on the vulcanisation network density, which is not weaker than the type and concentration of the filler (compare composites 1 and 6, 4 and 7 in Table 2). Since the concentration of polymer cross-links in peroxide vulcanisates prevails significantly over the concentration of longitudinal links (by SCTV end groups) in rubbers obtained by additive vulcanisation, it is evident that the mechanical modulus of the first composites is greater than that of the second ones. This is the reason for the differences in relaxation characteristics. In this regard, the increase in the “soft phase” in the composite due to the introduction of low-molecular SCTN elastomer softens the relaxation processes. This is evident from the decrease in the fast relaxation rate and the time of slow relaxation compared with those of similar composites containing no SCTN (compare composites 7 and 8, Table 2).

Conclusion

The mechanical relaxation processes in electrically conducting polymer composites, particularly in conducting rubbers, were measured by studying time-dependent processes of electrical conductance, because the behaviour of the conducting system is directly dependent on any changes in the polymer matrix.

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