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MACROMOLECULAR DIELECTRICS

G.P. Mikhailov and B.I. Sazhin

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INTRODUCTION

If a polymer is to be used as an electrical insulator or a dielectric, not only its electrical properties but also a number of other physicochemical properties must fulfil certain conditions. The fact that a given polymer has certain electrical properties is no guarantee that it will be of any practical use. For example, some polymers are ruled out because their thermal stability is poor, because they are difficult to work, or because their mechanical strength is low.

Our aim in this paper is to demonstrate certain regularities in the electrical properties of polymers, using data from our own publications and from those of other investigators. Attention will mainly be directed to dielectric loss and polarisation, and their relation to the structure of the polymers. In this connection we shall not only consider the chemical composition, stereochemical structure, and crystalline or amorphous state, but also the nature of the thermal motion, since the latter has a marked effect on the electrical properties. The main peculiarity of the thermal motion of a polymer macromolecule is that, because of its chain-like structure and relatively enormous dimensions, intramolecular thermal motions play an important part.

Polymers may be divided into polar and non-polar, according to the stereochemical structure of the monomers; the overwhelming majority are polar. The variation of the electrical properties of polar polymers may be explained in terms of the nature and strength of the molecular forces. Study of the effective dipole moment of these polymers has shown that intramolecular forces are predominant[1], while in substances of lower molecular weight the intermolecular forces are most important.

A number of the electrical properties of polymers are kinetic in nature, so the study of these substances in changing electrical fields is of great interest. This is also worth while from the practical point of view, because dielectrics are used more often in alternating than in constant electric fields.

1. DIELECTRIC LOSSES AND POLARISATION OF NON-POLAR POLYMERS

Non-polar polymers are extensively used as high-frequency dielectrics. The most important electrical properties of such substances are the tangent of the dielectric loss angle, $\tan\delta$, and the dielectric constant ϵ'.

We shall first consider the dependence of these quantities on frequency and temperature for the most widely investigated polymer, amorphous polystyrene (PS).

Fig. 1 shows $\tan\delta$, ϵ', and n_D^2 (the square of the refractive index) for PS as functions of temperature at a frequency of 10 kc/s,[2] and $\tan\delta$ and ϵ' as functions of frequency at two temperatures, one below and one above the vitrification temperature, $T_{vit} = 80°$. It may be seen from Fig. 1*b* that $\tan\delta$ and ϵ' are practically independent of the frequency for vitreous PS (i.e. for $T < T_{vit}$). The value of $\tan\delta$ is $(0.5-1) \times 10^{-4}$, and this does not vary much with the temperature for $T < T_{vit}$. The decrease of ϵ' on heating in this temperature range is connected with the thermal expansion of the sample. Thus, it may be seen from Fig. 1 that there is a break in the ϵ' vs. T curve at about the vitrification temperature, which is also found in the density vs. temperature curve. The values of ϵ' and n_D^2 for PS coincide within 1% over a wide range of temperatures.

All this shows that relaxation-dependent dipolar dielectric losses do not occur in vitreous PS. It may also be seen from Fig. 1 that at temperatures above T_{vit}, the $\tan\delta$ vs. T and $\tan\delta$ vs. $\log f$ curves both show maxima. Near these maxima the value of ϵ' begins to decrease with the frequency and increase with the temperature. These are signs of dipolar polarisation. The presence of dipoles in PS may be due either to impurities chemically bound to the chain or to the slight polarity of the monomer ($\mu \sim 0.1-0.3$ c.g.s. units).

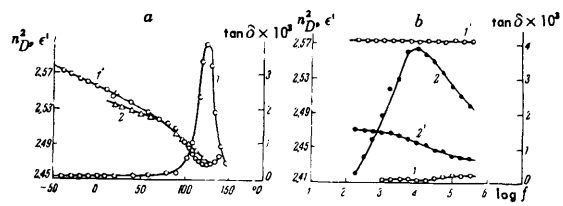


Fig. 1. The dielectric constant, square of the refractive index, and tangent of the dielectric loss angle of polystyrene as functions of temperature (*a*) and frequency (*b*)[2]. *a*: 1), 1') $\tan\delta$ and ϵ' at 10^3 c/s; 2) n_D^2. *b*: 1), 1') $\tan\delta$ and ϵ' at 39°; 2), 2') $\tan\delta$ and ϵ' at 134.5°.

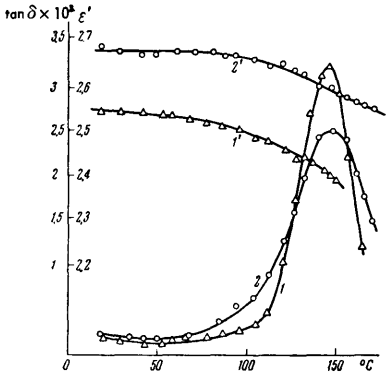


Fig. 2. ϵ' and tan δ for polystyrene as functions of temperature at 8.5×10^4 c/s: 1), 1') tan δ and ϵ' of atactic polystyrene; 2), 2') tan δ and ϵ' of isotactic polystyrene[3].

Fig. 2 shows ϵ' and tan δ as functions of the temperature for atactic and isotactic polystyrene[3]. It will be seen that both the values of these quantities and the way in which they vary with temperature are very similar for these two types of polystyrene. The slightly higher values of ϵ' for isotactic PS is due to the greater density of this substance. The temperature at which tan δ is maximum is the same for the two forms of PS, which is in accordance with the equality of the vitrification temperatures for these polymers[4]. Near the maximum the value of tan δ is nearly the same for both polymers. The slightly higher value for atactic PS may be due to the presence of traces of catalyst, which increases the value of tan δ as will be shown below for the case of polyethene (PE).

It may be expected that the dielectric properties of crystalline polymers will depend on the crystalline state of these substances: in fact, we have already seen how an increase in density on crystallisation of polystyrene is accompanied by a slight (about 1.5%) increase in the dielectric constant.

Fig. 3 shows tan δ as a function of temperature for low-pressure polyethylene, high-pressure polyethylene and polytetrafluoroethylene (PE_{LP}, PE_{HP}, and F-4)[5,6,7]. Some of these curves (curves *1'* and *2'* in Fig. 3*b* and curve *2* in Fig. 3*a*) refer to samples of low crystallinity, produced by rapid cooling from the liquid state. All the curves in Fig. 3 were determined at temperatures above T_{vit}: the vitrification temperature for F-4 is about -100°, and experiments on the dynamic mechanical losses of PE indicate that its vitrification temperature is about -140°.[8]

It will be seen that above the vitrification temperature the tan δ vs. T curve for F-4 has one maximum, and the corresponding curves for PE_{LP} and PE_{HP} have two and three maxima respectively. Since we are dealing with crystalline polymers, these dipolar losses may be associated with dipolar relaxation in the amorphous or in the crystalline part. It was found that the value of tan δ for F-4 in the region of the maximum is increased if the degree of crystallinity is reduced by rapid cooling from the liquid state, which suggests that these losses are connected with processes in the amorphous part of the polymer.

The picture is rather more complicated for polyethylene. The increase in the branching of the molecule on passing from PE_{LP} to PE_{HP} leads to a considerable change in the nature of the relation between tan δ and the temperature: at a frequency of 1 kc/s near 0° the more highly branched PE_{HP} shows a maximum due to the "medium-frequency relaxation losses" (m.f.r. losses), which is not found with PE_{LP}.

We have seen that ϵ' for polystyrene is constant to within 1% with respect to frequency, and that the decrease of ϵ'

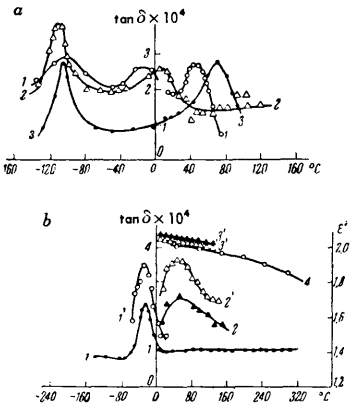


Fig. 3. ϵ' and tan δ for polyethylene (*a*) and F-4 (*b*) as functions of temperature[5,6,7]. *a*: 1), 3) high-pressure and low-pressure polyethylene; 2) "quenched" PE_{LP}. *b*: 1), 1'), 2), 2') tan δ of original and "quenched" samples at 10^3 and 5×10^8 c/s; 3), 3') ϵ' of original and "quenched" samples at 5×10^8 c/s; 4) ϵ' at 10^2 and 10^5 c/s.[4]

TABLE 1.

Polymer	t, °C	ϵ'	d, g/cm³	P, cm³, obs.	R_D, cm³, calc.	$\frac{(P-R_D)}{P} \times 100$,%
Atactic polystyrene	25	2.544	1.055	34.3	33.7	1.8
Isotactic polystyrene	25	2.680	1.075	35.0	33.7	4.0
Polyethylene	23	2.276	0.920	4.55	4.65	2.2
Polyethylene	23	2.320	0.940	4.56	4.65	2.0
Polyethylene	23	2.365	0.960	4.56	4.65	2.0
Isotactic polypropylene	25	2.28	0.912	13.6	13.9	2.2
Atactic polypropylene	25	2.16	0.865	13.6	13.9	2.2

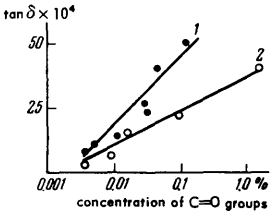


Fig. 4. The variation of tan δ for polyethylene with the concentration of C=O groups: 1) PE_{HP}, 25°C, 5×10^7 c/s[14]; 2) PE_{LP}, 20°C, 400 c/s[15].

with temperature is due to thermal expansion. Similar results are obtained for other non-polar polymers. For such polymers ϵ' lies between 2.0 and 2.6 (F-4 and PS), and is determined by the values of the density and the bond refraction. The accuracy of this relationship is shown in Table 1, in which are given measured values of ϵ' and the density for various polymers at various temperatures, the values of the molecular polarisation calculated from these data, and the molecular polarisation determined from bond-refraction data given in the literature[9]. The last column gives the percentage difference between the experimental[7,10,11] and calculated values. It will be seen that this difference never exceeds 4%. It may therefore be concluded that the value of ϵ' for non-polar polymers is practically entirely determined by deformation polarisation. Changes in the density can only have a slight effect on ϵ'. For example, PE_{HP} has $d = 0.92$ g/cm³ and $\epsilon' = 2.28$, while PE_{LP}, with $d = 0.96$ g/cm³ has $\epsilon' = 2.36$ to 2.37. The value of ϵ' for polystyrene or polyethylene foams may be 1.1–1.2. Investigation of the possibility of using such materials in cables is therefore of great interest.

A substance with a high dipolar or ionic polarisability is sometimes added to a non-polar polymer in order to increase ϵ'. However, this is always accompanied by an increase of $\tan\delta$ for certain temperatures and frequencies. This way of increasing ϵ' is only acceptable for capacitors to be used in relatively narrow ranges of frequency and temperature. For example, in the USA[12] F-4 containing 20% of barium titanate has been used for high-frequency capacitors. This material has $\epsilon' = 5$, and $\tan\delta$ of the order of 0.001.

The value of $\tan\delta$ near the maximum is proportional to the volume fraction of polar groups present, and to the square of their effective dipole moment μ_{eff}.[13] The presence of these groups in non-polar polymers may be due to either a disturbance in the structure of the macromolecular chain (oxidation, appearance of unsaturation) or impurities. Fig. 4 shows $\tan\delta$ for high-pressure and low-pressure polyethylene, as a function of the concentration of the highly polar C=O groups in the polymer molecule, determined from the infra-red absorption spectra[14,15]. It may be seen that concentrations of the order of 0.005% correspond to $\tan\delta = 0.0005$. This amount of C=O groups is so small that it can hardly be determined spectroscopically; but the value of $\tan\delta$ for these polymers is quite high, so that they cannot be used for some ultra-high-frequency applications. The oxidation of polypropylene (PP) also strongly increases the value of $\tan\delta$. It will be seen from Fig. 5 that rolling

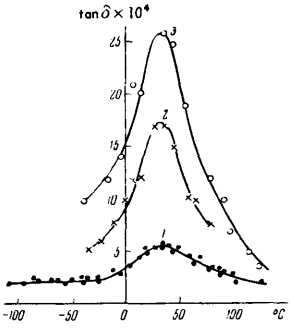


Fig. 5. $\tan\delta$ for polypropylene as a function of temperature at 7.5×10^4 c/s: 1) original sample; 2) after rolling for 10 min at 170°; 3) after rolling for 20 min at 170°.

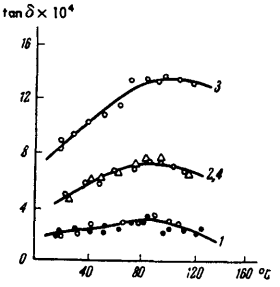


Fig. 6. $\tan\delta$ for polyethylene as a function of temperature at 3×10^9 c/s[16]: 1) PE_{LP}, ash content S = 0.03%; 2) PE_{LP}, S = 0.35%; 3) PE_{LP}, S = 1.9%; 4) PE_{HP}.

molten PP for only 10 min increases $\tan\delta$ more than three times, from $(2-5) \times 10^{-4}$ to $(6-17) \times 10^{-4}$. The data given above suggest that these losses are due to the presence of small amounts (0.01–0.001%) of polar groups (OH, C=O, etc.).

Organometallic catalysts are now very widely used. Polymers made with the aid of these catalysts should be very carefully purified.

Fig. 6 shows $\tan\delta$ as a function of the temperature at 3×10^9 c/s for samples of PE_{LP} which have been purified with varying thoroughness[16], as determined by the amount of inorganic material in the polymer. It may be seen from Fig. 6 that the removal of traces of catalyst has a considerable influence on the value of $\tan\delta$. Thus, at 80° and $f = 3 \times 10^9$ c/s, polyethylene with an ash content of 0.03% has $\tan\delta = 3 \times 10^{-4}$, while an ash content of 1.9% gives $\tan\delta = 13.5 \times 10^{-4}$. All this shows that in order to obtain non-polar polymer dielectrics with the lowest possible value of $\tan\delta$ (about 0.0001) over a wide range of frequency and temperature, extreme care must be taken in the production and processing to ensure the absence of impurities and of polar groups in the macromolecule.

Moreover, in a number of cases differences in the structure of the macromolecule can have a considerable effect on the value of $\tan\delta$. Thus, it has been mentioned above that PE_{HP} shows three sorts of dipolar losses, while PE_{LP} shows two. It is known that at room temperature and above PE_{HP} and PE_{LP} have a maximum in the dielectric losses at ultra-high frequencies[17], and that in the region of this maximum PE_{HP} shows two kinds of losses simultaneously, while PE_{LP} only shows one: it lacks the medium-frequency relaxation. This is why the value of $\tan\delta$ for PE_{HP} is about twice that for PE_{LP} at ultra-high frequencies, other things being equal (purity, moisture content, etc.) (see Fig. 6, curves *1* and *4*).

2. DIELECTRIC LOSSES AND DIELECTRIC CONSTANTS OF POLAR POLYMERS

Fig. 7 shows $\tan\delta$ and ϵ' as functions of temperature for poly-*p*-chlorostyrene (PPCS),[18] polyvinyl chloride (PVC)[19] and polytrifluorochloroethylene (F-3).[20] These substances differ from PS, PE, and F-4 respectively in that one atom of hydrogen or fluorine is replaced by chlorine in the monomer. This is accompanied by a considerable increase in

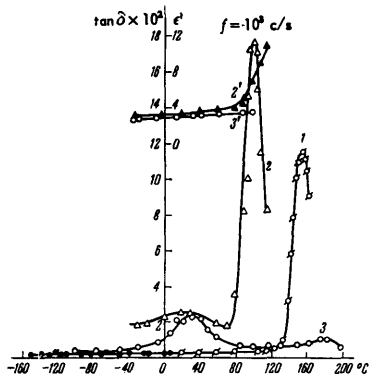


Fig. 7. ϵ' and tan δ for polar polymers as functions of temperature at 10^3 c/s: 1) tan δ for polyparachlorostyrene [section marked —·—· at 10^6 c/s (missing from figure. Ed. of Translation)] [18]; 2), 2') tan δ and ϵ' for polyvinylchloride [19]; 3), 3') tan δ and ϵ' for F-3 [20].

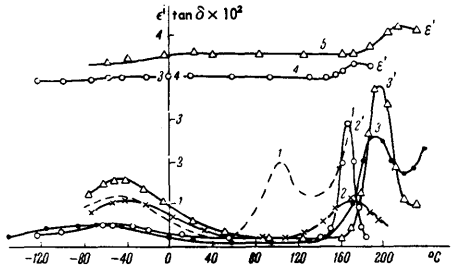


Fig. 8. ϵ' and tan δ for polyesters as functions of temperature at 10^3 c/s [23, 24]: 1) tan δ for polyethyleneterephthalate[23]; 2), 2') tan δ for poly-dian-carbonate (curve 2' — sample of reduced crystallinity); 3), 3') tan δ for poly-dian-isophthalate; 4), 5) ϵ' for poly-dian-carbonate and poly-dian-isophthalate.

the dipole moment μ_{eff}; in fact, all the physical and mechanical properties are changed. It may be seen from Fig. 7 that the maximum value of tan δ is 0.1–0.2, and $\epsilon' = 4$–10 for these polar polymers. This is doubtless due to the polarity of the monomer: the relationship between ϵ' and tan δ of polymers on the one hand and μ_{eff} and the concentration of dipoles n_0 on the other has received ample experimental confirmation.

Moreover, measurement of the dielectric losses has been successfully used in a number of cases to determine the value of the dipole moment or the concentration of dipoles [17]. As may be seen from Fig. 7, the maximum value of tan δ for polar polymers is 100 to 10 000 times larger than for non-polar polymers. This makes it difficult to use polar polymers as high-frequency dielectrics. It is interesting that at temperatures below T_{vit} the value of tan δ for PPCS hardly changes with temperature, and does not exceed 0.001. Similar data have been obtained with three other polymers of halogenated styrene [18]. This property of a given set of polar polymers is evidently connected with the specific properties of the polar side group.

It may also be seen from Fig. 7 that the curves of tan δ as a function of temperature for PVC and F-3 both have two maxima. The dipole losses occurring at low temperatures are called dipolar-radical (d.r.) losses, while those occurring where the polymer is highly elastic are called dipolar-elastic (d.e.) [3] losses. These two types of losses have been discovered in the vast majority of polymers investigated, both amorphous and crystalline [13,22]. Even when measurements of tan δ and ϵ' seem to indicate that d.r. losses are absent [18], more detailed analysis of the frequency-dependence of tan δ and ϵ' shows that both d.r. and d.e. losses are present, but cannot be distinguished at frequencies between 50 and 10^{10} c/s.

Fig. 8 shows tan δ and ϵ' as functions of temperature for three crystalline polyesters: polyethyleneterephthalate (PET), [23] poly-dian-carbonate* (PDC) and poly-dian-isophthalate* (PDIP), [24] and for the less crystalline samples of the last two (curves *2'* and *3'*).

It may be seen that, despite the differences in structure, the dipolar loss for all these polymers in the low temperature range has its maximum at the same temperature. Remembering that these polyesters contain highly polar carbonyl groups, the explanation of the constant value of T_{max} may be that the other atoms and groups play no essential part in the dipolar-radical relaxation process.

A different rule holds for the dipolar-elastic losses, occurring at higher temperatures: the temperature at which tan δ is a maximum increases with the number of aromatic groups in the macromolecule.

As may be seen from Fig. 8, crystallisation of the polymers is accompanied by a decrease in the value of tan δ. This has been observed in other crystalline polymers [25].

In Table 2 are given data on the effect of crystallisation of polychloroprene (PCP), PET, and F-3 on the value of the loss factor $\epsilon'' = \epsilon' \tan\delta$ in the region of maximum d.e. and d.r. losses, and also values of α, the characteristic width of the relaxation-time spectrum or the range of frequencies corresponding to the region of maximum dielectric loss. At the maximum the loss factor ϵ''_m is related to α, n_0, and μ_{eff} as follows:

$$\epsilon''_m = \epsilon' \tan\delta = A \frac{\alpha n_0}{T} \mu^2_{eff}. \qquad (1)$$

It may be seen from Table 2 that crystallisation decreases the value of ϵ'', and the value of α for d.e. losses, while the value of α for d.r. losses remains practically unchanged. This suggests that d.e. and d.r. losses in crystalline polymers are connected with relaxation processes in amorphous regions of the polymer. The decrease of ϵ' and tan δ on crystallisation may be related to a decrease of the concentration of dipoles in these regions. However, in the case of the d.e. losses this decrease in ϵ''_m is partly due to a decrease in the value of α as a result of the increase in the heterogeneity of the structure of the polymer on crystallisation. We may remark that orientation of the dipoles may occur in the well-ordered crystalline regions of polymers, leading to a sharp increase of ϵ' on crystallisation, as has been observed in certain substances of low molecular

* "dian" = "Bisphenol A" = di(P-hydroxyphenyl)dimethyl methane (Ed. of Translation).

TABLE 2. The effect of the degree of crystallinity X on the loss factor ϵ''_m and the parameter α governing the distribution of relaxation times [25].

Polymer	f, c/s	Sample 1, with lower degree of crystallinity			Sample 2, with higher degree of crystallinity			Remarks
		X_1	$\epsilon''_{m_1}=\epsilon'_{m_1}\tan\delta_1$	α_1	X_2	$\epsilon''_{m_2}=\epsilon'_{m_2}\tan\delta_2$	α_2	
Polychloroprene	10^4	0	1.0	0.48	0.04	0.75	0.43	dipolar-elastic losses
		0	1.0	0.48	0.19	0.66	0.36	
		0	1.0	0.48	0.36	0.58	0.32	
PET	$5\cdot10^2$	0	0.49	0.48	0.60	0.12	0.24	ditto
	$2\cdot10^2$	0	0.45	0.44	0.60	0.11	0.22	
	$6\cdot10^4$	0	0.067	0.30	0.60	0.041	0.31	dipolar-radical losses
	$9\cdot10^5$	0	0.055	0.31	0.60	0.039	0.31	
F-3	50	0.3	0.070	0.20	0.55	0.054	0.26	ditto
	$2\cdot10^4$	0.3	0.12	0.50	0.55	0.078	0.50	
	$4.5\cdot10^5$	0.3	0.13	0.60	0.55	0.082	0.60	

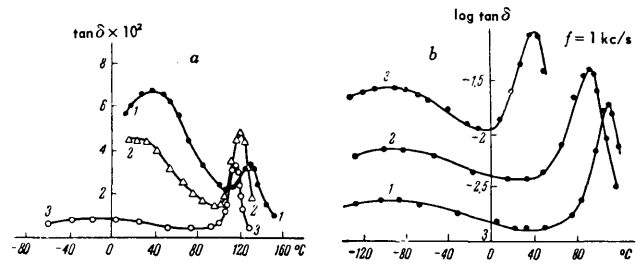
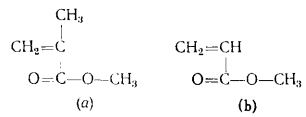


Fig. 9. tan δ for copolymers of styrene with methyl methacrylate (*a*) and with methyl acrylate (*b*) as a function of temperature. *a*: 20 c/s, 1), 2), 3) MMA content 100, 80.5, and 24.4%; *b*: 10^3 c/s; 1), 2), 3) MA content 14, 40, and 100%.

weight[26]. This also occurs to a certain extent in F-3, for which the value of ϵ' decreases by about 20–30% on fusion[20].

A convenient method of controlling the physicochemical properties of polymers is copolymerisation. Fig. 9 shows tan δ as a function of temperature for copolymers of styrene with methyl methacrylate (*a*) and methyl acrylate (*b*)[13,27].



Methyl methacrylate (MMA) differs from methyl acrylate (MA) in that the α hydrogen in the latter is replaced by a methyl group. This structural difference has a considerable effect on the properties of the polymers and copolymers of these substances. Thus, T_{vit} for PMMA is 110°–120°, while for PMA it is about 25°. It may be seen from Fig. 9 that increasing the concentration of styrene shifts the regions of maximum d.r. and d.e. losses to lower temperatures for copolymers of styrene and MMA. This shift is not found for d.r. losses in copolymers with MA, while the d.e. losses shift to higher temperatures.

It follows from Fig. 9 that the magnitude of the d.e. and d.r. losses of copolymers of polar and non-polar monomers decreases as the concentration of the polar component decreases. It may be remarked that in some cases the opposite behaviour is observed. For example, it may also be seen from Fig. 9 that on going from pure PMMA to the copolymer containing 40% of styrene, the maximum value of tan δ in the d.e. loss region increases. This is probably due to an increase in the mobility of the chain as the concentration of α methyl groups is decreased.

In some of the copolymers the presence of d.e. and d.r. losses is indicated in the plots of tan δ against frequency, as well as in the temperature curves. Thus, for the copolymer of styrene and MMA , the maximum of tan δ at low frequencies (Fig. 10) is due to d.e. losses and the maximum at high frequencies is due to d.r. losses. This example shows that in highly elastic states d.r. and d.e. relaxation may both be found at the same temperature.

The strong influence of the chain structure on its mobility is demonstrated by the example of copolymers of acrylonitrile with butadiene (SKN-26) and styrene (SN-28).[28] Both copolymers contain 26–28% of the polar acrylonitrile.

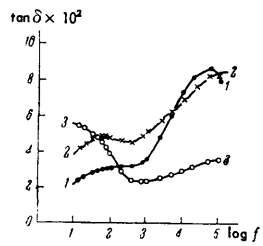


Fig. 10. tan δ as a function of the frequency for copolymers of styrene and MMA: 1) 90.2% MMA; 125°; 2) 80.5% MMA, 122.5°; 3) 55.5% MMA, 109°.

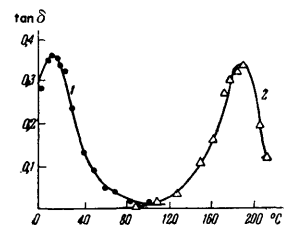


Fig. 11. tan δ as a function of the temperature at 1.5 × × 10^6 c/s for copolymers of: 1) acrylonitrile and butadiene, 26 : 74; 2) acrylonitrile and styrene, 28 : 72.

It may be seen from Fig. 11 that the d.e. losses for SKN-26 are maximum at 15°, while the corresponding maximum for SN-28 occurs at 185°. Moreover, the maximum value of tan δ is about the same for both copolymers, because they both contain about the same number of $-C\equiv N$ groups. The difference in the temperature of the maximum shows that the d.e. losses are due not only to the thermal motion of the individual polar groups, but also to the thermal motion of segments of the macromolecule.

In non-polar polymers ϵ' decreases with increasing temperature, but in polar polymers it increases with temperature in the regions of d.r. and d.e. losses. Fig. 12 shows

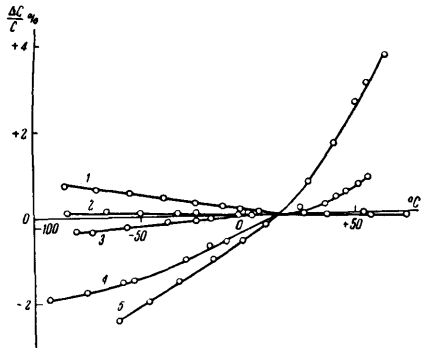


Fig. 12. The relative change of capacitance of capacitors made from copolymers of styrene and MMA, as a function of the temperature at 50 c/s: 1), 2), 3), 4), 5) 0.5, 10, 40, and 60% MMA [26] [one percentage missing (Ed. of Translation)].

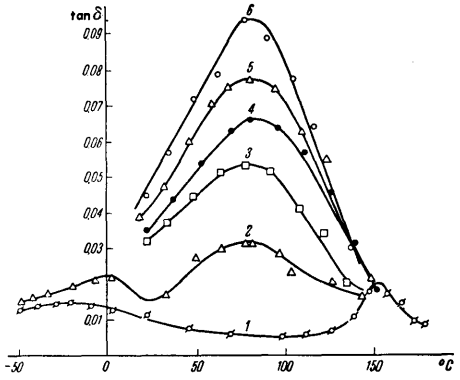


Fig. 14. tan δ as a function of temperature at 10^3 c/s for mixtures of grafted and homopolymers of cellulose acetobutyrate and PMMA: 1), 2), 3), 4), 5), 6) 0, 25, 60, 80, 90 and 100% MMA [28].

how the capacitance of capacitors made with copolymers of styrene with varying amounts of MMA, is related to temperature [26]. It will be seen that a change of temperature from -80° to +60° causes an increase of 6% in the capacitance when a copolymer containing 60% MMA is used, while for a copolymer containing 5% MMA the capacitance decreases by about 0.2%. These data show that copolymers of non-polar monomers with a small amount of polar ones may be used as materials for capacitors with a low temperature coefficient of capacitance.

Polymer dielectrics are quite often plasticised in order to improve their operational characteristics. Fig. 13 shows tan δ and ε' as functions of temperature for polystyrene plasticised with 6.4% of benzyl benzoate [2]. Comparison of these data with those for pure PS (Fig. 1) shows that the introduction of a polar plasticiser increases the value of tan δ about tenfold at temperatures below T_{vit}, and increases the value of ε' by about 10% in this temperature range. This is due to the fact that at low temperatures the values of tan δ and ε' for the PS–benzyl benzoate system are determined to a large extent by the dipolar losses of the second component, i.e. the system is heterogeneous in the vitreous state, and each component has the losses it would have in the pure state. Thus, it has been established that the introduction of a plasticiser has no effect on the temperature or frequency at which d.r. losses are maximum [13,29]. In the highly elastic state plasticising causes a considerable shift of the region of maximum d.e. losses to lower temperatures or higher frequencies, which gives the same results as a decrease in the vitrification temperature.

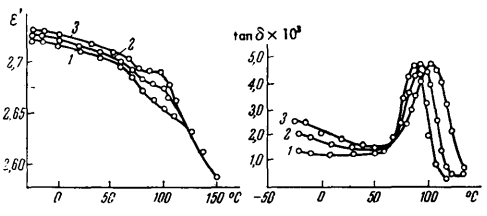


Fig. 13. ε' and tan δ as functions of temperature for polystyrene containing 6.4% benzyl benzoate [2]. 1), 2), 3) 178, 10^3, and 10^4 c/s.

Nowadays the mechanical properties are sometimes improved by grafting a polymer of different chain structure on to the macromolecule, or by making a block-polymer The isolation of the pure graft- or block-polymers from their mixtures with the original substances is sometimes complicated, but fortunately it is not necessary, since the mechanical properties are also improved without it.

The dielectric losses of such technical mixtures of graft- or block-polymers with the homopolymers have been investigated [28]. Fig. 14 shows tan δ as a function of T for poly-(methyl methacrylate), cellulose acetobutyrate (CAB) and mixtures of these substances, containing 25, 60, 80, and 90% MMA. In this case the "grafting" is accomplished by the polymerisation of MMA on the active centres produced in the CAB chain by ultra-violet light. It may be seen from Fig. 14 that at 1 kc/s and 80° PMMA shows a maximum in tan δ. The maximum value of tan δ decreases linearly as the concentration of CAB is increased. Similar data have been found for other polymers which have been modified either during the polymerisation or by a mechano-chemical treatment.

All these data suggest that the values of tan δ and ε' are mainly determined by the concentration of the components. Moreover, each component retains a practically constant relaxation time, which determines the position of the corresponding maximum of tan δ; as is also found with simple mechanical mixtures. Thus, the chemical bonds between the components of a block-polymer, which have a considerable effect on some mechanical properties, have practically no influence on the relationship between tan δ and the temperature and frequency for the separate components.

The orientation of polymeric films and threads gives a considerable improvement in the mechanical properties, and is used for this purpose, for example, in the construc-

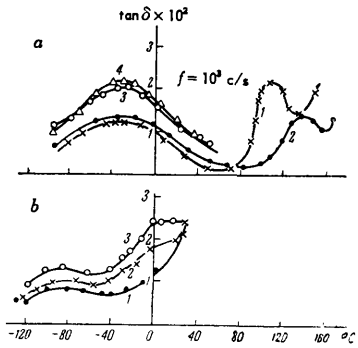


Fig. 15. tan δ as a function of temperature at 10^3 c/s for polyethylene terephthalate (*a*) and nylon (*b*)[30]. *a*: 1), 2), 3), 4) unoriented sample, and samples oriented at 120°, 60°, and 20°. *b*: 1), 2), 3) unoriented sample, and samples oriented in one and two directions.

tion of capacitors. Fig. 15 shows tan δ as a function of temperature for unoriented and oriented films of PET and poly-(hexamethylene adipamide) (nylon)[30]. It will be seen that orientation causes an increase in tan δ in the region of d.r. losses. Moreover, orientation at low temperatures, and in two mutually perpendicular directions, gives a greater increase in tan δ than uniaxial elongation at temperatures above T_{vit}. It may be seen from Fig. 15 that the values of tan δ for oriented PET are lower than for unoriented in the region of d.e. losses, and shifted towards higher temperatures. Similar results have also been found for various amorphous polymers[31].

Finally, Fig. 16 shows the logarithms of the frequencies of maximum d.e. and d.r. losses of certain polymers, plotted against the reciprocal of the absolute temperature[13]. These curves give an idea of the regions of temperature and frequency in which d.r. and d.e. losses are found, and give some information about the mechanism of these losses. D.r. losses are found in the temperature range in which the polymers are vitreous; in this state the polymers have a

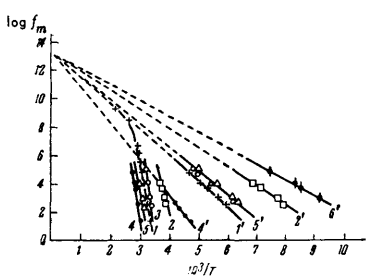


Fig. 16. The logarithm of the frequency of the maximum in tan δ for dipolar-elastic and dipolar-radical losses, as a function of $1/T$ (curve numbers with primes refer to d.r. losses): 1) polymethylacrylate; 2) polypropylacrylate; 3) polychloroethylacrylate; 4) polyvinylacetate; 5) poly-β-chlorovinylpropionate; 6) polyvinylbutyral.

large relaxation time, which is not affected by crystallisation, orientation, copolymerisation, or plasticising. Extrapolation of the curve of $\log f_m = \varphi(1/T)$ for the d.r. losses to $1/T = 0$ gives a frequency of 10^{13}–10^{14} c/s, which is characteristic of processes not related to changes in the short-range order. The activation energy of the d.r. losses can be calculated from the slope of these curves. It lies in the range 5–12 kcal/mole.

All this suggests that the d.r. losses are due to the orientation of small parts of the macromolecule such as separate side groups or a single unit of the chain. The latter probably occurs when a polar radical is firmly bound to the chain (PVC, F-3). In such polymers the relaxation time for d.r. losses is slightly changed by crystallisation or plasticising[13].

D.e. losses occur when the polymer is highly elastic, and the macromolecular chain is very mobile. The relationship between $\log f_m$ and $1/T$ is not linear over a wide range of temperatures (see curve *1* for PMA in Fig. 16). Similar results have been found for other polymers[13]; it is therefore impossible to determine the activation energy of the d.e. losses from the slope of these curves. Earlier, Kobeko[26] had shown that this is characteristic of processes connected with a reorganisation of the short-range order. Thus we may suppose that d.e. losses are due to the thermal motion of relatively large segments of the chain.

Sometimes d.r. and d.e. losses overlap very closely. A typical example is PMMA, for which it is only possible to distinguish the two types of losses in the temperature-dependence of tan δ at very low frequencies, 10–20 c/s. On the other hand, PMA only shows this overlapping at high temperatures and ultra-high frequencies. As Fig. 16 shows, the experimental points corresponding to the maximum of tan δ at frequencies of 10^8–10^9 c/s might refer to the curve for d.e. losses or to that for d.r. losses.

3. ELECTRICAL CONDUCTIVITY AND BREAKDOWN OF POLYMERS

While hundreds of papers have been written on the dielectric losses and polarisation of polymers, comparatively little work has been done recently on their electrical conductivity and breakdown.

The study of the electrical conductivity of polymers is complicated by the fact that the current flowing through a sample under the influence of a constant voltage decreases with time. For example, Fig. 17 shows the logarithm of the current flowing through samples of PE, PS, F-3, F-4, and PMMA as a function of the logarithm of the time for which the constant voltage has been applied[32]. It will be seen that the relationship is a linear one. The value of the current decreases about a thousand times between t = 10 sec and t = 1000 sec for PMMA, F-4 and F-3, so the value of the resistance determined by the usual equation $R_t = V_t/I_t$ is a function of the time.

Fig. 18 shows the volume resistivity of PVC plasticised with 4.5% dioctyl phthalate as a function of temperature, after the voltage has been applied for various periods of time. It will be seen that at temperatures up to about 80° the value of ρ_v increases considerably if the voltage is applied for longer periods, but that this is not the case at higher temperatures[33].

It has been shown by Ioffe[34] that this is due to the production of a large counter-e.m.f. by high-voltage polarisation as the current passes through the sample. This e.m.f.

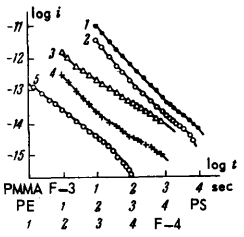


Fig. 17. The logarithm of the current flowing through a polymer as a function of time, with a constant applied voltage, at 20° [32]: 1) PMMA; 2) F-3; 3) PE_{HP}; 4) PS; 5) F-4.

decreases with an increase in the temperature, because of an increase in the diffusion [34]. It has been found for many low-molecular-weight dielectrics that the true value of the resistivity, taking this counter-e.m.f. P into account,

$$R_t = \frac{V_t - P_t}{I_t}$$

is independent of the time.

Unfortunately, all the existing data on the conductivity of polymers are not corrected for the polarisation: they refer either to the value of the current 1 min after the application of the voltage or to the "residual current". In the first case the value obtained is rather arbitrary since any period other than 1 min (suggested by the brothers Curie) could have been used. In the second case, the resistivity obtained refers to the maximum polarisation of the sample.

Information can be found in the literature about the effect of the time for which the voltage is applied, the value of the voltage, the temperature, and other factors, on the conductivity of polymers. But none of these data are corrected for the polarisation e.m.f. Moreover, the data refer to materials prepared in different ways and to different voltages applied for different lengths of time, etc. This makes it difficult to draw any general conclusions from them.

As is well known, the electrical conductivity of a substance depends on the presence in it of weakly bound or free charges, and on the mobility of these charges:

$$\kappa = \sum_i n_i e_i \lambda_i \qquad (2)$$

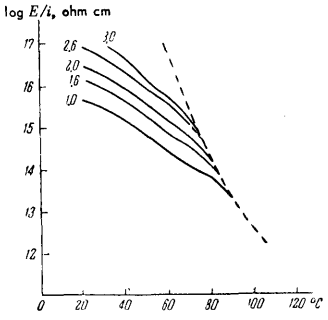


Fig. 18. The resistivity of PVC plasticised with 4.5% dioctyl phthalate, as a function of temperature. The number against each curve is the logarithm of the time [probably in seconds (Ed. of Translation)] for which the voltage was applied [33].

where n_i is the number of ions of a given type per cm^3, e_i their charge, and λ_i their mobility. It follows that factors which change these will affect the conductivity. For example, the composition and chemical structure of a polymer, temperature, and ionising radiation may all have a considerable effect on the concentration and mobility of charge carriers. Thus it has been shown that the presence in polymers of substances of low molecular weight, especially water and plasticisers, causes a considerable increase in the conductivity [35].

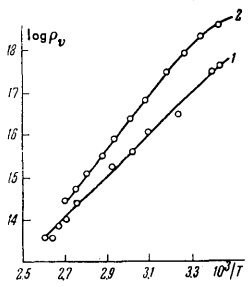


Fig. 19. The logarithm of the resistivity of PE_{LP} as a function of $1/T$: [29]: 1) ash content 0.30%; 2) ash content 0.03%;

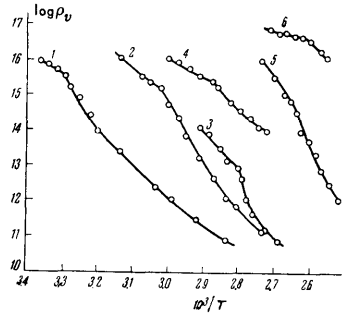


Fig. 20. $\log \rho_v = f(1/T)$ for: 1) polyvinyl acetate; 2) polyvinylbutyral; 3) polyvinylformal; 4) PMMA; 5) polyvinylethylal; 6) polystyrene [36].

As has been mentioned, it is necessary to remove as far as possible from polymers traces of heterogeneous catalysts used in their preparation. These traces may decrease ρ_v.

Fig. 19 shows the logarithm of resistivity of two samples of low-pressure polyethylene taken from the same batch, but purified to different extents, as a function of the reciprocal of the absolute temperature. The first sample contains 0.3% of catalyst residue, the second 0.03%. It will be seen that the decrease in the amount of residue leads to about the same decrease in the conductivity. The temperature has a considerable effect on ρ_v.

Fig. 20 shows the logarithm of resistivity of some polymers as a function of the reciprocal of the absolute temperature [36]. It will be seen that an increase in temperature decreases ρ_v, and that there is a break in the curves near the vitrification temperature.

It has been shown [37] that, for substances of low molecular weight, the change in kinetic properties in the neighbourhood

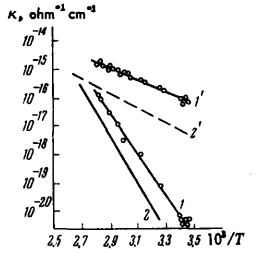


Fig. 21. The electrical conductivity of polyethylene (1) and PMMA (2) as a function of $1/T$: 1'), 2') the corresponding curves for samples irradiated with X-rays (7 to 8 r/min)[38].

of T_{vlt} is related to a sharp increase in the rate of molecular rearrangement. This may perhaps explain the break in the log ρ_v vs. $1/T$ curve, which has been observed for many polymers.

Fig. 21 shows the logarithm of the conductivity plotted against $1/T$ for samples of PE and PMMA before and during irradiation with X-rays of intensity about 7 r/min.[38] It will be seen that ionising radiation causes a considerable increase in the conductivity of polymers: for example, at room temperature the conductivity of PE increases 100 000 times. Similar results have been obtained with other polymers[38]. It is interesting to remark that on exposure to the radiation ρ_v first decreases sharply, and then slowly increases again [39,40]. Moreover, if the sample is irradiated again, it immediately assumes the conductivity it had at the end of the first irradiation. This "conditioning" of insulators is probably due to irreversible changes in the structure of the polymer caused by the irradiation, and may be of practical interest.

Even more than in the case of conductivity, the study of breakdown in polymers is complicated by the influence of factors which do not depend on the nature of the dielectric. For example, the breakdown voltage depends on the thickness and homogeneity of the dielectric, the shape of the electrodes, the atmosphere, and the frequency, wave-form, and duration of the applied voltage. By choosing standard experimental conditions, however, we can obtain a value of the breakdown voltage (E_{br}) characteristic of the polymer in question. For the purpose of establishing a relation between E_{br} and the structure of the polymer the greatest interest lies in the temperature dependence of this quantity. It is also undoubtedly of great practical value. However, we have found only a few papers dealing with this problem in the literature[41,42,43].

It seems to us that the work of Masson is the most interesting[43]. He determined E_{br} for a number of crystalline and amorphous polymers as a function of temperature, and his results are shown in Fig. 22. His measurements were carried out on samples containing a spherical cavity, and with silver or aquadag electrodes. Preliminary experiments showed that the value of E_{br} did not depend on the thickness of the sample, the rate of increase of E, the radius of the cavity, the polarity of the electrodes, or the nature of the atmosphere. It may therefore be concluded that the value of E_{br} found in these experiments is the true dielectric strength. The experiments were carried out at constant voltage.

It may be seen from Fig. 22 that as the temperature is increased, E_{br} does not vary much until the "critical" temperature is reached, after which it decreases sharply. However, in a number of cases (curve *1*, Fig. 22) there is no sharp break in the curve. The range of temperature in which E_{br} falls sharply corresponds to the melting of the polymer (PE, Fig. 22, curve *7*), or to the transition to the highly elastic state. It has been shown that the modulus of elasticity of PE and polyisobutene changes with temperature in much the same way as E_{br}, in the temperature range in which the latter shows its sharp decrease. The broken lines in Fig. 22 represent the variation of E_{br} with temperature, calculated from known values of the modulus of elasticity. There is good agreement between the experimental and calculated curves. It has therefore been concluded that the decrease of E_{br} at high temperature is probably due to the mechanical breakdown of the polymers under the influence of the electrostatic field[41,42].

The values of E_{br} given in this paper are about an order of magnitude higher than the values usually obtained by the standard methods[16]. This is obviously partly due to the quality of the polymer, and partly to the different experimental methods and conditions.

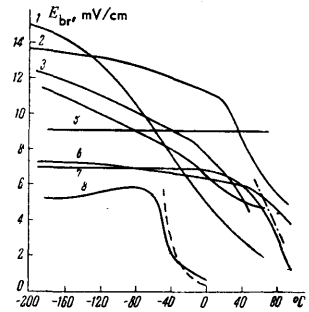


Fig. 22. The breakdown voltage of a number of polymers as a function of temperature[43]: 1) polyvinyl alcohol; 2) PMMA; 3) polyvinylchloroacetate; 4) chlorinated PE_{HP}; 5) mica; 6) PS; 7) PE_{HP}; 8) polyisobutene.

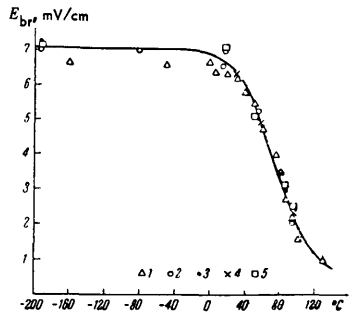


Fig. 23. The breakdown voltage of PE_{HP} as a function of temperature[42, 44-46]: 1), 2), 3), 4) unquenched samples; 5) quenched samples at 3300 Mc/s..

It may also be seen from Fig. 22 that E_{br} is higher for polar polymers than for non-polar ones. For example, comparison of curves *4* and *7* shows that the introduction of 8% of chlorine into polyethylene increases E_{br} to practically twice the value at low temperatures, although at higher temperatures the difference is no longer found.

Fig. 23 shows E_{br} for PE_{HP} as a function of temperature, as determined by a number of workers [42,44-6]. It may be seen from the figure that the values of E_{br} for quenched and slowly cooled samples are the same, i.e. the reduction of the degree of crystallinity from 60% to 50% by quenching has no effect on the breakdown voltage. However, comparison of the variation of the degree of crystallinity and the breakdown voltage with temperature shows that these two relationships are similar, which suggests that a considerable change in the degree of crystallinity would change E_{br}.

It is interesting that, as may be seen in Fig. 23, the values of E_{br} obtained at a frequency of 3.3×10^9 c/s and with direct current fall on the same curve.

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NEW STUDIES ON THE CHEMISTRY OF PROTOACTINIUM

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INTRODUCTION

The existence of an element occupying the position between thorium and uranium in the Periodic System was pre-