Stress-relaxation study of tetrafluoroethylene–propylene rubbers

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(Received 7 April 1994; revised 13 December 1994)

Stress-relaxation processes of tetrafluoroethylene-propylene (TFE-P) elastomer compositions (including crosslinked and carbon-black-filled samples) were studied within the temperature range from 298 to 573 K in air over times ranging from 10^1 to 3×10^5 s. Using the Tobolsky–Murakami method, discrete spectra of the relaxation times (τ_i) were determined. In the high elastic state, λ-relaxation region transitions proceed by segmental motion, with activation energies up to $55\,kJ\,mol^{-1}$. These processes are related to the rearrangement of domains formed by different microstructures of the fluoroelastomer chain, the so-called 'soft' rubber component. The activation energy, U_φ, of the φ-transition corresponds to a rearrangement of the carbon black filler network, i.e. 'hard' rubber component. Three relaxation processes were registered in crosslinked elastomers, which are associated with changes in the chemical network. They consist of several transitions: the δ_1-process has the lowest activation energy $(U_{\delta 1} = 64\,kJ\,mol^{-1})$ and can be related to the rearrangement of the dense sections of the chemical network, whereas the μ_F-transition can be connected with decomposition and recombination of cross-pseudo-hydrogen bonds between fluorine and hydrogen atoms. This energy is close to the viscous flow activation energy in the pseudo-plastic region in terms of the de Waele–Ostwald equation. The other δ-process can be assigned to the high-temperature destruction of C–C bonds in the chemical network. By dynamic mechanical experiments, the principal α-relaxation and three β-transitions below T_g were also registered.

(Keywords: tetrafluoroethylene–propylene rubber; stress relaxation; physical transitions)

INTRODUCTION

Fluorine-containing elastomers possess high thermal and chemical resistance, and good physico-mechanical and dielectric properties, facilitating their versatile technical application. Performance properties of fluoroelastomers are connected with their discrete structure. It is well known that there are a number of structural elements in these elastomers which differ in their morphology and molecular mobility[1].

Relaxation spectroscopy provides a means to obtain information about different structural elements and the corresponding relaxation transitions in order to clarify their nature and predict the deformation properties of the material under operational conditions.

Data on relaxation studies of fluorine-containing elastomers are very rare in the literature. In crosslinked copolymers of vinylidenefluoride (VDF) with hexafluoropropene (HFP), only one relaxation transition has been reported[2]. Investigation of the dynamic mechanical properties of this class of elastomers showed two transitions (α and β) in the amorphous region of non-crosslinked samples[3]. Studies of physical and chemical relaxations, including dynamic-mechanical properties of VDF and trifluorochloroethylene (TFCE) elastomers, revealed 10 relaxation transitions[4]. The stress relaxation under high temperature and γ-irradiation

from ^{60}Co has been studied on samples of crosslinked tetrafluoroethylene–propylene (TFE-P) copolymer[5,6]. Depending on the dose rate, the activation energy of the chemical relaxation has been found to be $105\,kJ\,mol^{-1}$ $(8.0 \times 10^4\,R\,h^{-1})$ and $122\,kJ\,mol^{-1}$ $(1.2 \times 10^5\,R\,h^{-1})$.

Using an oil-soluble initiator (tert-butyl peroxybenzoate), we synthesized a new type of TFE-P copolymer possessing a high degree of alternating regularity, and excellent chemical and thermal stability[7,8]. Analysis of mechanical relaxation spectra of these fluoroelastomers makes it possible to evaluate their physical and chemical structure.

In the present work, different types of relaxation processes are studied, mainly in the high elastic state of linear, filled and crosslinked TFE-P copolymers.

EXPERIMENTAL

Materials

TFE-P copolymer was obtained by a technique described previously[7]. The initial monomer mixture contained 80/20 mol% TFE and P. A trilon-rongalite redox system was used, containing tert-butyl peroxybenzoate (TBPB) and ammonium perfluorooctanoate as emulsifier[7]. The polymerization was carried out in a $500\,cm^3$ autoclave at 298 K and 2.0 MPa, with a stirring speed of $700\,min^{-1}$. The TFE/P feeding mixture $(50/50\,mol\%)$ was continuously supplied to maintain constant pressure during the polymerization. After

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coagulation of the emulsion obtained, the TFE-P copolymer was separated and used in our experiments.

TFE-P compositions were prepared on mixing rolls and consisted of (phr): TFE-P copolymer, 100; α, α'-bis-(tert-butylperoxi-*m*-isopropyl)benzene, 1; trialyliso-cyanurate, 5; MT carbon black, 25, MgO, 3; sodium stearate, 2. The reactants used were of guaranteed quality. On the basis of the above compositions, different types of samples were prepared. Original and carbon-black-filled non-crosslinked samples were prepared on a press at 433 K and 12.0 MPa, and cooled under pressure. The vulcanization was carried out in two steps: in the press at 20.0 MPa and 433 K for 15 min, and in an oven maintained at 473 K for 3 h.

Measurements

The stress-relaxation study was carried out by a 'Polyani' type relaxometer, similar to that used by Ito[6], supplied with thermostat and strain gauge system. Rectangular samples (70 mm × 5 mm × 1 mm) of the copolymers obtained were tested at static deformation of 20% in air. The relaxation of the linear, carbon-black-filled non-crosslinked TFE-P copolymer was studied in the temperature interval from 298 to 373 K, while that of crosslinked copolymers was investigated in the range from 298 to 573 K.

The dynamic-mechanical spectra were determined by means of a free oscillation pendulum at low frequency (3.5 Hz) in the temperature interval from 93 to 673 K.

Rheological characteristics of TFE-P copolymer were determined on a capillary viscometer working under conditions of constant shear stress (S), equipped with nozzles with length to aperture ratios of 10 and 20. The experiments were carried out in the temperature interval from 458 to 478 K and shear stress within the range from 160 to 285 N.

RESULTS

The data obtained from the stress relaxation were processed by a computer program[9] using the Tobolsky–Murakami method[10]. The different transitions in the mechanical relaxation spectra were identified by an approach developed by Bartenev *et al.*[1,4] for rubber-like polymers.

Figures 1 and *2* show the temperature dependences of the discrete relaxation times of the separate relaxation processes, determined from the stress-relaxation data. The linear curves observed obey the Boltzmann–Arrhenius equation:

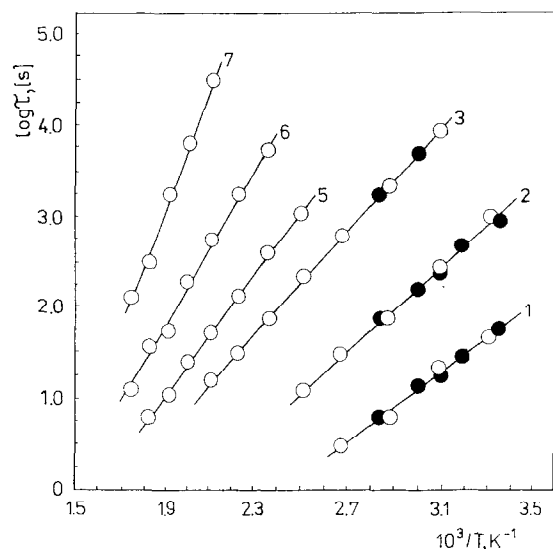$$\tau_i = B_i \exp\left(U_i/kT\right) \tag{1}$$

Figure 1 Temperature dependence of relaxation times of non-filled TFE-P copolymer: O, crosslinked; ●, non-crosslinked. Plot numbering corresponds to the numbering in *Table 1*
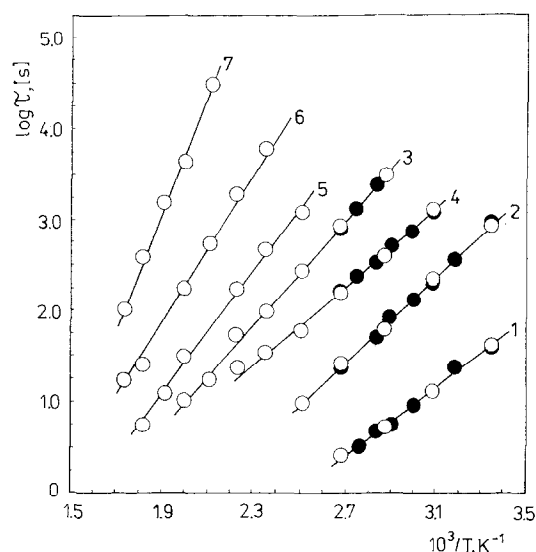

Figure 2 Temperature dependence of relaxation times of carbon-black-filled TFE-P copolymer: O, crosslinked; ●, non-crosslinked. Plot numbering corresponds to the numbering in *Table 1*

Table 1 Relaxation transitions in non-filled and carbon-black-filled crosslinked TFE-P copolymer and their constants, obtained from stress-relaxation data

| No. | Relaxation transition | B_i (s, ±20%) | | U_i (kJ mol^{-1}, +2) | T_i (K) at $\nu = 3.5$ Hz | |
		Non-filled	Filled		Non-filled	Filled
1	λ_1	4.6×10^{-5}	2.7×10^{-5}	36	471	445
2	λ_2	3.1×10^{-5}	1.8×10^{-5}	43	539	510
3	λ_3	1.4×10^{-5}		55	637	
4	φ	1.1×10^{-3}		37	741	
5	δ_1	4.2×10^{-6}		64	672	
6	μ_F	5.1×10^{-7}		82	720	
7	δ_c	3.8×10^{-10}		126	725	

where τ_i (s), B_i (s) and U_i (kJ mol^{-1}) are the discrete time, a coefficient depending on the dimension of the kinetic unit, and activation energy of the ith relaxation process, respectively. The relaxation processes observed and their constants are shown in *Table 1*.
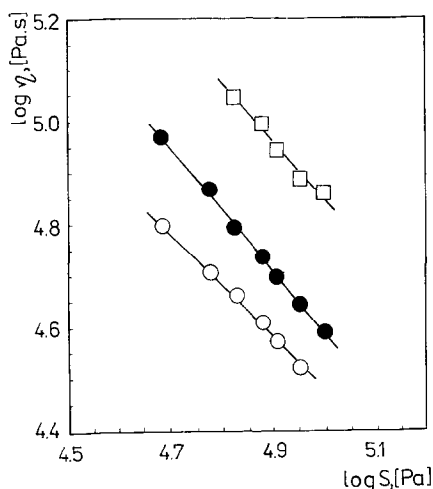

Figure 3 Logarithmic dependence of effective viscosity (η) of linear TFE-P copolymer on shear stress (S) at different temperatures: □, 458 K; ●, 468 K; ○, 478 K

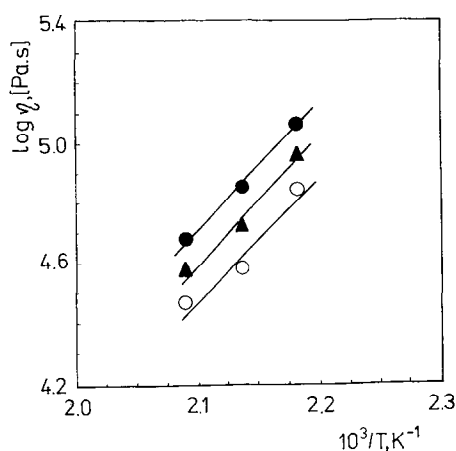**Figure 4** Dependence of effective viscosity of linear TFE-P copolymer on temperature in Arrhenius coordinates at different shear stresses: ●, 63 kPa; ▲, 79 kPa; ○, 100 kPa
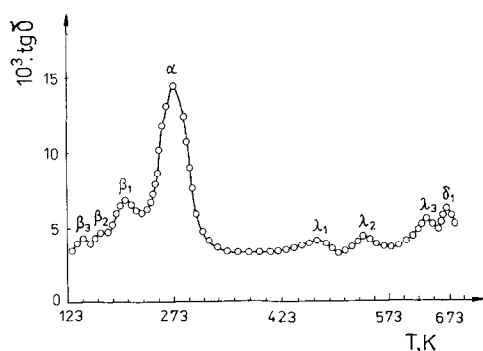

Figure 5 Dynamic-mechanical spectra of internal friction of non-filled crosslinked TFE-P copolymer at a frequency of $\nu = 3.5$ Hz

Data obtained from studies of shear stress *versus* shear rate ($\dot{\gamma}$) curves of TFE-P copolymer were processed by a technique described earlier[11]. From the intersects of log S *versus* log $\dot{\gamma}$ straight lines, the effective viscosities η were determined and the results are presented in log η *versus* log S plots (*Figure 3*). The activation energy of viscous flow was calculated from the dependence of log η on temperature in Arrhenius coordinates (*Figure 4*).

The temperature dependence of tg δ for non-filled crosslinked TFE-P copolymer is shown in *Figure 5*.

DISCUSSION

Six relaxation transitions were observed for the non-filled TFE-P crosslinked copolymers and three for non-crosslinked ones (*Figure 1*). It can be seen from the figure that in the low-temperature interval up to 400 K and times up to 3×10^5 s, high relaxation times, related mainly to chemical processes, cannot be registered. With increasing temperature, the shortest times, attributed to slow physical processes, are shifted towards the fast physical relaxation and cannot be observed in relaxation spectra. Three relaxation processes observed over the glass temperature (T_g) for the linear elastomer can be attributed to λ-transitions. They are slow physical relaxations connected with dissociation and rearrangement of microvolume physical nodes in the molecular network[12].

As can be seen in *Figures 1* and *2*, the λ-relaxation processes were observed in all the studied samples. Moreover, their activation energies are close to one another regardless of whether they are crosslinked, linear or filled. It is known[13] that they are related to domains formed by different microstructures of the fluoro-elastomer chain, the so-called 'soft' rubber component. λ-Transitions can be divided into three subgroups, each containing propylene, tetrafluoroethylene and mixed units. It is suggested that the λ_1-process ($U_{\lambda_1} = 36$ kJ mol^{-1}) can be connected with the mobility of the structural microblocks formed of TFE units. The λ_2-process ($U_{\lambda_2} = 43$ kJ mol^{-1}) is associated with the rearrangement of microvolume nodes formed of mixed units (TFE and P), which make up over 70% of the whole structure. The highest activation energy ($U_{\lambda_3} = 55$ kJ mol^{-1}) is exhibited by the λ_3-process, which can be attributed to propylene segments in the polymer chain. From its activation energy and B_i coefficients, this transition is close to λ-transitions observed in poly-propylene ($U_{\lambda_{1,2,3}} = 55$ kJ mol^{-1}, $B_{\lambda_{1-3}} = 0.8 \times 10^{-4} - 1.0 \times 10^{-6}$ s)[14]. The different values of B_i coefficients for the processes discussed show that there are micro-regions of different dimensions. Higher values of B_i correspond to larger microregions. It could be suggested that the destruction and formation of the domains takes place by rearrangement of segments as separate kinetic units. This follows from the value of the activation energy $U_{\lambda_{1,2,3}}$, which is in the range of the segmental rearrangements (35–45 kJ mol^{-1}).

A new transition appears in filled elastomers after the λ_2-process, and is connected with filler particle mobility, e.g. φ-process of relaxation of 'hard' rubber component with $U_\varphi = 37$ kJ mol^{-1}. The introduction of the filler does not lead to changes in activation energy of λ-processes, but slightly decreases their relaxation times and the corresponding coefficients B_λ.

Three other relaxation transitions were observed in the crosslinked elastomers. The first one is the δ_1-process of relaxation, which is characterized by its low activation energy of $64\,kJ\,mol^{-1}$. This process was observed for the first time in ethylene–propylene bi- and terpolymer[15] and was attributed to the chemical network of the vulcanizate.

The next process, designated by μ_F ($U_{\mu_F} = 82\,kJ\,mol^{-1}$), is connected with the dissociation and recombination of transverse pseudo-hydrogen bonds between fluorine and hydrogen atoms. One could expect that the activation energy of this process would be close to that of viscous flow of linear TFE-P copolymer. The rheological copolymer characteristics studied showed that in the viscous state the elastomer behaves like a pseudo-plastic liquid (*Figure 3*). In terms of the de Waele–Ostwald equation, the flow index changes within the range from 0.44 to 0.51. The calculated activation energy of the process of viscous flow is $81\,kJ\,mol^{-1}$ (*Figure 4*) and corresponds to the activation energy of the μ_F-transition ($82\,kJ\,mol^{-1}$).

A transition with a small value of B_i ($c.\ 3.8 \times 10^{-10}\,s$) and high activation energy ($126\ kJ\,mol^{-1}$) was observed after the μ_F-process, which can be attributed to chemical δ-processes of relaxation. The activation energy of the δ_c-process ($125 \pm 3\,kJ\,mol^{-1}$) is close to that observed for the destruction of similar TFE-P copolymers[16].

A typical temperature dependence of the coefficient of mechanical losses, $\mathrm{tg}\,\delta$, for crosslinked non-filled TFE-P elastomer is shown in *Figure 5*. Two regions can be observed, divided by the main α-relaxation transition, corresponding to T_g. In the rubber-like region on the right, the slow physical relaxation (λ-transitions) and chemical (μ_F and δ) relaxation transitions can be found. The fast relaxation transitions (α and β) take place in the non-arranged parts of the elastomers. Their relaxation times in the high elastic state are significantly smaller than 1 s so they were not observed over T_g. The α-relaxation transition is associated with the motion of the segments and corresponds to T_g (273 K for TFE-P elastomer). The result is in accordance with the T_g determined experimentally by d.s.c. The triplet β-maximum corresponds to small-scale motion of polymer-chain regions of length close to that of the units, but significantly shorter than the segments[1]. They probably correspond to the three types of structural elements in TFE-P rubber.

The temperatures of the relaxation transitions T_i are plotted on the internal friction spectra of filled cross-linked TFE-P copolymer (*Figure 5*) over $T_g = 275\,K$ (α-transition). T_i values were calculated by the formula[4]:

$$T_i = \frac{U_i}{2.3R}\left(\log\frac{C_i}{2\pi\nu B_i}\right)^{-1} \qquad (2)$$

where ν is linear frequency, and C_i is a numerical constant, approximately 10 for segmental motion in large structural elements. The values of B_i, U_i and T_i are presented in *Table 1*.

Good correlation was observed between experimental and calculated values of T_i, which proves the identification of separate transitions by the method of relaxation spectroscopy.

CONCLUSION

By the use of mechanical relaxation spectroscopy, some aspects of the physical structure and chemical network of alternating TFE-P elastomers and their compositions were considered.

Different groups of physical and chemical relaxation processes were found: λ-processes of domain rearrangements, φ-processes of the carbon-black network, and μ_F- and δ-processes of the elastomer vulcanizate network. α-Relaxation at the glass transition temperature and β-relaxations in the glassy state were also observed.

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