

Dielectric Behavior of Some Polar High Polymers at Ultra-High Frequencies (Microwaves)

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Synopsis

The dielectric behavior of different polar high polymers at ultra-high frequencies has been investigated by means of a dielectrometer, suitably modified to permit measurements at different temperatures. Experimental measurements were made at about 9×10^9 cps over the temperature range of -150 to 200°C . for polyoxymethylene, polythiomethylene, poly(3,3'-chloromethyl)oxetane (Penton), polycarbonate of 4,4'-dioxydiphenyl-2,2'-propane (Makrolon), poly(vinyl alcohol), poly(vinyl acetate), poly(vinyl chloride), vinyl chloride-vinyl acetate copolymer, and two ABS plastics, type B (blend) and type G (graft). On comparing the dielectric behavior of the examined materials at ultra-high frequencies with the corresponding ones determined at low or at radiofrequencies, it is observed that, in the microwave region, all relaxation peaks, either connected with cooperative motions in main chain (primary processes) or with local motions in the backbone or in side chains (secondary processes), usually observed at lower frequencies, tend to disappear; the corresponding relaxation effects, however, manifest themselves through a progressive increase of losses with increasing temperature, which is particularly marked above the glass transition temperature T_g . The latter transition, in spite of the very high frequency, is easily distinguished, in most cases, by the sudden change of slope in the $\tan \delta$ versus temperature curve which accompanies its onset. This is explained on the basis of the very wide distribution times of molecular relaxation processes in polymers and the increase in strength of the secondary relaxation effects, which is verified at T_g , as a consequence of the increased kinetic energy of macromolecules and of the larger free volume for orientation of side chains. Each case is discussed separately and the experimental results interpreted on the basis of the molecular structure and chain mobility of the examined polymers.

The increased interest in dielectrics for ultra-high frequency applications makes desirable a better knowledge of the dielectric properties of high polymers, which are employed in various sectors of electronics, in the microwave region of the electromagnetic spectrum. In the literature, in fact, there are not many data regarding this subject, and often the experimental results from different sources are not in a good agreement. In order to dispose of other experimental data and in an attempt to give to them a structural interpretation, a systematic investigation has been initiated in our laboratories on different classes of high polymers. Some of our first results are presented in this paper.

EXPERIMENTAL

Methods

For the determination of the complex dielectric constant $\epsilon^* = \epsilon' - i\epsilon''$, the method described by Roberts and von Hippel^{1,2} has been utilized, a microwave dielectrometer of the Central Research Laboratories (Model 3, Serial no. 37) being used. This method, described in detail in a preceding paper,³ together with the modifications made to the instrument to allow measurements at different temperatures, enables one to calculate the complex dielectric constant through determination of the following quantities: d = sample thickness; Δ = shift of the node towards the termination, passing from the empty guide to a guide partially filled with the specimen under examination; λ_g = wavelength in the guide; Δx = distance between the double power points on the right and on the left of a node, which allows calculation of the standing wave ratio R .*

$$R = \sqrt{1 + \operatorname{cosec}^2 [(\Delta x/\lambda_g)\pi]} \quad (1)$$

Measurements were carried out in a circular pipe, working on the TE₁₁ mode, first empty and then partially filled with the specimen.

Figure 1 shows the situations which are encountered in the two cases and the relevant quantities of interest, in particular,

$$\Delta = N_e - N_c \quad (2)$$

where N_e is the position of the node in the empty guide and N_c the same position with the guide partially filled with the specimen, while Δx_m is the distance between the double power points with the specimen inserted, and Δx_e is the same distance without specimen, that is, referred to the losses for the empty guide, due in part to the terminations and in part to the walls. A discussion of various contributions is given in the Appendix, where the correction in Δx_m required in order to get the Δx value introduced in eq. (1) is also precisely given.

As already pointed out,³ the dielectrometer has been suitably modified in order to permit measurements either at low or at high temperatures (covering a temperature range from about -150 to about $+200^\circ\text{C}$). Error analysis was also carried out, and the corrections for Δ to take into account the length variation of the guide due to thermal expansion were determined.

Finally it was necessary to take into account the losses in the guide, which, for low-loss materials, cannot be neglected, since the modifications carried out on the instrument increased the distance between the upper face of specimen and the section into which measurements are carried out.

* In effect, the exact relation is: $R = \sqrt{1 + \{[(E'_z/E_{\min})^2 - 1] \operatorname{cosec}^2 [(\Delta x'/\lambda_g)\pi]\}}$ where E_{\min} is the electric field value in a minimum and $\Delta x'$ is the distance between two points on either side of the same minimum, for which the value of the field is E'_z . Such an expression is reduced to eq. (1) when $(E'_z/E_{\min})^2 = 2$. Nevertheless, it is opportune to consider the exact relation, since, if R is too large, it is convenient to measure it, making readings between points at which $(E'_z/E_{\min})^2 > 2$.

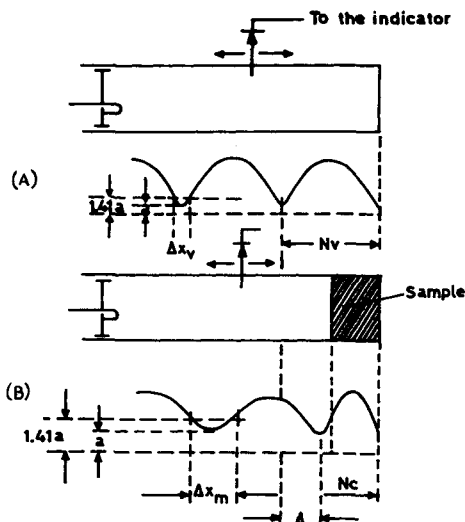


Fig. 1. Behavior of standing waves in the empty guide (A) and in the guide partially filled with the specimen (B).

Materials

Some of the examined polymers were commercial products; others were materials prepared in our laboratory.

Polyoxymethylene was prepared by a method developed by Baccaredda et al.^{4,5} through topochemical polymerization of trioxane from concentrated solutions in cyclohexane in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$. The polymerization product was successively stabilized by esterification with acetic anhydride at 180°C . The main characteristics of the examined specimen were: inherent viscosity (in 0.5% solution in *p*-chlorophenol at 60°C .) = 1.1 dl./g.; density at 20°C . (annealed) = 1.44 g./cm.³; crystallinity (from density data) = 78%; melting point = $174\text{--}176^\circ\text{C}$.

Polythiomethylene was prepared by solid-state polymerization of tri-thiane (CH_2S)₃ in mineral oil suspension at 210°C . in the presence of H_2SO_4 as catalyst. The monomer was prepared by Baumann's method,⁶ consisting in saturating a 40% solution of formaldehyde acidified with HCl with hydrogen sulfide at 30°C . and successive purification by repeated recrystallizations and sublimations. The polymer was insoluble in all the most common solvents; the density at 20°C . was 1.20 g./cm.³; crystallinity (x-ray) = 70%; melting range = $220\text{--}230^\circ\text{C}$.

Poly(3,3'-chloromethyl)oxetane was a commercial product of the Hercules Powder Co. (Penton), with the following characteristics: density at 20°C . (annealed) = 1.41 g./cm.³; crystallinity (from density) = 30%; melting point = $178\text{--}180^\circ\text{C}$.

Polycarbonate was a commercial polymer (Makrolon) produced by the Bayer A.G. having a viscosity-average molecular weight of 3×10^5 ; density at 20°C . = 1.19 g./cm.³.

Poly(vinyl alcohol) was prepared by ester interchange reaction of poly(vinyl acetate) in methanol solution with alkali as catalyst.⁷ The reaction product was treated with cold water for some hours and successively centrifugated to remove by-products (sodium acetate). This treatment was followed by prolonged washing with methanol and then with a 0.25*N* NaOH solution in methanol. Such treatments were followed by final washing and purification treatments. Residual acetate groups and residual sodium acetate were estimated to be about 0.032 mole-% and 0.07 wt.-%, respectively. The polymer showed an intrinsic viscosity in aqueous solutions of 0.821 dl./g.; density at 20°C. = 1.30 g./cm.³.

Poly(vinyl acetate) was prepared by radical polymerization (benzoyl peroxide: 0.03 mole/100 mole of monomer) at 60–70°C. in benzene solutions. The polymer was precipitated from the solution with *n*-hexane at –10°C. and successively purified by successive solubilization in benzene followed by reprecipitations with *n*-hexane. Intrinsic viscosity in acetone solution at 25°C. was 1.267 dl./g.; average molecular weight = 360,000; density at 20°C. = 1.18 g./cm.³.

Poly(vinyl chloride) was a commercial product (Solvic 334) having a chlorine content of 56.5% (theor. 56.76); intrinsic viscosity = 1.20 dl./g.; density at 20°C. = 1.4 g./cm.³.

Vinyl chloride–vinyl acetate copolymer was a commercial product (Solvic 513 P), composed of about 85% vinyl chloride and 15% vinyl acetate; density at 20°C. = 1.35 g./cm.³.

ABS plastic, type B (blend) was a commercial product (Montecatini) and constituted a mechanical blend of styrene–acrylonitrile (76/24) copolymer and butadiene–acrylonitrile (80/20) rubber; rubbery component \simeq 10%.

ABS plastic, type G (graft) was also a commercial product (Montecatini) and constituted a mixture of styrene–acrylonitrile copolymer (76/24) and a graft copolymer of styrene–acrylonitrile onto polybutadiene plus ungrafted polybutadiene; rubbery component \simeq 10%.

All polymer samples, except for polythiomethylene and poly(vinyl alcohol) were in the form of circular plates (24.45 mm. diameter, 17.5 mm. thickness), obtained by molding at temperatures above the corresponding softening or melting points, in inert atmosphere, then ground on a lathe and finally annealed at suitable temperatures (about 20–30°C. below the corresponding softening or melting point) for about 60 hr., under vacuum. The polythiomethylene and poly(vinyl alcohol) samples were shaped by compression of the powders at about 2000 atm. at 30°C. This was so done to avoid thermal degradation of the polymers.

RESULTS

The dielectric constant ϵ' and the loss tangent $\tan \delta$ for polyoxymethylene are shown as functions of temperature in Figure 2. ϵ' , at the lowest temperature reached in measurements (–150°C.), has the value 2.64; it remains practically constant with increasing temperature up to about –10°C. and, then rises at an increasing rate with further temperature

increase, reaching values of the order of 4.0 at about 200°C. The loss tangent is quite low at the lowest temperature of measurements (-150°C .; $\tan \delta = 2 \times 10^{-3}$); remains constant up to about -60°C ., then, increases

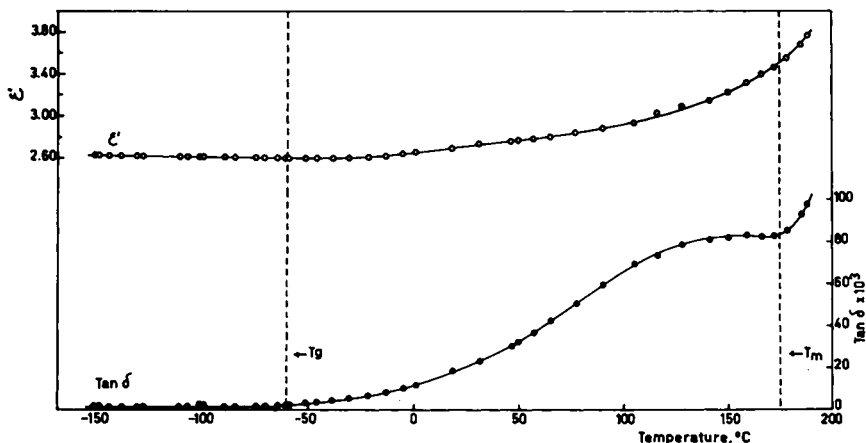


Fig. 2. Dielectric constant ϵ' and dissipation factor $\tan \delta$ for polyoxymethylene as functions of temperature. $f = 8.6 \times 10^9$ cps.

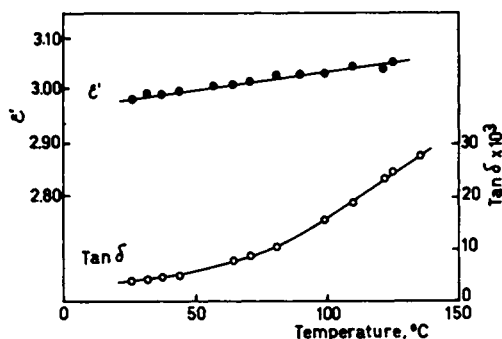


Fig. 3. Dielectric constant ϵ' and dissipation factor $\tan \delta$ for polythiomethylene as functions of temperature. $f = 8.6 \times 10^9$ cps.

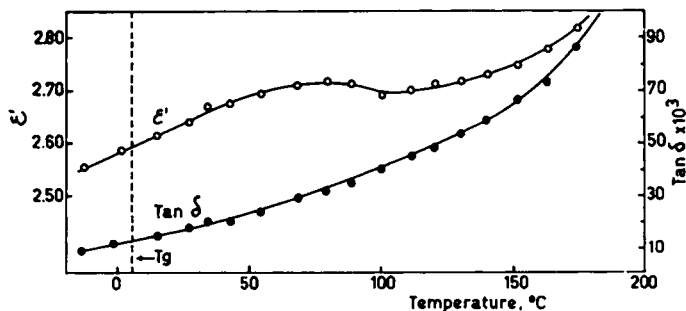


Fig. 4. Dielectric constant ϵ' and dissipation factor $\tan \delta$ for poly(3,3'-chloromethyl)oxetane (Penton) as functions of temperature. $f = 8.6 \times 10^9$ cps.

markedly with increasing temperature, passing through a very flattened maximum at about $+160^{\circ}\text{C}$. and, finally increases again, when the melting point T_m is reached.

In Figure 3 the dielectric constant and loss tangent for polythiomethylene are reported against temperature. The dielectric behavior of this polymer is quite simple; ϵ' , which is about 2.98 at room temperature, tends to increase approximately linearly with rising T , showing a maximum increase of ϵ' of about 3% passing from room temperature to the highest temperature reached in measurements ($+140^{\circ}\text{C}$.). The loss tangent, at room temperature, is quite low ($\tan \delta = 3 \times 10^{-3}$), but shows a marked increase with increasing temperature, reaching at 140°C . a value about ten times larger than that shown at room temperature.

In Figure 4 the dielectric constant and the loss tangent for poly(3,3'-chloromethyl)oxetane are reported against temperature over the range -20 to 180°C . At room temperature, the dielectric constant is 2.62, while the loss tangent is relatively high (about 1×10^2). With increasing temperature, ϵ' , at first increases, then passes through a flat maximum at about 80°C . and finally, in the higher temperature region, after having reached a minimum value, increases markedly with further temperature rise. The loss tangent exhibits a definite tendency to increase over the whole temperature range; such a tendency is particularly strong when temperatures above about 140°C . are reached.

In Figure 5 the experimental values of the real part of the complex dielectric constant and of the dissipation factor for polycarbonate are reported as functions of temperature. At room temperature, the dielectric constant is 2.76, while the losses are relatively low ($\tan \delta = 7 \times 10^{-3}$). The dielectric constant shows a steady tendency to increase with increasing temperature over the whole temperature range at a growing

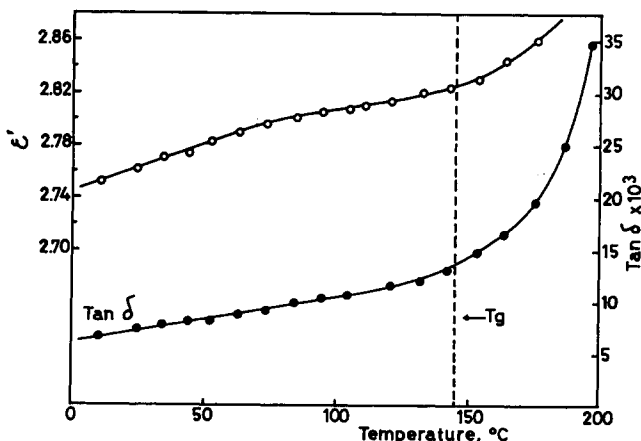


Fig. 5. Dielectric constant ϵ' and dissipation factor $\tan \delta$ for polycarbonate of 4,4'-dioxydiphenyl-2, 2'-propane (Makrolon) as functions of temperature. $f = 8.6 \times 10^9$ cps.

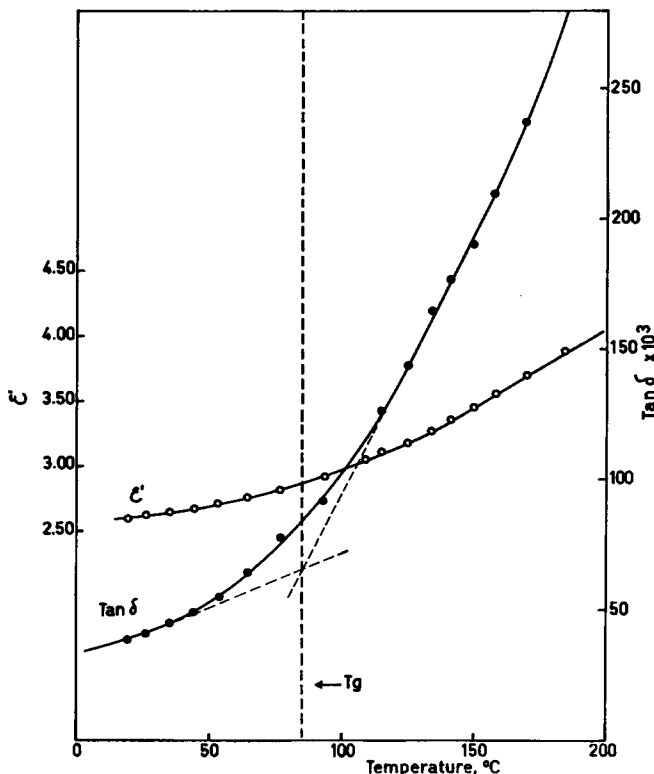


Fig. 6. Dielectric constant ϵ' and dissipation factor $\tan \delta$ for poly(vinyl alcohol) (dried sample) as functions of temperature. $f = 8.6 \times 10^9$ cps.

rate; the rate of increase becomes particularly high when temperatures higher than about 145°C . are reached, to which the dilatometric glass transition point of the specimen corresponds. The loss tangent, which assumes values of the order of 5×10^{-3} at the lowest temperature reached in measurements, also increases with increasing temperature, at first, with a nearly constant rate and, then, above the glass transition point, almost exponentially, attaining values of the order of some units $\times 10^{-2}$ in the vicinity of the softening point.

In Figure 6 the dielectric constant and loss are reported for poly(vinyl alcohol) as functions of temperature. ϵ' for poly(vinyl alcohol) is about 2.6 at room temperature, but increases with increasing temperature over the whole temperature range, at a rate which is particularly high when temperatures above the glass transition point are reached. The loss tangent for this polymer, at room temperature, is quite high ($\tan \delta = 40 \times 10^{-3}$), tending to increase more and more with raising temperature. At temperatures either above or below the glass transition point ($T_g = 85^{\circ}\text{C}$.), the variation of the loss tangent with temperature is almost linear, but with different slopes before or after the transition point. The dielectric behavior

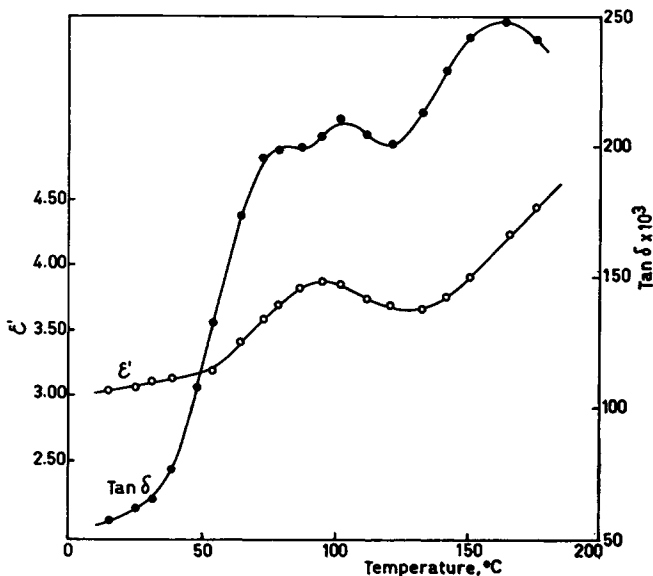


Fig. 7. Dielectric constant ϵ' and dissipation factor $\tan \delta$ for poly(vinyl alcohol) ($\text{H}_2\text{O} = 5\%$ by weight) as functions of temperature. $f = 8.6 \times 10^9$ cps.

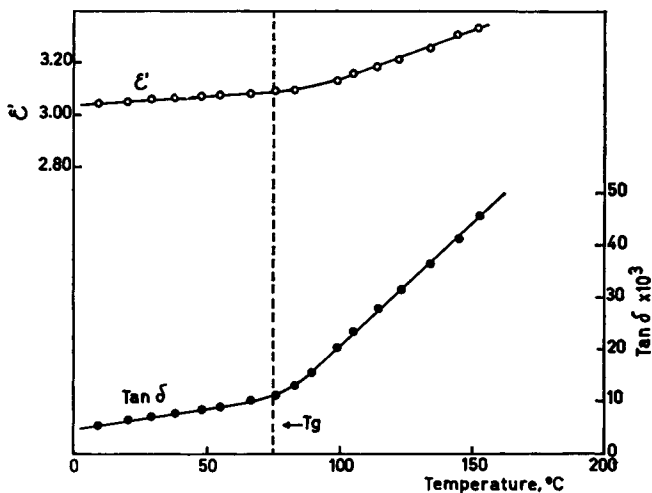


Fig. 8. Dielectric constant ϵ' and dissipation factor $\tan \delta$ for poly(vinyl chloride) as functions of temperature. $f = 8.6 \times 10^9$ cps.

of the water-containing poly(vinyl alcohol) specimen is shown in Figure 7. At room temperature, the wet sample, containing about 5% water in weight, shows higher values for both dielectric constant and loss as compared with the corresponding dry specimen. With increasing temperature, the dielectric constant, at first, increases approximately linearly; then, above about 50°C., it shows a rapid rise up to about 100°C. At still higher tempera-

tures, it first decreases and then increases again with increasing T , after having passed through a minimum value at about 130°C . The loss tangent, on the contrary, increases very strongly when temperature rises from room temperature to about 80°C ., then, after remaining practically constant between 80 and 130°C ., augments again with further temperature increases, reaching a maximum value at about 165°C .

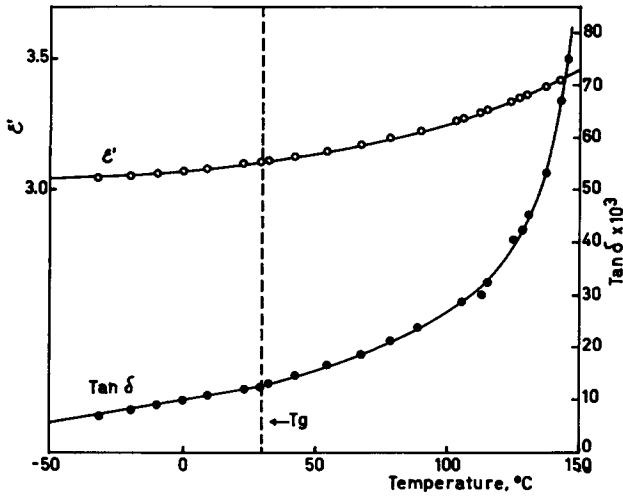


Fig. 9. Dielectric constant ϵ' and dissipation factor $\text{tan } \delta$ for poly(vinyl acetate) as functions of temperature. $f = 8.6 \times 10^9$ cps.

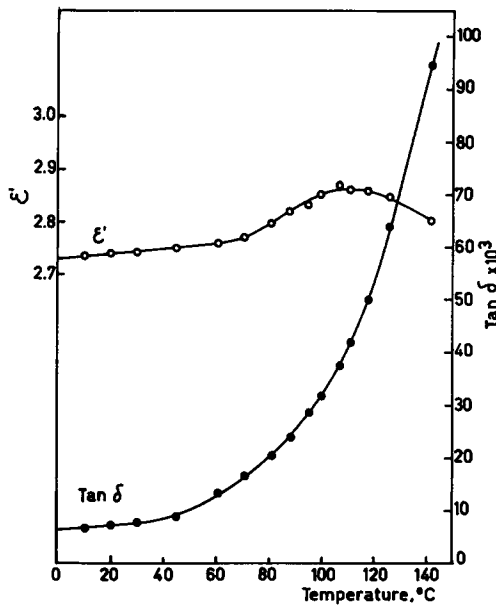


Fig. 10. Dielectric constant ϵ' and dissipation factor $\text{tan } \delta$ for vinyl chloride-vinyl acetate copolymer as functions of temperature. $f = 8.6 \times 10^9$ cps.

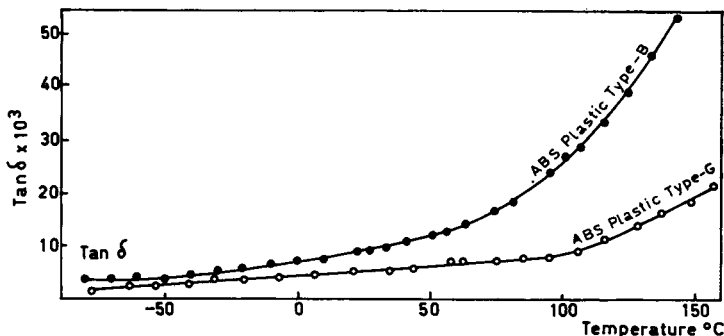


Fig. 11. Plot of dielectric dissipation factor as function of temperature for two ABS plastics: (●) type B; (○) type G. $f = 8.6 \times 10^6$ cps.

In Figure 8 are shown the variations of dielectric constant and dielectric loss for poly(vinyl chloride) as functions of temperature. At the lowest temperature reached in measurements ($0^\circ\text{C}.$), ϵ' is about 3.0, while $\tan \delta$ is about 5×10^{-3} . Both quantities increase with increasing temperature over the range examined, particularly when temperatures higher than the glass transition point are considered. This is particularly evident for the losses.

Behavior analogous to that of poly(vinyl chloride) is shown by poly(vinyl acetate) (Fig. 9). For this polymer, however, the change of slope which occurs in the loss tangent versus temperature curve at T_g is much less marked.

The dielectric behavior of the vinyl chloride–vinyl acetate copolymer is shown in Figure 10. The dielectric constant is about 2.75 at room temperature; it shows a small increase when temperature is raised from room temperature to about $70^\circ\text{C}.$ and, successively a stronger increase up to about $100^\circ\text{C}.$, tending to decrease when temperature is furtherly increased. Much simpler is the loss tangent behavior as function of temperature; it tends to increase over the whole temperature range, with particularly high rates when the glass transition point is passed.

In Figure 11 is shown the dielectric loss behavior for the ABS plastic, type B (blend of a styrene–acrylonitrile copolymer with a butadiene–acrylonitrile rubber). At the lowest temperature ($-90^\circ\text{C}.$), the loss tangent is about 4×10^{-3} ; it remains practically constant up to about $-50^\circ\text{C}.$, but, with further temperature increase, tends to rise, at first, approximately linearly (between -50 and $+80^\circ\text{C}.$) and then, when the glass transition point T_g is reached, nearly exponentially. $\tan \delta$ is of the order of 20×10^{-3} at T_g and about three times higher at $150^\circ\text{C}.$

For the ABS plastic, type G (styrene–acrylonitrile copolymer grafted onto polybutadiene), for which data are also shown in Figure 11, the loss tangent is about 5×10^{-3} at $0^\circ\text{C}.$, showing only small variations when temperature rises up to T_g . At still higher temperatures, a strong rise of the loss is observed with increasing T , but either the $\tan \delta$ values at each

temperature or the rate of increase with T , are always smaller as compared to the corresponding data for the corresponding blend.

DISCUSSION OF RESULTS

As the polarization mechanisms operating in polar high polymers in the microwave region seem to be the same as those occurring at low and radio frequencies,⁸ it is useful, for the interpretation of the dielectric behavior of these substances at very short wavelengths to take into consideration the results obtained at lower frequencies, which in most cases, have been fully elucidated.

Polyoxymethylene

In Figure 12 is reported the dielectric-loss behavior of this polymer, as determined by Ishida et al.⁹ at low frequencies (100 cps). As can be seen from the curve reported, a well-defined loss peak is found at about -70°C ., followed by another high-loss region at higher temperatures, characterized by a rapid increase of $\tan \delta$ with increasing T . While the higher-temperature loss region is due to ionic conduction (connected with the presence of ionic impurities in the specimen), the low-temperature loss peak has been attributed to the thermal excitation of particular motions in chain segments. The results of Ishida are substantially similar to those obtained by many other authors,¹⁰⁻¹⁴ who investigated the latter phenomenon either by electrical or mechanical methods. Various interpretations have been given to the molecular mechanism responsible for the low-temperature relaxation in polyoxymethylene, but it seems to consist of a rotational *gauche-trans* isomerism, that is, a process very similar to that found in polyethylenes at low temperature (γ -transition), classified among secondary relaxation phenomena of the local mode.¹⁵ The position of the loss peak, which, is of course, frequency-dependent, shifts towards higher temperature when the measurement frequency is increased, but, contrary to the general case for secondary relaxation processes, the frequency dependence of the maximum loss temperature does not follow an Arrhenius-type equation but an empiri-

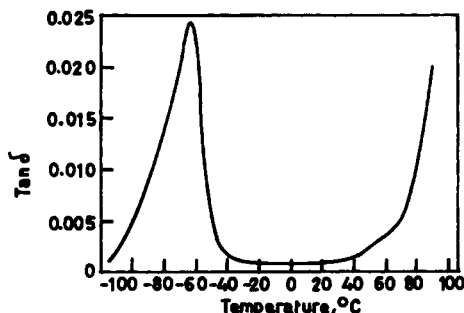


Fig. 12. Dielectric loss vs. temperature for polyoxymethylene at 100 cps. Data of Ishida et al.⁹

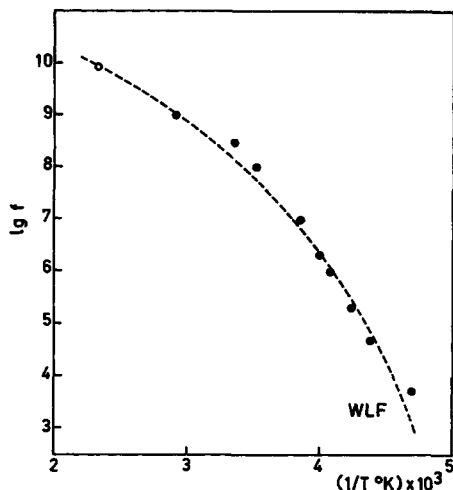


Fig. 13. Frequency dependence of the main relaxation peak for polyoxymethylene: (O) present data; (●) Thurn's data.¹³

cal equation of the WLF-type, as happens for primary processes, connected with cooperative motions in the main chain (Fig. 13). Thus, the apparent activation energy is temperature-dependent, tending to decrease with increasing T .

In the light of the results obtained from low- or radiofrequency measurements, the increase of the dielectric loss with temperature, starting from about -60°C . and the maximum of $\tan \delta$ at about 160°C . observed in microwave measurements may be reasonably associated with the same molecular process responsible for the low-temperature relaxation in lower-frequency measurements. This suggestion is, on the other hand, supported by the fact that the temperature location of the loss maximum found at ultra-high frequency, falls quite well on the $\log f$ versus $1/T$ curve (Fig. 13) representing the shift of the maximum damping temperature of the process under discussion with frequency, calculated from data at radiofrequencies, taking into account the WLF equation. The apparent activation energy, calculated over the temperature range in which the loss maximum is found at ultra-high frequencies, is of the order of 5 kcal./mole.

Polythiomethylene

There is a complete lack of information in the literature about the dielectric behavior of this polymer at radiofrequencies. However, the steady increase of the dielectric constant and the approximately exponential increase of losses with increasing temperature, observed in the microwaves region, may be associated with an increase in kinetic energy of the macromolecules arising from the temperature increase, which favors orientational polarization of dipolar groups. This is confirmed by the fact that the glass transition point for this polymer, as determined by sound velocity measurements¹⁶ is located around -30°C .

Poly(3,3'-chloromethyl)oxetane

In the literature there are not many data regarding the dielectric behavior of this polymer at radio frequencies. However, it is known that two dielectric relaxation phenomena exist: one at lower temperature, below the glass transition point, and another, of much greater intensity, at higher temperature, above T_g ^{17,18} (Fig. 14). The higher-temperature relaxation (α -process) has been attributed to cooperative motions in main chain; its apparent activation energy, as calculated from the shift of the maximum-loss temperature with frequency, is of the order of 70 kcal./mole. The lower-temperature relaxation, which has been carefully investigated through mechanical measurements at acoustic and low-ultrasonic frequencies by Baccaredda and co-workers,¹⁹ has been attributed to local motions of $-\text{CH}_2-\text{O}-$ segments (γ -process). The apparent activation energy for the latter process is of the order of 20 kcal./mole.

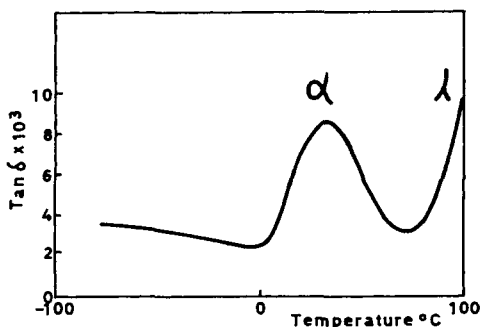


Fig. 14. Loss tangent $\tan \delta$ for poly(3,3'-chloromethyl)oxetane at radiofrequencies. $f \sim 10^8$ cps.¹⁷

Neither of the above loss peaks are found in dielectric data at microwave frequencies; however, the onset of cooperative motions in the main chain can easily be deduced from the rapid exponential increase of dielectric losses, which can be observed above the glass transition point. Moreover, at temperatures still below the glass transition point, the losses are relatively high and the microwave dielectric constant is higher than the optical dielectric constant n_D^2 (n_D = refractive index). This is an indication of the contribution of the partial orientation of dipolar groups to the microwaves dielectric constant associated with the secondary process.

Polycarbonate

The dielectric behavior of the polycarbonate of 4,4'-dioxydiphenyl-2,2'-propane was investigated by Krum²⁰ and by Muller and Huff²¹ at radiofrequencies. Also for this polymer, the radiofrequency measurements indicated the existence of two loss maxima, one (β) located at temperatures below the glass transition point (-80°C . at 10^8 cps) and another (α), of greater intensity, located at 175°C . for the same frequency. The higher-

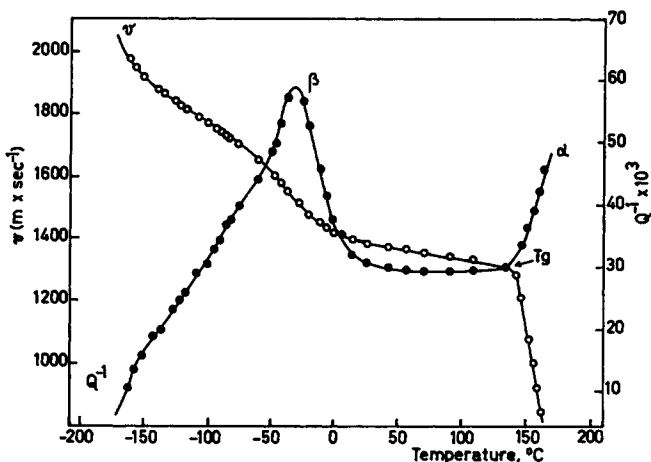


Fig. 15. Sound velocity and mechanical damping factor of polycarbonate (Makrolen) as functions of temperature ($f \sim 10^4$ cps) (unpublished data of M. Baccaredda, E. Butta, and V. Frosini).

temperature maximum has been attributed to segmental motions arising as a consequence of the glass transition ($T_g = 145^\circ\text{C}.$); the other loss peak has been ascribed to reorientation of carboxyl dipoles.²² Similar results have been obtained from mechanical measurements by Illers²² at low frequency and in our laboratory at acoustic frequencies (Fig. 15).

In microwave measurements for polycarbonate, the relaxation phenomena found at radiofrequencies, do not manifest themselves with characteristic loss peaks. Nevertheless, even at ultra-high frequencies the contributions of dipolar orientations associated with thermal excitation of the carboxyl group motions and with cooperative motions of chain elements are operating; this can be deduced by the progressive increase of the loss with increasing temperature observed below T_g and by the rapid exponential rise of $\tan \delta$ with increasing T which occurs above the glass transition point. In particular, the onset of the latter transition is accompanied by an abrupt increase of slope in the $\tan \delta$ versus temperature curve, thus, permitting its individuation.

The disappearance of the β -loss peak in microwave measurements can be explained quite easily; because of the low activation energy, it is shifted considerably towards higher temperatures, to fall well above the glass transition point, thus becoming completely masked by the higher losses provoked by the excitation of macro-Brownian motions of macromolecules. On the other hand, the α -peak associated with the latter motions must fall at some temperature above the highest one reached in our measurements.

Poly(vinyl Alcohol)

The radiofrequency dielectric behavior of poly(vinyl alcohol) has not yet been accurately investigated, but from dynamic mechanical measurements made by Takayanagi²³ at low frequency, it has been found that at least four

different relaxation effects (each characterized by its own loss maximum) are operating; these have been assigned to torsional motions of solvated chain parts, torsional motions of nonsolvated chain segments, cooperative motions in the amorphous regions, and torsional motions in crystalline regions.

The plot of dielectric loss against temperature, as deduced by measurements at ultra-high frequencies, is, on the contrary, quite simple; no maxima are found in the $\tan \delta$ versus temperature curve, which only shows a marked upswing when the glass transition point is reached. This may be explained on the basis of the shift of the various relaxation effects towards higher temperatures, because of the frequency increase, and with the melting together of the various loss regions, associated with different relaxation mechanisms. However, at temperature below T_g , relatively high values for $\tan \delta$ are found, whereas the microwave dielectric constant is considerably higher than the square of the refractive index; in addition, these quantities both tend to increase significantly with increasing temperature; this may be due to traces of water molecules, which, acting as a plasticizer, favor orientational polarization of chain segments.

As concerns the microwave dielectric behavior of the water-containing poly(vinyl alcohol) sample, shown in Figure 7, while the shift of the glass transition towards lower temperature may be interpreted as due to the plasticizing action of water molecules, which reduces intermolecular attractions, the anomalous behavior observed at higher temperature, may be related to the loss of water as a result of the temperature rise (which tends to decrease both dielectric constant and loss) and to the antagonistic effect due to the increase in the average kinetic energy of chain segments.

Poly(vinyl Chloride)

The dielectric behavior of poly(vinyl chloride) either at low or at radiofrequencies (up to 10^6 cps) has been extensively investigated by many different authors.²⁴⁻³⁰

In general, two loss regions have been found in this polymer; the α -relaxation, characterized by a loss peak located at temperatures above the dilatometric glass transition point, and the β -relaxation, characterized by a flat loss maximum, extending over a wide temperature range. While the α -transition, characterized by a high apparent activation energy (77 kcal./mole) has been attributed to cooperative motions of chain segments, the β -transition, whose activation energy is of the order of 15 kcal./mole, has been the object of much controversy regarding the assignment to a particular molecular mechanism. At present, it is believed to consist in small-scale motions of small segments in the main chain and is classified among the secondary local mode motions.

Analogously to the above discussed polymers, also for poly(vinyl chloride) the dielectric loss-peaks observed at radiofrequencies, fail to appear when measurements are carried out at ultra-high frequencies. The β - and

the α -relaxations, responsible for the dipolar polarization at temperatures below and above the glass transition point, respectively, manifest themselves simply through a definite increase of dielectric constant and loss with increasing temperature, which is particularly marked above T_g . The latter temperature can be very well identified by the upswing of the $\tan \delta$ versus temperature curve.

Poly(vinyl Acetate)

For this polymer, radiofrequency dielectric measurements indicated, in addition to the principal loss maximum (α -process), localized above the glass transition point, the existence of a secondary very broad maximum, probably formed by the superimposition of two or more loss maxima.^{31,32} The latter relaxation has been attributed to motions of polar side groups, probably involving some cooperation from a small portion of the main chain.

The observation made for poly(vinyl chloride) as regards the dielectric behavior at ultra-high frequencies (microwaves) as compared to that observed at lower frequencies, can be repeated for poly(vinyl acetate). The β -process, at frequencies of the order of $\sim 10^{10}$ cps, is, most probably, melted together with the α -process. This suggestion is supported by the results of mechanical loss measurements (Fig. 16),³³ from which it resulted that, even at frequencies of the order of 10^4 cps, the β -region is so much overlapped to the α -region, that it becomes difficult to distinguish the two peaks.

As regards the α -process, connected with cooperative motions in the main chain, in this case no maximum is found, but a progressive marked loss increase with increasing temperature above the glass transition point can be observed.

Because of the existence of an important secondary dielectric relaxation process below T_g , the microwave dielectric constant for glassy poly(vinyl acetate), is much higher than the optical dielectric constant n_D^2 ; at room

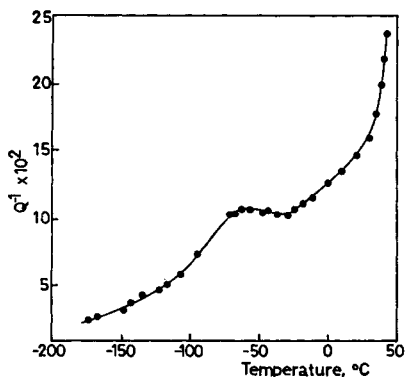


Fig. 16. Mechanical damping factor in poly(vinyl acetate) as function of temperature. $f \sim 10^4$ cps.³³

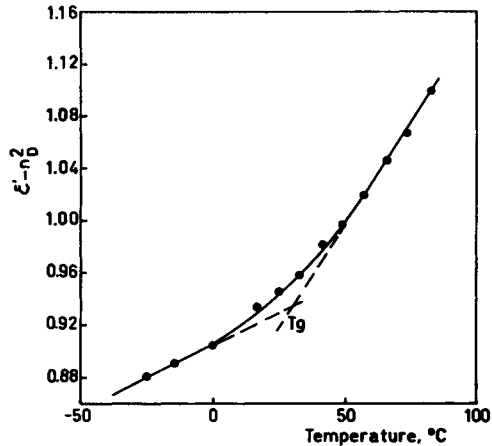


Fig. 17. Plot of the difference between the microwave dielectric constant and optical-dielectric constant in poly(vinyl acetate).

temperature, a difference of the order of 29% between those quantities is observed; such a difference becomes much more accentuated, when temperatures above the glass transition point are considered, as a consequence of the increased contribution of the orientational polarization to the dielectric constant (Fig. 17).

In comparing the microwave dielectric behavior of poly(vinyl acetate) with that of poly(vinyl chloride), it can be noted that the increase in slope of the dielectric loss versus temperature curve, which occurs at the corresponding T_g , is less accentuated for the former than for the latter polymer. The rate of increase of $\tan \delta$ with increasing T for poly(vinyl acetate) becomes, however, quite large when temperatures about 100°C. above the glass transition point are reached. This may be attributed to the effect of the greater bulkiness of acetate groups as compared with chlorine atoms, so that the orientational freedom of the former is much more hindered and requires more volume.

Vinyl Chloride-Vinyl Acetate Copolymer

In comparison with poly(vinyl chloride) this material exhibits a lower transition temperature, as is to be expected for the lowering of intermolecular forces caused by statistical introduction of vinyl acetate units along the chain. It is surprising, however, that in the copolymer the dielectric constant at room temperature is a little lower than those of the two homopolymers; this may be due to the different methods of polymerization, which may introduce different quantities of impurities in the examined materials.

ABS Plastics

There are, at present, no data regarding the radiofrequency dielectric behavior of these materials; nevertheless, it can be easily predicted on the

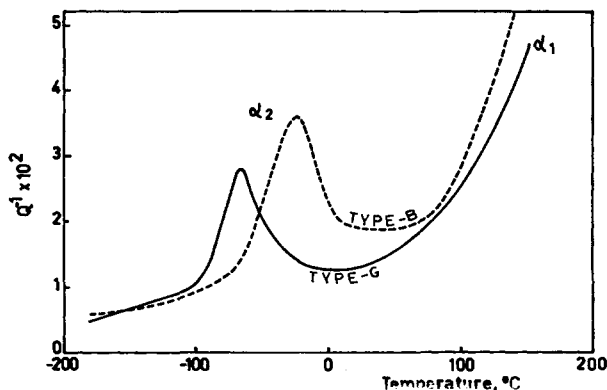


Fig. 18. Plot of mechanical damping factor as function of temperature for two ABS plastics. $f \sim 10^4$ cps.

basis of mechanical loss measurements made by us on the specimens under discussion at acoustic frequencies over a wide range of temperature.

In Figure 18 is reported a plot of mechanical loss against temperature for the ABS plastic, type B, and for the corresponding type G sample at a frequency of about 10^4 cps. For both materials two mechanical high-loss regions are distinguished: one α_2 , located at a temperature below the dilatometric glass transition point, and another α_1 , above this temperature. The α_2 loss region is characterized, for both materials, by a single mechanical damping peak of limited height (Q^{-1} = reciprocal of the resonant coefficient = 3×10^{-2}); for the type B sample, such a peak is located at about -25°C ., whereas for the type G sample, the corresponding maximum is located at a much lower temperature (about -70°C .). The α_1 loss region is, on the contrary, characterized by a rapid increase of mechanical damping with increasing temperature, starting from the glass transition point; the relevant loss peak could not be distinguished because of the softening of the specimen, which impeded further measurements at higher temperatures. The glass transition temperature, as determined experimentally by dilatometry, for the type G sample coincides practically with the glass transition point of the pure rigid component (styrene-acrylonitrile 76/24 copolymer), whereas that for the type B sample is a little lower, due to the plasticizing effect of the more compatible butadiene-acrylonitrile rubber.

The α_2 loss peak can be interpreted as due to cooperative motions in the main chain of the rubbery component. It is located at higher temperature for the type B sample than for the type G specimen, since the butadiene-acrylonitrile copolymer, which constitutes the rubber-phase component for the former material, is more rigid than polybutadiene, which constitutes the rubber-phase component for the type G sample.

The radiofrequency dielectric loss versus temperature plot, for the type B sample is expected to be quite similar to that observed in mechanical measurements, while for the type G specimen it has to be somewhat differ-

ent. In particular, for the latter, the α_2 -peak should be either completely missing or very much attenuated, inasmuch as the almost nonpolar polybutadiene rubber is not expected to show important dielectric relaxation effects.

Finally, in the light of the preceding results and comments, it seems now quite easy to explain the differences observed in the behaviors of the two ABS plastics at ultra-high frequencies. The higher losses shown by the blend as compared with the G type sample, at temperatures below T_g , derive from the existence of an important dielectric relaxation effect in the rubber-phase component; the higher values of $\tan \delta$ and the more rapid increase of this quantity with increasing temperature, observed for the same blend above T_g , may be explained on the basis of the larger number of polar groups (per volume unit) and to the plasticizing effect of the butadiene-acrylonitrile rubber, which enhances the molecular mobility of the rigid component and shifts the average relaxation times for the α_1 process towards shorter values.

GENERAL REMARKS AND CONCLUSIONS

On the basis of the present results, the substantial differences which can be noted between the dielectric behavior of polar polymers at ultra-high frequencies and that at very low or at radiofrequencies are summarized schematically in Figure 19.

At low frequencies, one notes, in addition to the α -relaxation peak localized above T_g , which is associated with cooperative motions in the main chain, one or more secondary relaxation effects (β , γ , etc.), associated with local motions in the main chain or to motions in side chains which become excited below the glass transition point. Finally, in the softening region, another high loss region is noted (λ), characterized by a rapid increase of dielectric losses with increasing temperature. This is due to ionic conduction.

Passing from low to radiofrequencies (up to 10^6 cps), the primary and secondary relaxation peaks are shifted towards higher temperatures, the former following an empirical equation of the WLF-type, the latter an Arrhenius-type equation. The differences in the activation energies for primary and secondary effects (ΔE^* is much higher for the former) causes progressive merging of the corresponding high-loss regions when frequency is increased.

Passing, finally, to ultra-high frequencies (microwaves) all relaxation peaks, either primary or secondary, tend to disappear: the corresponding relaxation effects, however, manifest themselves with a progressive increase of losses with increasing temperature, which is particularly marked above T_g . The disappearance of the α -peaks may be explained on the basis of the fact that, at ultra-high frequencies, these are localized at too high a temperature (near the decomposition temperature of the material), as can be roughly seen from the extrapolation of the $\log f$ versus $1/T$ curve (WLF

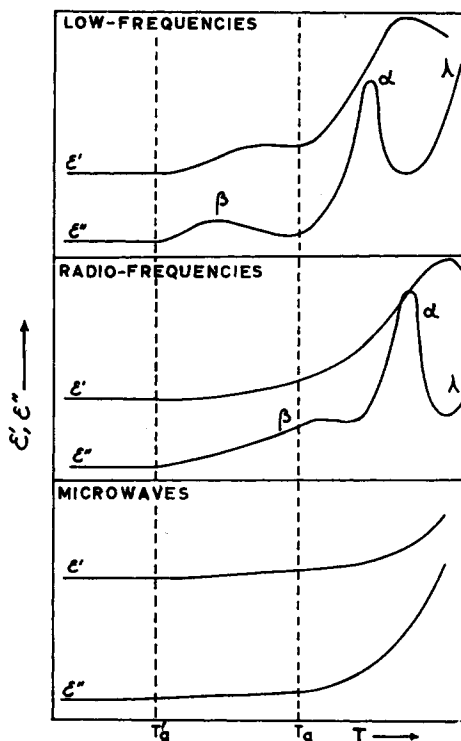


Fig. 19. Schematic representation of the dielectric behavior (dielectric constant and loss factor) as a function of temperature for an hypothetical amorphous linear high polymer over different frequency ranges.

equation) (Fig. 20). The disappearance of secondary peaks is, on the contrary, due to the fact that these, in the microwave region, either fall in the α -loss region, becoming thus completely masked by the latter (much more important), or because the corresponding loss region merges with the α -region, giving place to a single macroscopic relaxation effect, which sometimes may appear as a flattened loss maximum. The latter seems more probable when some cooperation exists between side-chain and backbone motions, frequently occurring in polymers containing bulky side groups.

The conduction losses, which vary with σ/ω (where σ is the conductivity and ω the angular frequency), become negligible at ultra-high frequency and so do also interfacial losses (Maxwell-Wagner effect), particularly important in heterogeneous materials at low and middle frequencies.

As concerns the glass transition, it can be observed that, in spite of the very high frequency used in our measurements, its onset, in most cases, can be easily determined from the experimental $\tan \delta$ versus temperature curves. This may be explained either on the basis of the very wide distribution of relaxation times, which characterizes molecular relaxation processes in polymers, or more probably by the fact that, when the glass transition point

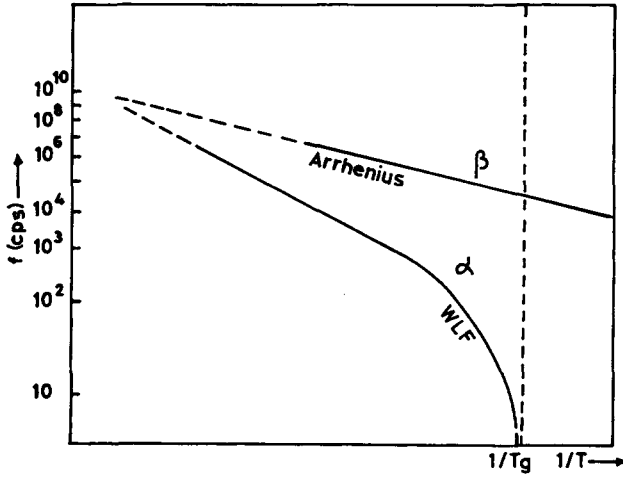


Fig. 20. Frequency dependence of the dielectric loss peaks for primary (α) and secondary (β) relaxation processes.

is reached, the increased kinetic energy of macromolecules and the larger free volume available increases the strength of the secondary relaxation effects (practically present in all polymers), whose average relaxation times at T_g may be sufficiently short to give important contributions to the dielectric polarization of the material, even at ultra-high frequencies.

APPENDIX

In Figure 21 a simplified scheme of the modified section of the guide is represented.

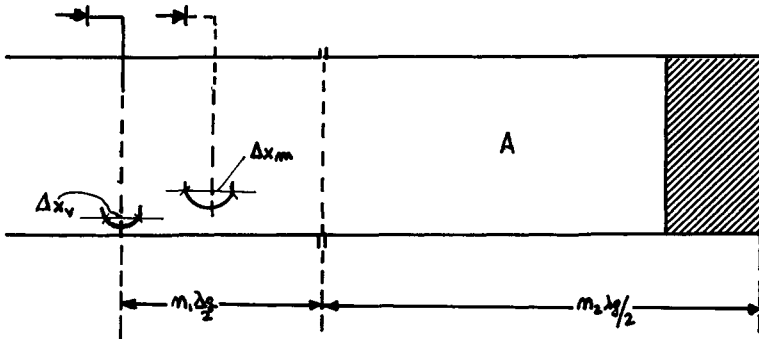


Fig. 21. Modified section of the guide and relevant quantities of interest.

With the empty guide Δx_s is measured at a given abscissa. As already stated, such a value takes into account the losses in the terminal short-circuit and the losses on the guide walls. If, corresponding to the various nodes, the relevant Δx_s are measured and then plotted against the position

of the nodes, starting from the short-circuited extreme, a straight line following the equation

$$\Delta x_v = n(\Delta \cdot \Delta x_v) + b \quad (3)$$

is obtained, where n is the distance of the n th node from the terminal short-circuit, measured in half wavelengths, $\Delta \cdot \Delta x_v$ is the difference in Δx_v between two successive nodes, and b is the contribution due to the losses in the terminal short-circuit, which, in general, can be ignored (in our case, $b = 0.002$ mm.).

Measurements carried out with the empty guide, without the A extension, allowed formulation of eq. (3).

$$\Delta' x_v = n_1 \cdot 0.007 \quad (4)$$

To obtain eq. (4) the quantity $\Delta' x_v$ was measured on successive nodes, namely on the first, second, third, fourth, and fifth, starting from the short-circuit, all accessible through the slotted line.

With the A guide section added, $\Delta'' x_v$ values, related to the new situation, were determined in correspondence of the slotted zone. Assuming that the terminal losses in the two situations are equal (which can be taken for granted either because the same short-circuit was employed or because the losses themselves are very low), we can write, for a given node:

$$\Delta x_v = \Delta' x_v + \Delta'' x_v = \Delta' x_v + n_2 (\Delta \cdot \Delta'' x_v) \quad (5)$$

where n_2 expresses the length of the guide extension in $\lambda_g/2$, we obtain:

$$\Delta \cdot \Delta'' x_v = 0.011 \text{ mm.} \quad (6)$$

i.e., the guide extension exhibits higher losses.

Let us examine, then, the corrections to be made on Δx_m in order to obtain the Δx value to be introduced in eq. (1). When the specimen is inserted, the wall losses are to be divided between the contribution of the walls of the empty guide and the contribution of the guide containing the sample.

The first term can be immediately deduced from measurements carried out with the empty guide. Referring to Figure 21 we can write:

$$\Delta x = \Delta x_m - \Delta' x_v (1 - 2\Delta/n_1\lambda_g) - \Delta'' x_v (1 - 2d/n_2\lambda_g) \quad (7)$$

The other term can be determined by considering that the propagation constant of a guide section filled with dielectric can be expressed by means of the equation:

$$\gamma = \alpha_2 + \alpha' + j\beta_2 \quad (8)$$

where $\alpha_2 + j\beta_2 = \gamma_2$ is the propagation constant related to the dielectric, while α' is the attenuation due to the wall losses. Such losses are conveniently expressed by means of loss tangent, which depends on the dielectric constant and magnetic permeability of the dielectric. For a circular guide working on the TE₁₁ mode, the ratio of the loss tangent of the walls in

presence of the specimen, $\tan \delta_{w_0}$, to the loss tangent of same walls for the empty guide, $\tan \delta_w$, is:

$$\frac{\tan \delta_{w_0}}{\tan \delta_w} = \frac{0.42 + (\lambda_0/\lambda_c)^2 (1/\mu' \epsilon')}{\mu' [0.42 + (\lambda_0/\lambda_c)^2]} \quad (9)$$

where λ_0 is the free-space wavelength, λ_c is the cutoff wavelength for the TE₁₁ mode, and μ' is the permeability of the specimen.

Experimentally, we determined:

$$\tan \delta_w = (\Delta \cdot \Delta x_0) (2/\lambda_0) \{ [1 - (\lambda_0/\lambda_c)^2] \} \quad (10)$$

Thus, putting $\mu' = 1$, from eqs. (8) and (9) we obtain:

$$\tan \delta_{w_0} = (\Delta \cdot \Delta x_0) (2/\lambda_0) (1 - \eta^2) [(0.42 + \eta^2)(1/\epsilon')]/(0.42 + \eta^2) \quad (11)$$

where $\eta = \lambda_0/\lambda_c$.

In the present case, for $\lambda_0 = 60$ mm., $\lambda_c = 43.43$ mm., and $\Delta \cdot \Delta x_0$, given from eq. (6) we have:

$$\tan \delta_{w_0} = 0.000054(1 + 1.55/\epsilon') \quad (12)$$

In conclusion, the losses due to the walls of the empty guide are taken into account by modifying Δx_m and those due to the walls of the guide in contact with the specimen are taken into account by subtracting the value of $\tan \delta_{w_0}$ calculated by means of eq. (12) from the experimental $\tan \delta$.

Another aspect which has to be considered is the loss changes in the empty guide caused by temperature variations. Numerous preliminary measurements carried out showed that up to $120 \div 130^\circ\text{C}$. $\Delta'' x_0$ does not change. A small increase is observed at higher temperatures, but it can be ignored.

Finally, a further consideration has to be made regarding the thermal expansion of the specimen. The specimen thickness has been corrected, taking into consideration the thermal expansion coefficient of the material under examination. It seemed more suitable to consider the linear coefficient instead of the cubical one, since the guide also expands transversally, even if with a smaller expansion coefficient.

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Résumé

Le comportement diélectrique de différents copolymères polaires a des fréquences ultra-élevées a été étudié au moyen d'un diélectromètre adapté de façon à effectuer des mesures à différentes températures. Les mesures expérimentales ont été effectuées à environ 9×10^9 cycles/sec sur un domaine de température de -150 à $+200^\circ\text{C}$ pour le polyoxyméthylène, pour le polythiométhylène, le poly-3,3'-chlorométhylloxétane (Penton), le polycarbonate de 4,4'-dioxydiphényl-2,2'-propane (Makrolon), le polyvinylalcool, le polyvinylacétate, le chlorure de polyvinyle, le copolymère de chlorure de vinyle-acétate de vinyle et les plastiques ABS type B (blend) et type G (greffé). Comparant le comportement diélectrique des matériaux examinés à des fréquences très élevées avec le comportement déterminé à basse ou à radio-fréquences, on observe que dans la région de micro-ondes tous les pics de relaxation tendent à disparaître soit à se relier à des mouvements coopératifs dans la chaîne principale (processus primaire) ou aux mouvements locaux dans la chaîne principale ou les chaînes latérales (processus secondaire) ce que l'on observe généralement aux faibles fréquences, les effets correspondants de relaxation toutefois, se manifestent eux-mêmes à travers un accroissement progressif des pertes avec température croissante, ce qui est particulièrement marqué au-dessus de la température de transition vitreuse T_g . Cette dernière transition malgré la très haute fréquence de mesure est facilement remarquée dans la plupart des cas par suite du changement soudain de la tangente δ en fonction de la température qui accompagne son apparition. Ceci est expliqué avec les temps de distribution très larges du processus de relaxation moléculaire dans les polymères et avec, l'accroissement de la force des effets de relaxation secondaire, qui est vérifiée à T_g comme conséquence de l'énergie cinétique des macromolécules et d'un volume libre plus grand pour l'orientation des chaînes latérales. Chaque cas est discuté séparément et les résultats expérimentaux

interprétés sur la base de la structure moléculaire et la mobilité des chaînes des polymères examinés.

Zusammenfassung

Das dielektrische Verhalten verschiedener polarer Hochpolymerer bei ultrahohen Frequenzen wurde mit einem zur Ausführung von Messungen bei verschiedenen Temperaturen geeignet modifizierten Dielektrometer untersucht. Messungen bei etwa 9×10^9 Hz wurden im Temperaturbereich von -150 bis 200°C an Polyoxymethylen, Polythiomethylen, Poly(3,3'-chlormethyl)oxetan (Penton), Polycarbonat von 4,4'-Dioxydiphenyl-2,2'-propan (Makrolon), Polyvinylalkohol, Polyvinylacetat, Polyvinylchlorid, Vinylchlorid-Vinylacetat-Copolymeren und ABS-Plastomeren vom Typ-B (Mischung) und Typ-G (Pfropfung) durchgeführt. Beim Vergleich des dielektrischen Verhaltens der untersuchten Stoffe bei ultrahohen Frequenzen mit dem entsprechenden bei niedrigen oder Radiofrequenzen zeigt sich, dass im Mikrowellenbereich alle Relaxationsmaxima, sowohl die durch kooperative Bewegung in der Hauptkette (Primärprozesse) bedingten, als auch die mit lokalen Bewegungen in der Hauptkette oder in Seitenketten (Sekundärprozesse) zusammenhängenden, die gewöhnlich bei niedrigeren Frequenzen beobachtet werden, zu verschwinden trachten; die entsprechenden Relaxationseffekte äussern sich jedoch durch eine ständige Zunahme der Verluste mit steigender Temperatur, was sich besonders oberhalb der Glasumwandlungstemperatur T_g bemerkbar macht. Diese Umwandlung kann in den meisten Fällen trotz der sehr hohen Messfrequenz leicht aus der plötzlichen Neigungsänderung der Kurve $\tan \delta$ gegen Temperatur, welche ihr Einsetzen begleitet, lokalisiert werden. Das wird durch die sehr breite Verteilung der Dauer der Molekülrelaxationsprozesse in Polymeren und durch die Zunahme der Stärke der sekundären Relaxationseffekte, die bei T_g verifiziert wird, als Folge der erhöhten kinetischen Energie der Makromoleküle und des grösseren, für die Seitenkettenorientierung zur Verfügung stehenden freien Volumens erklärt. Jeder Fall wird für sich diskutiert und die Versuchsergebnisse werden auf Grundlage der Molekülstruktur und der Kettenbeweglichkeit der untersuchten Polymeren gedeutet.

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