

Relaxation Processes in the Surface Layers of Polymers at the Interface

YU. S. LIPATOV and F. Y. FABULYAK, *Institute of Macromolecular Chemistry, Academy of Science of the Ukrainian SSR, Kiev, U.S.S.R.*

Synopsis

The proton spin-lattice relaxation and dielectric relaxation were studied in some polymers at the solid-polymer interface was constructed from several filled polymers. A useful model of surface layer which can be considered as consisting of a great number of small solid particles covered with a polymer layer. The following systems were studied: polystyrene, poly(methyl methacrylate), their copolymers and cellulose acetate in the presence of different content of fine particles of aerosil and Teflon.

It was established that the decrease of surface layer thickness shifts the minimum of spin-lattice relaxation time T_1 of high temperature process to higher temperature and minimum T_1 of low temperature process to lower temperature. The same was found for dielectric losses reflecting the motion of side groups and of segments. From temperature dependence of T_1 and $\tan \delta$ for both relaxation processes the apparent energies of activation were calculated. On the base of dielectric relaxation data the circular diagram of complex dielectric constant was constructed and by the Cole-Cole method the dispersion parameter α for polymers at the interface was calculated. These data also show the broadening of relaxation spectra in surface layers. The results are discussed in terms of the restriction of possible conformation of chains at the interface and their interaction with surface. It was established that character of molecular motion changes at the interface is dependent on the mode of molecular motion.

INTRODUCTION

The study of the relaxation processes in polymers at the interface with solids is of theoretical and practical importance with regard to the formation of filled polymer materials as well as to finding the most appropriate conditions for their processing.

We were first in closely studying the relaxation processes in surface layers of polymers at the interface¹⁻⁴. It was observed that the existence of interface brings about a substantial change in the relaxation behavior in polymer surface layers as well as in glass transition temperatures and the mean relaxation time, etc., which facts are undoubtedly associated with varying density of molecular packing and restriction in the motion of segmental and larger kinetics elements of polymer chains due to their interaction with solid particles.

The purpose of the present report is to study the factors influencing molecular motion.

EXPERIMENTAL

Poly(methyl methacrylate), polystyrene, copolymer of methyl methacrylate and styrene, various polyurethane elastomers, and cellulose acetate, all noted for molecular-chain flexibility as well as for the presence of functional groups in their chains (potentially ready to interact with solid particles), were the chosen objects of our investigation. The surface layers of polymers were formed by introducing into a polymer various amounts of finely dispersed particles which allowed the filled polymer to be treated as consisting of particles bearing on their surface polymer layers of various thicknesses. The amounts of fillers used enabled the formation of surface layers of thicknesses in the range of 0.5–1.3 μ . A solid of high surface energy (Aerosil) and a solid of low surface energy were used as fillers.

Molecular mobility was investigated with the technique of nuclear magnetic resonance and by means of dielectric relaxation study. The techniques and calculations used have been described before.^{5,6}

RESULTS AND DISCUSSION

The effect of surface behavior on polymer chains in the surface layers can be described by a shift in the maximum dielectric losses in the $\tan \delta$ -versus-temperature curve. Figure 1 shows the temperature dependence of $\tan \delta$ for polystyrene and poly(methyl methacrylate) in the presence of Aerosil and Teflon, the filler content with regard to particle dimensions being chosen in such a way that the thicknesses of the surface layers would be approximately equal. As the thickness of the surface layers decreases, a shift in the $\tan \delta$ maximum corresponding to the side-chain relaxation process to lower temperatures and in segmental relaxation maximum to higher temperatures takes place. It is evidence of a change in mean relaxation times of the corresponding processes in the surface layers. From the above considerations it follows that the curves corresponding to the correlated surface layers thickness on the surfaces of high and low surface energy possess similar shift magnitudes in both maxima. The same behavior (Fig. 2) was observed by us in the nuclear magnetic resonance study of temperature dependence of spin-lattice relaxation time of protons in surface layers for all polymers in question. This phenomenon, in particular, bears out that the effects of dielectric relaxation observed in the study are brought about by the Maxwell-Wagner effect of medium inhomogeneity characteristic for permeable and unpermeable regions.⁷

The results obtained allowed us, by means of Cole-Cole circle diagrams (some of them are given in Fig. 3), to calculate the temperature dependence of the relaxation time parameter of distribution α in the surface layer (see Fig. 4).

Figure 4 shows that the reduction in distribution parameter occurs in the surface layers, corresponding to the broadening of the relaxation spectra;

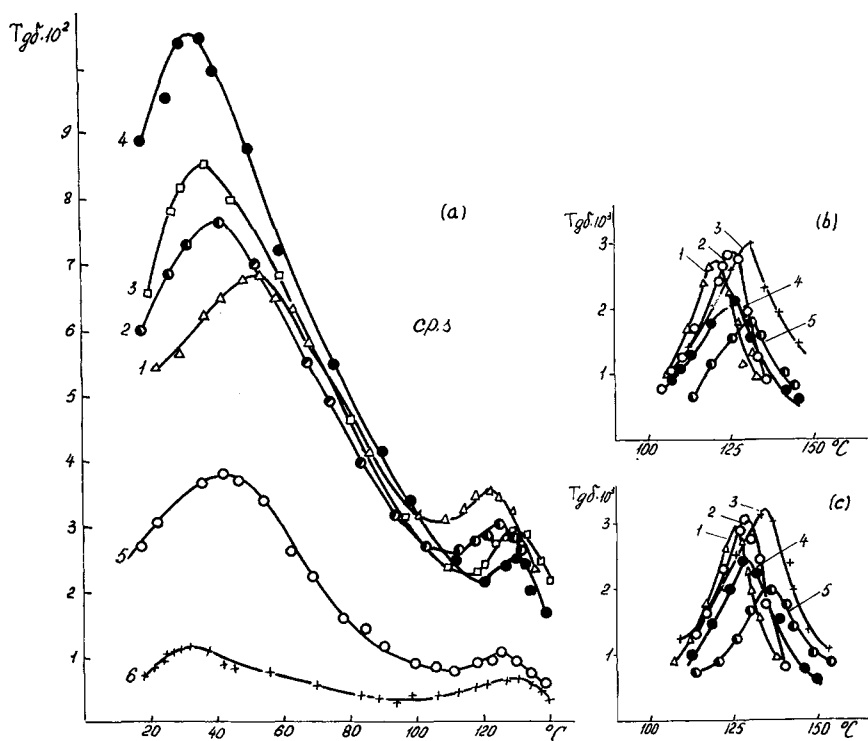


Fig. 1. Temperature dependence of $\tan \delta$. (a) Poly(methyl methacrylate): (1) pure PMMA; (2) with 1.32% Aerosil; (3) 16.63% Aerosil; (4) 23.08% Aerosil; (5) 49.2% Aerosil; (6) 75.0% fluoroplast. (b) Polystyrene samples at 0.5 kHz and (c) PS polystyrene samples at 1.0 kHz: (1) pure PS; (2) with 1.32% Aerosil; (3) 23.08% Aerosil; (4) 49.2% fluoroplast (5) 75.0% fluoroplast.

and it agrees with the above-mentioned maxima divergence of side chain and dipole segmental losses.

The above data suggest that the surface behavior by no means affects the shift in the loss maxima or spin-lattice relaxation time. It is worth noting that such a dependence is observed in the study of molecular motion in the surface layers brought about by the mobility of the larger structural units, which can be described by the mean relaxation time for the processes of isothermic decrease in volume.⁴

We have also made measurements of dielectric and spin-lattice relaxation in volume and on Aerosil particles with dimethyldichlorosilane-modified and nonmodified surfaces. Such a modification brings about a substantial change in the surface energy of particles. Experiments have been made for the polymers with more flexible chains (polyurethane resins of various chemical properties) as compared with polystyrene and poly(methyl methacrylate). The order of the temperature shifts of the dispersion regions of polymers appeared to be similar to that described above. Moreover, the change in molecular motion of chains at the interface was practi-

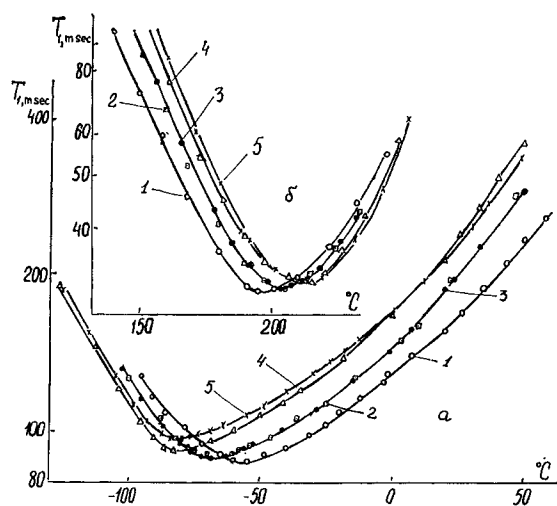


Fig. 2. Temperature dependence of spin-lattice relaxation time for various samples of copolymer: (1) pure copolymer; (2) with 8.83% Aerosil; (3) 26.5% fluoroplast; (4) 24.9% Aerosil; (5) 75.0% fluoroplast. (a) Low-temperature relaxation process—relaxation of $-\text{CH}_3$ groups; (b) high-temperature relaxation process—relaxation of chains segments.

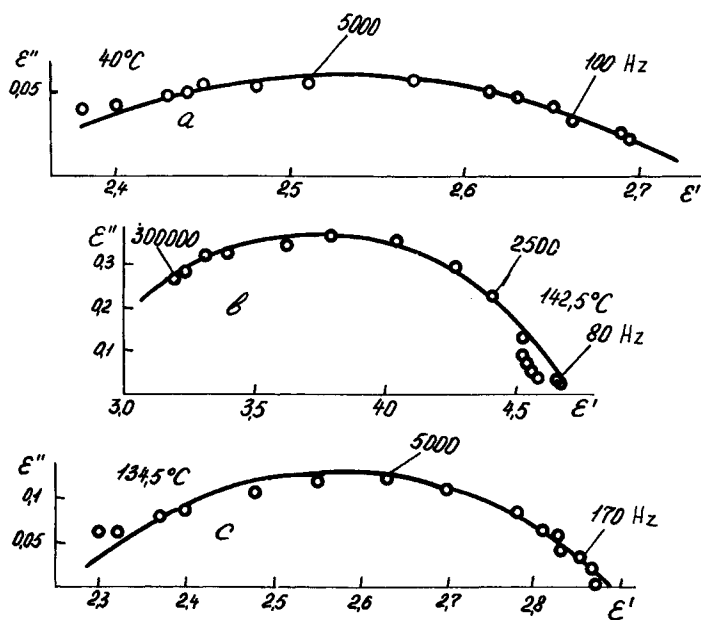


Fig. 3. Circle diagrams of Cole-Cole: (a) pure copolymer; (b) with 24.9% Aerosil; (c) with 75.0% fluoroplast.

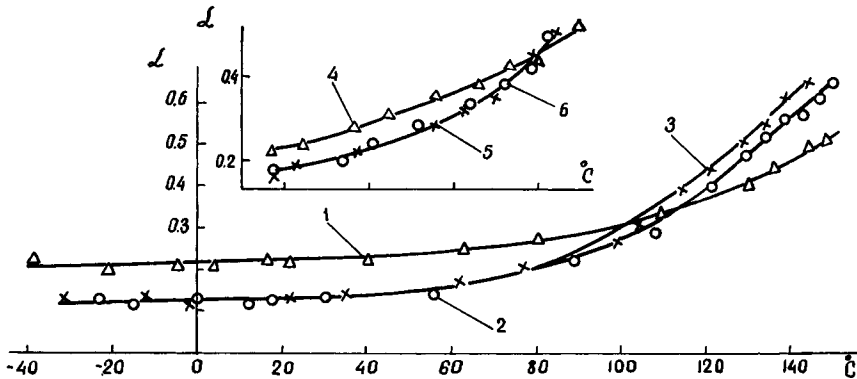


Fig. 4. Temperature dependence of distribution parameter of relaxation time. (a) For copolymer samples: (1) pure copolymer; (2) with 24.9% Aerosil, 75.0% fluoroplast. (b) For poly(methyl methacrylate) samples: (4) pure PMMA; (5) with 49.2% fluoroplast; (6) 1.32% Aerosil.

cally equal for nonmodified as well as modified surfaces. Such behavior is undoubtedly consistent with the above-mentioned principles of the independence of the effects on the surface nature, despite the fact that in our experiment polymers having in their molecular chains active functional groups which readily interact with Aerosil particles and form hydrogen bonds have been used.

Based on the data reported here, one is led to conclude that the change in molecular motion of chains is accounted for by some other phenomena and not by the change in energy of interaction at the interface. It is also appropriate to mention here that the change in molecular motion occurs not only in the layers close to the surface (macroscopy effects would not be observed), but also extends from the surface to considerable depth, the effect itself in this case being nonlinearly dependent on the thickness of the surface layer.

In order to ascertain the phenomena causing the change in molecular motion, let us consider some data from the study of surface layers of the stiff-chain polymer, namely cellulose acetate. Figure 5 shows the temperature dependencies of $\tan \delta$ for cellulose acetate on volume and on the surfaces of modified and nonmodified Aerosil; in the case of stiff-chain polymer, any effects of molecular motion change at the interface are completely lacking.

From the above considerations it follows that the main part in the change in molecular motion in the polymer chains of surface layers is played by the change in conformation of polymer at the interface and not by the energetic interaction of chains with the surface, which behavior is not encountered with layers not closely containing the surface.

The theoretical concepts on the chain conformation of polymer molecules near the interface were developed by Simha et al.⁹ and Frish et al.¹⁰ As reported by these authors, the function of distance distribution between

the polymer chain ends near the interface differs from that in volume; the surface of the solid serves as a barrier hindering the formation of such a number of molecular conformations that the macromolecule may have in volume.

As a consequence, impoverishment of conformational set of macromolecules occurs, the phenomenon which is equivalent to chain stiffness and, as we assume, is the main cause of inconstancy of relaxation behavior of macromolecules in surface layers.

Judging from the above data we consider the restriction of chain mobility in surface layers to be above all associated with the entropy factor, i.e., with impoverishment of the conformational set of macromolecules near the interface. The fact provides sufficient explanation for this effect independent of the surface nature, for the extension of the mobility change to

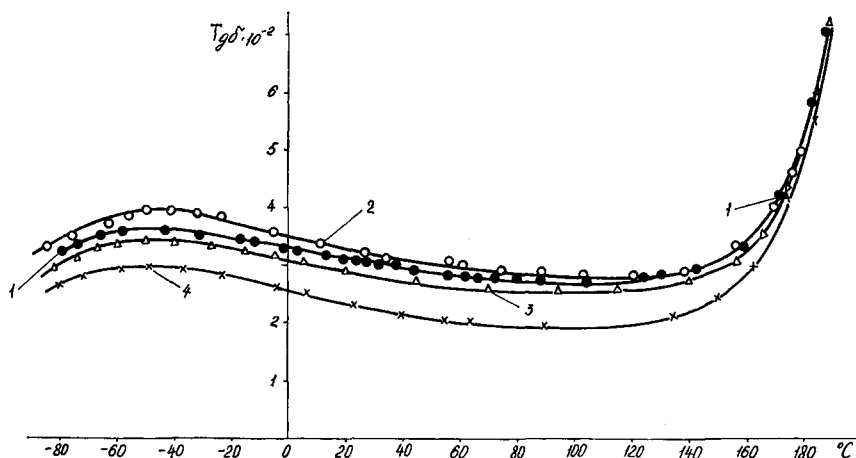


Fig. 5. Temperature dependence of $\tan \delta$ of acetylcellulose samples: (1) pure acetylcellulose; (2) with 8.1% diethyldichlorsilane-modified Aerosil.

the layers not closely contacting the surface, as well as for the dependence of these effects on polymer chain flexibility. Actually, the conformational set of molecules of stiff-chain polymer, being highly restricted as compared to flexible molecules, can not undergo such great changes near the interface owing to chain stiffness as do flexible molecules. In this case, no change in chain mobility occurs.

Consequently, change in molecular mobility can be associated with lowering the flexibility of chains in the surface layer among to conformational restrictions imposed by surface geometry. As we have stated, it is of no importance whether the conformational change is brought about by the surface itself or by some degree of bonding of molecules by the surface. The last factor, highly important for adhesive strength, is not so important for restriction of molecular motion inasmuch as this process is not associated with bonds rupture at the interface.

TABLE I
 Activation Energy of Relaxation Processes of Polymers in Thin Layers Determined
 by NMR and Dielectric Methods^a

Aerosil content, %	Fluoro- plast content, %	Activation energy of T_1 relaxation, kcal/mole			Activation energy of dielectric relaxation, kcal/mole		
		PMMA	PST	Copolymer MMA-ST	PMMA	PST	Co- polymer MMA- ST
Group Motion							
0.0	0.0	1.75	—	2.05	23.7	—	14.9
8.83	—	—	—	1.72	—	—	12.6
1.32	—	1.36	—	—	18.5	—	—
23.08	—	1.18	—	—	15.4	—	—
24.9	—	—	—	1.47	—	—	10.7
—	26.5	—	—	1.72	—	—	12.6
—	49.2	1.48	—	—	20.0	—	—
—	75.0	1.39	—	1.46	18.8	—	10.6
Segmental Motion							
0.0	0.0	14.5	11.3	13.3	—	90.0	99.0
8.83	—	—	—	12.0	—	—	—
1.32	—	9.78	—	—	—	60.9	—
23.08	—	9.20	12.3	—	—	57.1	—
24.9	—	—	—	11.5	—	—	85.5
—	26.5	—	—	12.0	—	—	89.5
—	49.2	11.0	—	—	—	69.2	—
—	75.0	10.1	13.1	11.4	—	63.2	84.6

^a For spin-lattice relaxation of protons T_1 , the group motion is restricted to that of CH_3 .

It should be noted that the above examples do not concern strong interactions at the interface, which behavior would be somewhat different from that described above.

The above-mentioned point of view being taken into consideration, there is good reason to evaluate the contribution of energetic and entropy factors to the change of molecular motion near the interface. We base this evaluation on the data from activation energies of relaxation processes in surface layers, obtained from temperature dependence of mean relaxation times. Some activation energy values are presented in Table I.

We proceed from the equation

$$\tau = \tau_0 \exp (\Delta F/RT)$$

where ΔF = free activation energy of relaxation process, τ = correlation (relaxation) time, and $\tau_0 = \tau$ value at $1/T = 0$.

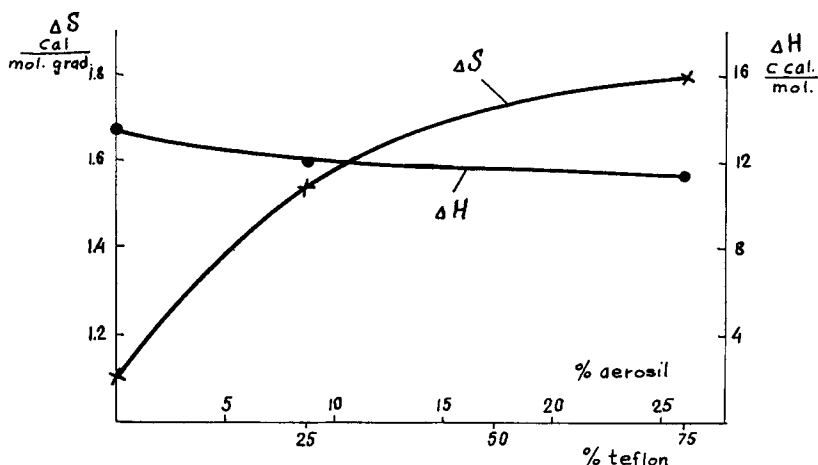


Fig. 6. Dependence of activation entropy and enthalpy on per cent content of fillers for copolymer samples.

Hence, it follows that

$$\ln \frac{\tau}{\tau_0} = \frac{\Delta F}{RT}$$

$$\frac{\partial \ln \tau / \tau_0}{\partial (1/T)} = \frac{\Delta F}{R} + \frac{1}{RT} \frac{\partial \Delta F}{\partial (1/T)} = \frac{\Delta F}{R} - \frac{T}{R} \frac{\partial \Delta F}{\partial T} = \frac{\Delta F}{R} - \frac{T \Delta S}{R} = \frac{\Delta H}{R}$$

or

$$\Delta H = R \frac{\partial \ln(\tau/\tau_0)}{\partial (1/T)} = -RT^2 \frac{\partial \ln \tau}{\partial T}$$

where H = activation energy, and τ_0 = const.

$$T \Delta S = -\Delta F + \Delta H = -RT \ln \frac{\tau}{\tau_0} - RT^2 \frac{\partial \ln \tau}{\partial T}$$

$$\Delta S = -\frac{\partial [RT \ln(\tau/\tau_0)]}{\partial T}$$

Thus, experimental dependencies $\ln \tau = f(1/T)$ determine the thermodynamics of the activation process. The dependences of ΔH and ΔS on the surface layer thickness for styrene and methyl methacrylate are presented in Figure 6. A considerable increase in activation entropy change has been observed whereas activation enthalpy negligibly decreases, the main contribution to the molecular motion change of chains near the interface being made by conformational effects. Corresponding values for other systems investigated are tabulated in Table II.

The above data show that as the surface layer thickness decreases, a considerable increase in the change of activation entropy takes place.

TABLE II
Enthalpy and Entropy Values of Activation in Surface Layers of Polymers*

Fluoroplast and Aerosil content, %	Copolymer		Polyester-based polyurethane		Polyether-based polyurethane	
	ΔH , kcal/mole	ΔS , cal/ mole-grad.	ΔH , kcal/mole	ΔS , cal/ mole-grad.	ΔH , kcal/mole	ΔS , cal/ mole-grad.
	Segmental motion					
—	13.3	1.10				
8.83 n.a.	12.0	1.52				
24.9 n.a.	11.5	1.81				
26.5 f.	12.0	1.50				
75.0 f.	11.4	1.82				
—			2.0	0.13		
13.3 n.a.			1.8	0.20		
13.3 n.a.			1.8	0.21		
—					4.38	1.15
14.8 n.a.					3.8	1.79

* n.a. = Nonmodified Aerosil; f. = fluoroplast.

The increase in ΔS is quite understandable, taking into account that the field-effect transformation calls for much more conformational changes in the case of stiff molecules than of flexible ones, the energetic barrier height being constant.

The data obtained show a pronounced effect of the interface with solid on the mobility of surface molecular chains of polymers as well as on their dependence on the surface layer thickness. In this situation, broadening of the relaxation time spectrum testifies to the fact that the interface does not equally affect the mobility of those or other relaxation agents participating in overall motion. In addition, the main reason for the change in relaxation behavior of polymer chains in surface layers lies in the impoverishment of the conformational set of chains near the interface due to conformational surface restrictions or to interaction with it.

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