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Comparative Study of Mechanical and Dielectric Properties of Glassy Acrylic Polymers Containing 1,3-Dioxane Rings in their Structures

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SUMMARY: A comparative study of mechanical and dielectric relaxation behaviour in the glassy region of some acrylic polymers containing 1,3-dioxane rings in the side chain is reported. Earlier results for similar polymers containing cycloaliphatic rings are used to interpret the results obtained. This study suggests that simple mechanisms based on chair-to-chair inverse conformational transitions are not able to explain in a unified way the responses of these polymers in the glassy region to mechanical and electric perturbation fields.

Introduction

Measurements of the complex dielectric permittivity and the complex relaxation modulus have been used to elucidate the molecular origin of polymer responses to perturbation fields[1,2]. The interest in these studies arises from the fact that physical performance of polymer materials depends on their relaxation behaviour. Both mechanical and dielectric relaxation spectra of polymers present one or more relatively weak absorptions in the glassy state followed by a prominent relaxation associated with the glass-rubber transition[3,4]. In semicrystalline polymers, an additional relaxation associated with motions of crystalline entities of crystalline-amorphous interphase may appear.

Mechanical relaxation spectra of polymers in the liquid state display an additional absorption in the low-frequency region, called the normal mode process, arising from the motion of the whole molecule. However, only dielectric relaxation spectra of polymers containing a dipole moment parallel to the chain contour exhibit normal mode processes. The relaxation time associated with this process scales with the exponent 1 or 3.4 of molecular weight depending, respectively, on whether the chains are unentangled or entangled in the melt[5,6].

Relaxation activity in the glassy state of molecular chains without flexible side groups is believed to arise from local conformational transitions in which some sort of cooperativity

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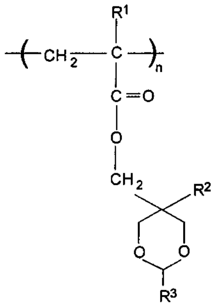
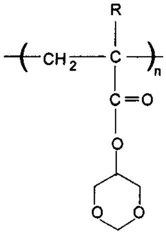
occurs so that the volume swept by the molecular tails during these transitions is negligible. This interpretation explains that the mean relaxation times associated with the subglass absorptions are independent of molecular weight for long chains. On the other hand, the relaxation behaviour of polymers with flexible side groups was attributed to motions in which conformational transitions about the skeletal bonds of these groups intervene.

Acrylic polymers with cyclohexane and 1,3-dioxane moieties in their structure present in most cases a strong subglass mechanical/dielectric dispersion or β-absorption which was attributed to chair-to-chair inverse conformational transitions of the rings[7]. In order to gain a better understanding of the mechanisms involved in the development of this often unusually high mechanical/dielectric activity, it is advisable to perform combined mechanical and dielectric studies on polymers containing these groups as a function of their chemical structure. This was the approach used in this work which reports a comparative study on the mechanical and dielectric relaxation behaviour of the following acrylic polymers in the glassy state:





Code	R^1	R^2	R^3
PAMED	H	Et	H
PAMMD	H	Me	H
PMAMED	Me	Et	H
PAEDP	H	Et	Ph
PAD	R = H		
PMAD	R = Me		

Experimental

Monomers were prepared by dropwise addition of acryloyl (or methacryloyl) chloride to a solution of the corresponding alcohol under stirring and in nitrogen atmosphere. The reaction was carried out in an ice bath for 5 h. The polymers were obtained by radical polymerization of the corresponding monomers in benzene at 60 °C using AIBN as initiator, precipitation with methanol, and drying in vacuo at 70 °C. The glass transition temperatures of the polymers corresponding to the maxima of the peaks associated with this transition at 1Hz are given in Table I.

Dynamic mechanical experiments were performed on 1x10x40 mm specimens using an DMTA Mark-II apparatus of Rheometrics, in flexural form from -140 to 40 °C above the corresponding glass transition temperature of each polymer. Measurements were conducted in multiplexing mode at 1 °C/min and five frequencies (0.3,1,3,10 and 30 Hz) up to 20 °C below the glass transition temperature. For higher temperatures, data were collected in thermal equilibrium to avoid non-equilibrium thermal effects on the glass transition. Owing to their brittleness, the specimens were clamped above the respective glass transition temperatures of the polymers.

Table I Glass transition temperatures

Polymer	T_g (°C)	Polymer	T_g (°C)
PAMED	34	PMAD	132
PAMMD	32	PAEDP	53
PMAMED	126	PCHA	30
PAD	26	PCMMA	78

Dynamic dielectric results were obtained with circular disk pills ca. 24 mm in diameter, using a DEA 2970 dielectric analyzer of TA Instruments at nineteen frequencies from 10^{-4} to 10^2 kHz. The measurements were performed in the same temperature range and utilizing the same thermal history as that used in the mechanical measurements.

Results

Temperature dependences of the dielectric loss for the acrylic polymers used in this study, in the glassy state, are shown in Fig. 1.

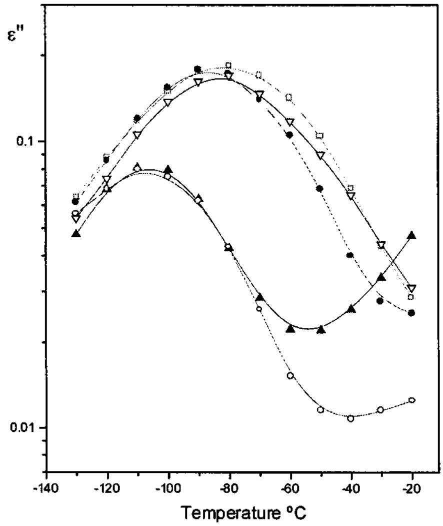


Fig. 1 Dielectric loss permittivity (ε'') of PAMED (□), PAMMD (●), PMAMED (∇), PAD (▲), PMAD (O) at 1 Hz as a function of temperature

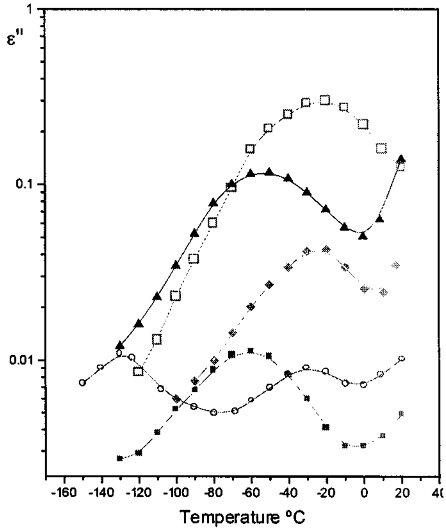


Fig. 2 Dielectric loss permittivity (ε'') of PAMED (□), PAD (▲), PCHA (◆), PCMMA (O), PAEDP (■) at 1 kHz as a function of temperature

Most of the isochrones present a prominent absorption, called β-relaxation. The results corresponding to PAEDP are not included in this figure due to a comparatively low intensity of the subglass relaxation of this polymer. A close inspection of the isochrones obtained at 1 Hz indicates that the β-relaxation of polymers with a CH_2 spacer between the oxygen of the ester group and the 1,3-dioxane ring occurs at a temperature 20 - 25 °C above that corresponding to PAD and PAMD.

The dielectric response of acrylic polymers containing 1,3-dioxane rings is compared with that of poly(cyclohexyl acrylate) (PCHA)[8] and poly(cyclohexylmethyl methacrylate) (PCMMA)[9] in Fig. 2. The isochrones of this figure correspond to 10^3 Hz. An inspection of the curves reveals that the β-relaxations of poly(1,3-dioxan-5-yl acrylate) and poly(1,3-dioxan-5-yl methacrylate) occur at temperatures 20 - 25 °C below that of PCHA. However, the introduction of a methylene group between the ester moiety and the 1,3-dioxane ring places again the β-relaxation in the same position as that of PCHA. On the other hand, the β-relaxation of PAEDP is located 10 - 15 °C below that of PAD. Moreover, the intensity of the relaxation in terms of ε''_{max} follows the order PAMED > PAD > PCHA > PAEDP. This indicates that phenyl substitution not only shifts the peak to lower temperatures, but also decreases its intensity.

Owing to the fact that PCMMA has a methylene group between the oxygen of the ester moiety and the cyclohexane group, it is important to compare the relaxation behaviour of this polymer in the glassy state with that of PCHA and other acrylate polymers containing 1,3-dioxane moieties in their structure. The isochrone corresponding to PCMMA, shown in Fig. 2, exhibits two maxima, one located roughly in the same region of the spectrum as the β-relaxation of PCHA and PAMED, and the other called γ, centred at -130 °C, not observed in the spectra of the other polymers.

Mechanical relaxation spectra of the polymers at 1 Hz, expressed in terms of the tensile loss modulus are shown in Fig. 3. In general, mechanical subglass relaxations of PAMED, PAMMD, PMAMED and PCHA are roughly centred at the same temperatures as the alternative dielectric absorptions. It is worth noting that the β-absorption of PCHA is significantly narrower than the absorptions of the other polymers. Moreover, though the dielectric behaviour differs, the intensity of the β-relaxation of PCHA is similar to that of PAMED, PAMMD, and PMAMED. The location of the β-relaxation in the spectra of polymers without a methylene spacer between the oxygen atom of the ester moiety and the 1,3-dioxane ring, specifically PAD and PMAD, is shifted 20 - 25 °C below that of PCHA. At the same time, the β-relaxation of PAEDP has lower intensity and is located 10 to 15 °C below that corresponding to PAD and PMAD. This behaviour is similar to that observed in the dielectric relaxation spectra of these polymers and is also in good agreement with mechanical data reported earlier by Heijboer[10].

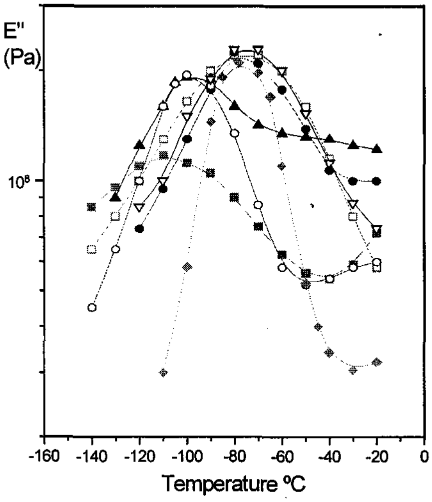


Fig. 3 Tensile loss modulus of PAMED (□), PAMMD (●), PMAMED (∇), PCHA (◆), PAEDP (■), PAD (▲), PMAD (O) at 1 Hz as a function of temperature

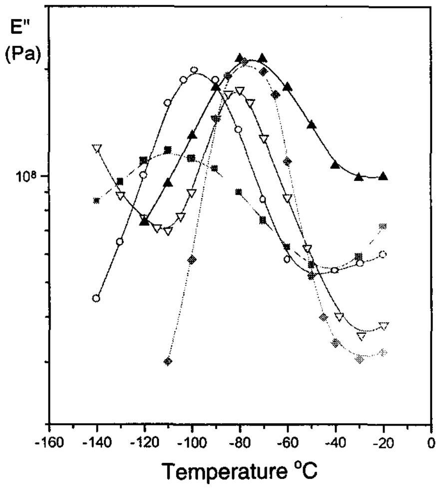


Fig. 4 Tensile loss modulus of PAEDP (■), PCHA (◆), PCMMA (∇), PAMMD (▲), PMAD (O) at 1 Hz as a function of temperature

The subglass relaxations corresponding to PCMMA[11] are compared in Fig. 4 with those of PMMAD, PCHA[8], PMAD and PAEDP. It can be seen that, though the intensity of the β-relaxation of PCMMA is slightly lower than that of PCHA, it is located in the same temperature region.

Discussion

The temperature dependence of both mechanical and dielectric relaxations follows the Arrhenius behaviour and the pertinent activation energies are given in Table II.

The locations of mechanical relaxation peaks at 1 Hz, and those of dielectric relaxations at both 1 Hz and 10^{3} Hz are also shown in this table. With the exception of PAEDP, the activation energies associated with mechanical relaxation are roughly 1.2 - 2.5 kcal mol^{-1} above those of the dielectric relaxations. The peak maximum of the mechanical subglass relaxation for any of the polymers under study is located at a temperature 4-11 °C below that of the corresponding dielectric relaxation. An important difference between the mechanical and dielectric spectra is that the intensities of mechanical relaxations show only a weak dependence on the chemical structure in contrast to what occurs with dielectric relaxations whose intensities can vary from 10^{-2} for PAEDP to ca. $3x10^{-1}$ for PAMED. Accordingly, the dielectric activity is strongly dependent on the chemical structure.

Table II Activation energies and location of maxima

Polymer	Mechanical		Dielectric		
	E_a (kcal mol^{-1})	T_{max} (^oC) 1 Hz	E_a (kcal mol^{-1})	T_{max} (^oC) 1 Hz	T_{max} (^oC) 1 kHz
PAMED	12.5	-74	10.0	-78	-25
PAEDP	7.2	-106	8.8	-	-60
PAMMD	11.1	-74	9.6	-80	-20
PAD	10.8	-94	9.6	-105	-53
PMAD	10.7	-95	9.3	-106	-51
PMAMED	13.1	-75	10.1	-81	-21
PCHA	14.2	-78	11.9	-82	-25
PCMMA	12.5	-82	11.8	-	-30

Though most acrylic polymers with cyclohexane or 1,3-dioxane moieties in the side chains present a strong subglass mechanical dispersion region centred in the vicinity of –80 °C at 1 Hz, this dispersion disappears if the cycloaliphatic rings in these polymers are replaced by benzene rings[12]. Moreover, it is worth noting that the mechanical relaxation spectra of polymers plasticized with cyclohexyl derivatives, such as dicyclohexyl phthalate, also show that relaxation[13]. Similar dispersion appears in the dielectric relaxation spectra of polymers containing cycloaliphatic groups[14,15]. The fact that the dispersion is not observed when either the chair or the inverse chair of the cyclohexyl group are identical, or when the steric hindrance impedes the chair-to-chair transition, led Heijboer[7] to postulate that flipping motions in cycloaliphatic moieties are responsible for the relatively strong mechanical and dielectric subglass absorptions of these polymers.

Molecular motions of model compounds of the side groups of poly(2-chlorocyclohexyl acrylate) (PCCHA)[16], PAMED[17] and PAEDP[18] were earlier investigated by using molecular dynamics (MD). Simulations carried out on the dynamics of 5-acetoxy-5-ethyl-1,3-dioxane[17], a model of PAMED, indicate that the time spent by the ester grouping in the equatorial and axial conformations is nearly the same, the energy barrier associated with the chair-to-inverse-chair conformational transition being nearly 8.0 kcal.mol^{-1}. This energy is ca. 1 kcal.mol^{-1} below that reported for 1,3-dioxane. According to these results, conformational transitions occurring in the 1,3-dioxane ring in the glassy region could give rise to the subglass absorption. However, this hypothesis may not be supported by the results of the MD simulation carried out in *cis/trans*-5-acetoxymethyl-5-ethyl-2-phenyl-1,3-dioxane (HEDPA)[18], a model compound of PAEDP, as will be discussed below.

HEDPA presents two configurations, trans and cis. The former configuration is taken as that one in which the ester grouping and the phenyl group are either eq-eq or ax-ax; accordingly, the positions of these groups are either ax-eq or eq-ax in the cis configuration. The calculations show[18] that the fractions of eq-eq and ax-ax conformations in the trans configuration at 30 °C are, respectively, 0.98 and 0.02. The conformational transition eq-eq → ax-ax in this configuration has an energy barrier of 6.8 kcal.mol^{-1} while the barrier of the reverse transition, ax-ax → eq-eq, is only 3.4 kcal.mol^{-1}. The results also show that the life-time at 300 K of the eq-eq conformation is 18 ns while that of the ax-ax one is only 0.14 ns.

In the cis configuration[18], the fraction of conformations in which the ester grouping is in axial and the phenyl group in equatorial also amounts to ca. 0.98 while the fraction of the alternative conformation (the ester grouping equatorial and the phenyl group axial) is approximately 0.02. The conformational transition ax-eq → eq-ax has a barrier of 7.0 kcal.mol^{-1} while the eq-ax → ax-eq of only 3.8 kcal.mol^{-1}. It should be pointed out that the MD simulations give a good account of the equilibrium and dynamic dielectric properties of the model compounds of PCCHA, PAMED and PAEPD[16-18] .

The fact that the barrier energy associated with the chair-to-inverse-chair conformational transition in the 1,3-dioxane ring of the two configurational isomers of PAEDP seems to be similar to that of PAMED suggests that both polymers should exhibit similar subglass absorptions if the dielectric activity in the glassy state is produced by chair-to-chair conformational transitions. The fact that this is not the case, as the isochrones of Figs. 2 and 4 show, seems to rule out the hypothesis that simple flipping motions in the 1,3-dioxane ring cause the ostensible subglass absorptions displayed in the relaxation spectra of some of these polymers. Rather, the absorptions may arise from conformational transitions occurring in the side groups. The bulkiness of the phenyl group in PAEDP presumably impedes the type of motions that develop an important dielectric activity appearing in the spectrum of PAMED. The lower activation energies of both mechanical and dielectric relaxations of PAEDP in comparison with those of PAMED suggest that the motions producing the subglass relaxations are less complex in the former polymer than in the latter.

The cooperativity of the molecular motions involved in the development of the β-relaxation can be analyzed in terms of the width of the peak. For this purpose, a quantitative comparison between the parameter *m* values appearing in the Fuoss-Kirkwood[19] equation is meaningful. As it is well known, the Fuoss-Kirkwood equation is useful to represent dielectric as well as dynamic mechanical data in a relaxational zone according to $\Gamma'' = \Gamma_{\max} \sec h m \ln \frac{f_{\max}}{f}$ where Γ is the loss permittivity as well as the loss modulus. In the former equation, *m* is the parameter indicating the width of the relaxation peak, being $m = 1$ for a Debye relaxation.

In Table III, the values of parameter *m* and those of the loss maxima together with the calculated relaxation strength $\Delta\varepsilon$ are given.

Table III Parameters appearing in Fuoss-Kirkwood equation and strength of the relaxations

Polymer	m	ε''_{max}	$\Delta\varepsilon = 2\varepsilon''_{max}/m$
PAMED	0.28	0.21	1.50
PAEDP	0.45	0.01	0.04
PAMMD	0.34	0.21	1.23
PAD	0.36	0.11	0.61
PMAD	0.40	0.11	0.55
PMAMED	0.33	0.21	1.27
PCHA	0.40	0.04	0.20
PCMMA	0.18	0.01	0.11

From the inspection of this table, we conclude that the width and the strength of the relaxations follow trends similar to the intensity, suggesting that the cooperativity of the mechanisms involved in the relaxation increases from PAEDP to PAMED. In other words, except for PAEDP, the polymer with a substituted phenyl group, and for PCMMA, where the motions of the lateral chain give rise to two relaxations, the β-peak due to 1,3-dioxane seems to be more influenced by the environment than that corresponding to the cyclohexane ring.

It is worth noting that the intensity and location of the β-relaxation is similar for PAMED and PMAMED, the two polymers the only structural difference of which is methyl group in the repeating unit. Since the methyl group severely reduces the conformational mobility of the repeating unit of the latter polymer, a similar relaxation behaviour of both polymers suggests that coupling motions of the side group and local motions of the main chain may not intervene in the development of the β-absorption.

The dielectric relaxation behaviour of PCMMA shows a striking difference from that of PCHA. Thus, whereas the latter polymer presents a relatively well developed single peak, PCMMA presents two relatively weak peaks, one located at the same temperature as that of

PCHA and the other located 100 °C below. It is clear that PCMMA has more degrees of freedom in the lateral chain than PCHA. Obviously, both polymers should exhibit the same relaxation spectrum if only flipping motions of the cycloaliphatic rings were responsible for the subglass relaxations.

Summing up, this study shows that the considerable mechanical and dielectric activity exhibited by the spectra of polymers with cyclohexane and 1,3-dioxane rings in their structure cannot exclusively be attributed to simple chair-to-chair conformational transitions as it is usually done. More efforts involving MD simulations are required to elucidate the molecular origin of the subglass relaxations of these polymers.

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