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Polymer 40 (1999) 971–981

polymer

On the viscoelastic and plastic behaviour of methylmethacrylate-*co*-*N*-methylglutarimide copolymers

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Received 25 November 1997; revised 23 February 1998; accepted 27 April 1998

Abstract

Both viscoelastic and plastic properties were investigated on random copolymers of methylmethacrylate (MMA) and *N*-methyl-glutarimide (GIM) in the range 0–76 mol%. All the measurements were performed on samples quenched from the melt in order to break free from physical aging effects. Dynamic mechanical experiments were performed at very low deformation and temperatures ranging from − 150°C up to the glass transition temperature (T_g) region. Increase in GIM amount improves the thermomechanical stability of the copolymers, as revealed by the increase of both T_g and α relaxation temperature. In the β relaxation region, the E'' loss peak first decreases in amplitude with increasing GIM content and then broadens further and finally spreads out till the onset of the α peak at the largest GIM amounts. A quantitative analysis of the β relaxation phenomena was performed by considering the loss compliance J'' instead of the loss modulus E''. It turns out that in the low temperature range (−80°C–0°C) the mechanical damping associated with the MMA motions is stronger for MMA–GIM than for MMA–MMA linkages; in addition, the mechanical damping associated with the motions of the GIM units is very low. By contrast, in the high temperature range (30°C to about 100°C), the mechanical damping associated with the MMA motions drops with increasing GIM amount, whereas a significant damping coming from the GIM units is observed. These results suggest that the β relaxation would mainly consist of MMA isolated motions at low temperature and of cooperative motions at higher temperature, involving the MMA units at GIM amounts lower or equal to 58 mol% and the GIM units at higher GIM content. The stress–strain curves were determined at low strain rate ($2 \times 10^{-3}\ s^{-1}$) and temperatures ranging from −120°C to T_g. Analysis of the plastic deformation region shows that the yield stress decreases with increasing GIM amount at low temperatures. The opposite trend shows up on the high temperature side of the β relaxation, where strain softening peaks at intermediate GIM amounts. As a plausible explanation, the cooperative β motions, whenever they exist, are suspected to be responsible for the decrease of both yield stress and strain softening. These conclusions agree well with those of a previous study on methylmethacrylate-*co*-maleimide copolymers. They are also consistent with our earlier identification of the microdeformation mechanisms involved in the stretching of methylmethacrylate-*co*-*N*-methylglutarimide thin films. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Polymethylmethacrylate; Methylmethacrylate copolymers; *N*-methyl-glutarimide

1. Introduction

During the past decades, numerous studies have been devoted to such mechanical properties of glassy polymers as elasticity, anelasticity, yielding, crazing, shear banding and fracture. However, it remains to some extent hazardous to search for suitable relationships between these properties and the chemical structure of the polymeric materials. Some pioneering papers were published with the aim of elucidating the macroscopic mechanical properties on the basis of polymer chain motions [1–4]. They were the starting point for further theoretical models [5–7] and experimental evidences [8,9].

Our laboratory also carried out some studies, at the molecular level, on the mechanical behaviour of amorphous thermoplastic polymers. Fourier-transform infrared measurements allowed Theodorou et al. [10] and Xu et al. [11] to give the experimental proof of the occurrence of an increase in the amount of higher-energy conformations at the yield point, regardless of the fact that they are gauche conformations in the case of the conventional polystyrene or trans conformations in the case of amorphous isotactic polystyrene. In recent years, we embarked in studies involving several series of methylmethacrylate-based random copolymers containing a comonomer in variable amounts

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PII S0032-3861(98)00337-1

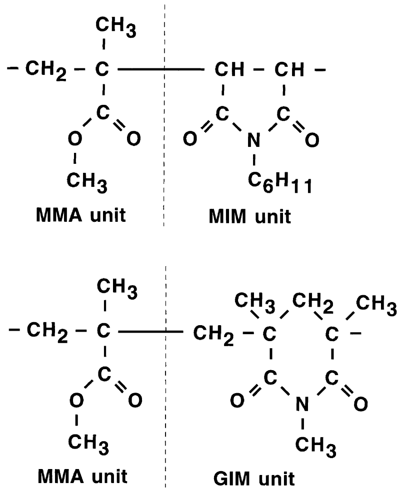

Fig. 1. Chemical formulae of the copolymer units: top, methylmethacrylate-*co*-*N*-cyclohexylmaleimide (MIM); bottom, methylmethacrylate-*co*-*N*-methylglutarimide (GIM).

[12–18]. Three types of comonomer were investigated, namely: (1) styrene, in the composition range 0–100 mol% [12–14,18]; (2) *N*-substituted maleimides in the range 0–25 mol% with cyclohexyl, phenyl and isopropyl substitutes [14,17,18]; and (3) *N*-methylglutarimide in the range 0–76 mol% [15–17]. In the methylmethacrylate–maleimide series, so-called MIM (Fig. 1), the presence of the maleimide rigid rings was shown to be responsible for increases in both glass transition temperature, T_g, and molecular mass between entanglements, M_e. In the methylmethacrylate–styrene series, it was observed that the presence of styrene is accompanied by rapid decreases of both T_g and mean monomeric friction coefficient [13], and by a substantial increase in Me. In both series of materials, addition of comonomer led to marked increase in strain softening, as revealed by the stress–strain curves [18] and to embrittlement of the materials, as deduced from thin film deformation experiments [14]. It was recently proposed to explain these effects by putting emphasis on the role of the β relaxation motions of the MMA units [18]: a condition for strain softening to be negligible and shear banding to develop in these series would be that the molecular motions involved in the high-temperature side of the secondary relaxation region are precursors of the α relaxation processes which occur in the T_g region. In addition, the β motions of the MMA units, which involve a coupling of the motion of the ester side-group with main-chain conformational changes [19], do present a cooperative character with each other over a sufficiently large spatial scale in the high-temperature part of the broad β relaxation peak. Addition of maleimide or styrene comonomer is shown to prevent this condition to be fulfilled as the result of the decoupling of the α and β relaxation processes.

In this context, the purpose of the study of the glutarimide-*co*-methylmethacrylate copolymers, so-called GIM (Fig. 1), is to check whether the above observations and findings are confirmed by the study of another series of MMA-based random copolymers. There are many factors which make the series of GIM copolymers attractive. First, the GIM copolymers are available over a much larger composition range than the MIM copolymers, as the result of both the refined syntheses performed by one of us [20] and the availability of additional samples from Röhm & Haas Ltd. Then, in contrast with our previous determinations for the MIM series, the sensitivity of M_e to the glutarimide comonomer amount is very weak, which means that the influence of this factor can be neglected while examining the fracture behaviour. And finally the GIM copolymers may offer an attractive alternative to the polymethylmethacrylate homopolymer in certain applications, because of their improved thermomechanical stability and their ability to develop shear deformation zones upon stretching, at least in the case of the glutarimide-rich thin films [16].

In the present paper, we will concentrate on both viscoelastic and plastic behaviour of the GIM copolymers. Data relative to their fracture behaviour will be the subject of a forthcoming publication [21,22].

2. Experimental

2.1. Materials

Designation, origin, chemical composition and molecular weight characteristics of the materials are given in Table 1. The characters following the acronym GIM in the entry ‘designation’ stand for the mol% of glutarimide units in the copolymers, as deduced from Fourier-transform infrared spectroscopy measurements in chloroform. In all the materials under study, the amount of acrylic acid or anhydride residual functions was found to be less than 0.6 wt% and neglected, as a first approximation, in the composition calculations. Synthesis of the Enichem’s GIMs was based on the reaction of methylamine with PMMA. Details on the reaction conditions may be found in Ref. [20]. With the exception of GIM8, these samples were prepared from the so-called PMMA b. The other GIMs under study were kindly supplied by Röhm and Haas Ltd and their original designation is recalled in brackets. Weight and number average molecular weights, $\overline{M}_w$ and $\overline{M}_n$, respectively, were determined by g.p.c., and are given in Table 1 in PMMA equivalents. The polydispersity $I = \overline{M}_w/\overline{M}_n$ of all the materials is close to 2. It was also checked by ^{13}C n.m.r. that all the copolymers are actually distributed at random and that the tacticity of the two homopolymer parents (PMMA a and PMMA b) is roughly the same (typically: 58% ± 1% rr, 36% ± 1% mr, 6% ± 1% mm).

2.2. Sample preparation

Before use, the polymer powders were dried under vacuum at 110°C for 24 h, in order to eliminate water

Table 1
Characteristics of the materials

Designation	Origin	Glutarimide amount (mol%)	$\overline{M_n}$ (g mol^{-1})	$\overline{M_w}$ (g mol^{-1})
PMMA a		0	66 000	119 000
PMMA b	Enichem	0	37 000	77 000
GIM4	Enichem	4.0	37 000	75 000
GIM8	Enichem	8.0	138 000	330 000
GIM21	Enichem	21.0	37 000	80 000
GIM36	Röhm and Haas (Paraloid HT 510)	36.1	37 000	76 000
GIM58	Röhm and Haas (Kamax T 240)	58.5	50 000	110 000
GIM63	Enichem	63.0	20 000	54 000
GIM76	Röhm and Haas (Kamax T 260)	75.7	49 000	106 000

which might be associated with the carbonyl groups. Then, sheets were prepared from the powders by compression-molding under vacuum at a temperature around $T_g + 60°C$, followed by a progressive cooling down through the glass transition region. Samples of suitable dimensions for mechanical testing were cut from the sheets by using a Krautkramer Isomet saw. The samples were stored under vacuum at $T_g + 5°C$ for 15 h and finally cooled rapidly to room temperature. As a consequence, one can assume that all the samples, quenched from the melt, are free of physical aging effects which are known to affect the molecular relaxations [18].

2.3. Dynamic mechanical analysis

Dynamic mechanical properties of these materials were determined using a servohydraulic viscoelasticimeter MTS 831.10 operated in tensile mode. Sample size was of 75 (direction of testing) × 15 × 3 mm. The samples were subjected to a static strain of 40 μm on which a sinusoidal strain of ± 20 μm was superimposed; as a consequence, the deformation was very low, never exceeding 0.1%. The measurements were performed from $-80°C$ to $T_g + 15°C$, if applicable. Using this piece of equipment, the driving sinusoidal frequencies can be fixed at values in the range 0.04–70 Hz. However, most of the results reported in the present study are just relative to the frequency 1.2 Hz.

Experiments yielded directly the storage modulus E', the loss modulus E'', and the damping tan δ by using a commercial routine available on the equipment. The values of storage compliance, $J' = E'/(E'^2 + E''^2)$, and of loss compliance, $J'' = E''/(E'^2 + E''^2)$, were derived by automatic computer calculations.

2.4. Characterization of yield point and plastic deformation

Stress–strain curves were obtained from mechanical experiments in compression by using a MTS 810 hydraulic testing machine. Samples were 3 × 3 mm^2 in section and 7 mm in height (direction of compression). A fresh sample was used for each experiment, and the recorded curves were an average of at least three separate measurements. Although the deformation can be easily imposed at rates ranging from 5×10^{-4} to 3×10^{-1} s^{-1}, most measurements were performed at the strain rate 2×10^{-3} s^{-1}. Usually, the temperature range covered by the experiments was from $-70°C$ to T_g. In certain cases, the lowest temperature of the measurements was just the ambient temperature, owing to the excessive brittleness of the samples.

A usual analysis of the stress–strain curves consisted in the determination of both yield stress, σ_y, and plastic flow stress, σ_{pf}, defined as the value of maximum load and as that of minimum load encountered at larger deformation, respectively. The amplitude of plastic softening, *SA*, was defined as the average difference between σ_y and σ_{pf}, extracted from three separate experiments at least.

3. Results and discussion

3.1. Viscoelastic analysis of the molecular mobility

3.1.1. Glass transition region

Figs 2 and 3 show the temperature dependence of the storage modulus E' and of the loss modulus E'', respectively, determined at the frequency 1.2 Hz for the materials under study. It is obvious from Fig. 2 that the addition of the

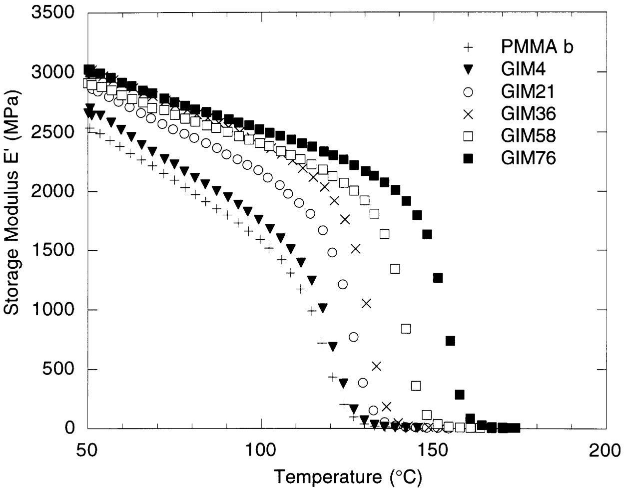

Fig. 2. Storage modulus E' at 1.2 Hz versus temperature in the glass transition region.

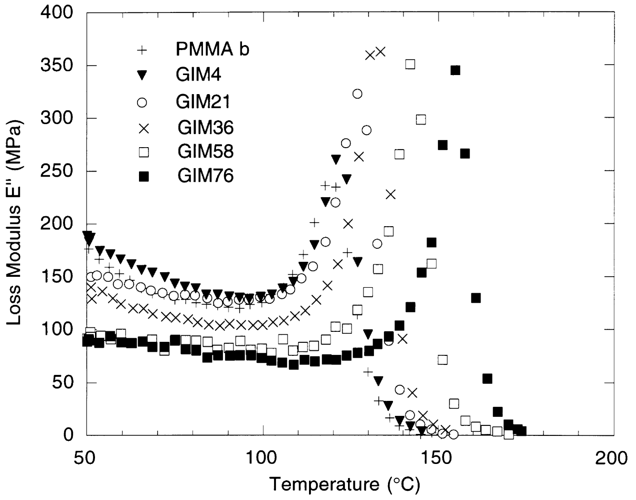

Fig. 3. Loss modulus E'' at 1.2 Hz versus temperature in the glass transition region.

comonomer glutarimide improves, as expected, the thermomechanical stability of the materials, as compared with polymethylmethacrylate homopolymer. E'' data (Fig. 3) yield the values of T_α (1.2 Hz), conventionally defined as the temperature at which the loss modulus E'' passes through a maximum at the frequency 1.2 Hz. These values are compared in Table 2 with the glass transition temperatures, T_g, taken as the onset of the differential scanning calorimetry traces, recorded at a heating rate of 10°C min^{-1}. Although more marked than in previous evaluations on similar systems [12,14,18], the gap between T_α and T_g remains very small. Besides, as shown in Fig. 4, plots of ($T_{\alpha\mathrm{GIM}}-T_{\alpha\mathrm{PMMA}}$) and ($T_{g\mathrm{GIM}}-T_{g\mathrm{PMMA}}$) as a function of the comonomer amount are identical within the experimental error. Comparison of these data with those obtained in the MMA–cyclohexylMIM series [18] shows that the increase in T_g with increasing comonomer content is much weaker in the GIM series than in the MIM series. This is in qualitative agreement with the idea that the glutarimide units are more rigid than the MMA units but less rigid than the maleimide ones, mainly as the result of the presence of an additional CH_2 group adjacent to the ring (Fig. 1).

3.1.2. Secondary relaxation region

Typical traces of E'', tan δ, and J'' (1.2 Hz) versus temperature of the GIM copolymers are given in Fig. 5a–c, respectively, in the secondary relaxation region. At the first sight, Fig. 5a reveals that the amplitude of the broad β peak (which overlaps in part the α peak for pure PMMA and GIM 21) decreases with increasing glutarimide amount. This means that the damping associated with the β relaxation is mainly due in GIM21 and GIM36 to motions of the MMA units. This behaviour is consistent with the observations reported in the case of the MMA–maleimide copolymers [18]. In the case of the glutarimide-rich copolymers (GIM 58 and GIM 76), the shape of the mechanical relaxation is changing: the β peak, of quite small amplitude, broadens still further and spreads out till the onset of the α peak.

Table 2
Values of T_α (1.2 Hz) and T_g in the GIM series

Designation	T_α (1.2 Hz) (°C)	T_g (°C)
PMMA b	119	112
GIM4	120	115
GIM21	127	121
GIM36	134	127
GIM58	147	140
GIM63	144	144
GIM76	158	151

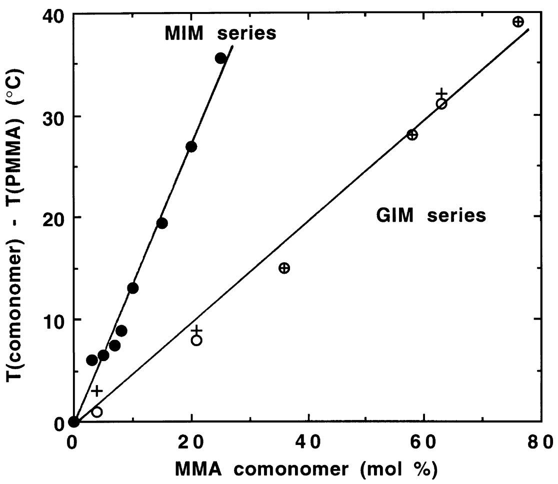

Fig. 4. Effect of the comonomer amount on the improvement of the thermomechanical resistance of PMMA: $T_{\alpha\mathrm{GIM}}-T_{\alpha\mathrm{PMMA}}$ (open circles); $T_{g\mathrm{GIM}}-T_{g\mathrm{PMMA}}$ (+); $T_{g\mathrm{cyclohexylMIM}}-T_{g\mathrm{PMMA}}$ (filled circles).

That being the case, it is never possible to determine with confidence the position of the maximum of the β peak and, therefore, to analyse, as usual [18], its composition dependence. This conclusion holds for tan δ (Fig. 5b) and J'' (Fig. 5c) traces as well. The alternative route we propose in this study is to take benefit from the agreement between the measured values of J'' in the secondary transition region and those calculated by simple addition of the contributions of the various groups to the J'' response of a copolymer [23]. This approach sounds good when applied (as here) to the secondary transition region, it would be misleading in the glass transition region, i.e. at higher cooperation of motions of the monomer species.

Let $J''(\mathrm{GIM}x)$ and $J''(\mathrm{PMMA})$ be the loss compliances of the GIM copolymer containing the mole fraction $x/100$ of glutarimide units, and of the homopolymer PMMA, respectively. Assuming that the MMA motions in the copolymer are unaffected by the presence of comonomer, the contribution to $J''(\mathrm{GIM}x)$ of the MMA units would be:

$$\left(1-\frac{x}{100}\right)J''(\mathrm{PMMA})$$

Therefore, the contribution of the glutarimide units to

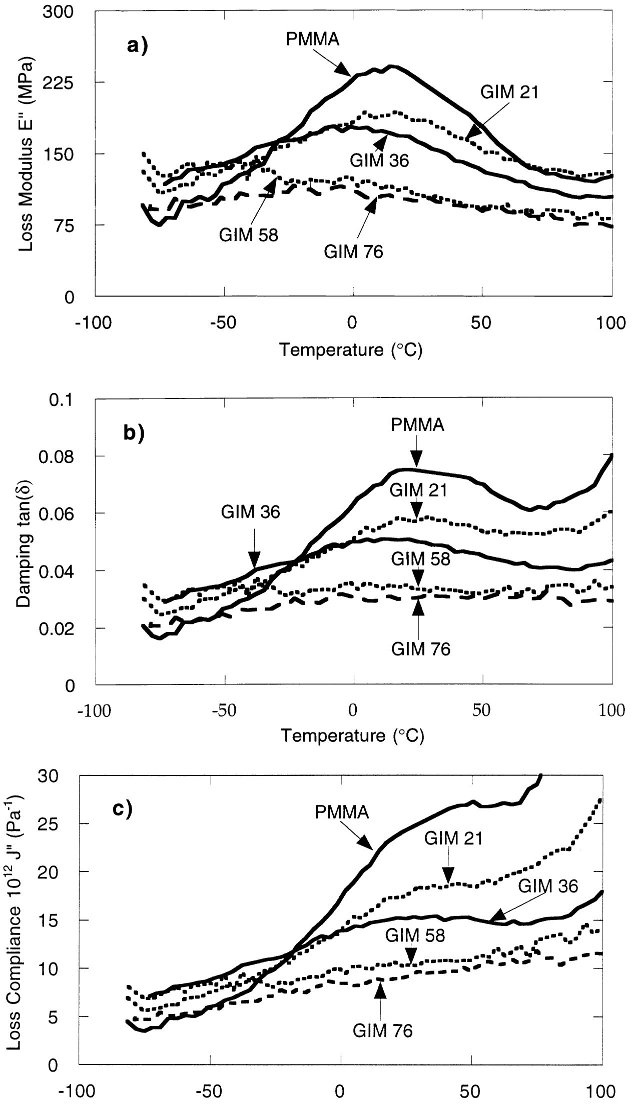

Fig. 5. Temperature dependence of the viscoelastic characteristics at 1.2 Hz of some typical GIM copolymers in the secondary relaxation region: plot (a), loss modulus; plot (b), tan δ; and plot (c), loss compliance.

J''(GIMx) could be defined as:

$$J''(\mathrm{GIM}x) - \left(1 - \frac{x}{100}\right) J''(\mathrm{PMMA})$$

or, after normalization for the number of GIM units:

$$\Delta J''_{\mathrm{G}}(\mathrm{GIM}x) = \frac{100}{x}\left[J''(\mathrm{GIM}x) - \left(1 - \frac{x}{100}\right) J''(\mathrm{PMMA})\right] \tag{1}$$

In the same way, the normalized contribution of the methylmethacrylate units to J''(GIMx) would be:

$$\Delta J''_{\mathrm{M}}(\mathrm{GIM}x) = \frac{100}{100 - x}\left[J''(\mathrm{GIM}x) - \frac{x}{100} J''(\mathrm{GIM100})\right]$$

Unfortunately, J''(GIM100) is unknown since the polyglutarimide homopolymer cannot be synthesized. As a first approximation, let us consider that:

$$J''(\mathrm{GIM100}) = \Delta J''_{\mathrm{G}}(\mathrm{GIM76})$$

Therefore, $\Delta J''_{\mathrm{M}}$(GIMx) would be given by the relation:

$$\Delta J''_{\mathrm{M}}(\mathrm{GIM}x) = \frac{100}{100 - x}\left[J''(\mathrm{GIM}x) - \frac{x}{100}\Delta J''_{\mathrm{G}}(\mathrm{GIM76})\right] \tag{2}$$

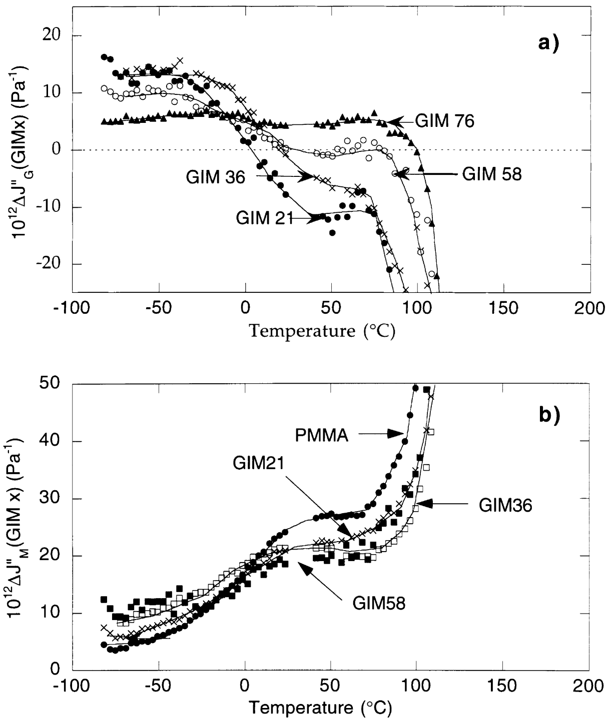

Fig. 6. Normalized contributions of the GIM and MMA units to the copolymer loss compliance in the secondary relaxation region: plot (a), $\Delta J''_{\mathrm{G}}$(GIMx) versus temperature for $x = 21$, 36, 58 and 76; and plot (b), $\Delta J''_{\mathrm{M}}$(GIMx) versus temperature for $x = 0$ (pure PMMA), 21, 36 and 58.

Systematically, Eqs. (1) and (2) were used to derive the values of $\Delta J''_{\mathrm{G}}$(GIMx) and $\Delta J''_{\mathrm{M}}$(GIMx) at any temperature and comonomer amount. Fig. 6a and b illustrate the influence of both temperature and composition on $\Delta J''_{\mathrm{G}}$(GIMx) and $\Delta J''_{\mathrm{M}}$(GIMx), respectively. From the inspection of these figures, it turns out that the effects of composition changes strongly depend on whether the domain of low temperatures (typically less than 0°C) or the domain of higher temperatures is under consideration.

In the low temperature range, $\Delta J''_{\mathrm{G}}$(GIMx) presents very low values (Fig. 6a), which means that the motions of the GIM units are scarce or characterized by a very low mechanical damping. In addition, $\Delta J''_{\mathrm{G}}$(GIMx) increases with increasing amount of MMA units in the copolymer, which is indicative of the fact that the presence of MMA units leads to an increase in damping per glutarimide unit. Similarly, $\Delta J''_{\mathrm{M}}$(GIMx) increases with increasing amount of GIM units in the copolymer (Fig. 6b). Thus, the presence of GIM units leads to an increase in damping per

Table 3
Percentages of the different types of triads as a function of copolymer composition (calculations performed on the basis of a random distribution of the GIM and MMA units)

Copolymer	Triad percentage			
	GIM–GIM–GIM	MMA–GIM–GIM (GIM–GIM–MMA) MMA–GIM–MMA	MMA–MMA–MMA GIM–MMA–MMA (MMA–MMA–GIM) GIM–MMA–GIM	
GIM76	43.9	32.1	1.4	22.6
GIM63	25.0	38.0	5.1	31.9
GIM58	19.5	38.5	7.4	34.6
GIM36	4.7	31.3	26.2	37.8
GIM21	0.9	20.1	49.3	29.7
GIM8	0.1	7.9	77.9	14.1
GIM4	0.01	4.0	88.5	7.5

methylmethacrylate unit. The two aforementioned conclusions unambiguously show that the increase in damping on the temperature range under consideration involves MMA–GIM linkages. The mechanical damping is stronger for MMA–GIM linkages than for MMA–MMA linkages (whereas it is very weak for GIM–GIM linkages). Consideration of a couple of units (of same or different chemical nature) rather than individual units is supported by the high probability of finding such couples in our copolymers (Table 3). This motion assignment is also consistent with the conformational energy calculations on GIM copolymers [24] which demonstrate that the MMA ester motion is less impeded by glutarimide than by methylmethacrylate neighbours. On the other hand, we have at the moment no means to ascertain the molecular origin of the GIM–GIM mechanical damping, as the pure polyglutarimide is not available.

Let us consider now the temperature range 0°C–100°C, which is sufficiently below T_g so that the J'' analysis remains unquestionnable. it appears clearly (Fig. 6a) that the copolymers GIM21 and GIM36 exhibit negative values of $\Delta J''_G$(GIMx). Therefore, the assumption that the MMA motions are the same in the copolymers and in the PMMA homopolymer leads to overestimate the MMA contribution while calculating the damping of a GIM unit. As a matter of fact, any MMA unit in the vicinity of a GIM unit exhibits in this temperature range a weaker damping than in the vicinity of other MMA units. This conclusion is corroborated by the fact that $\Delta J''_M$(GIM21), $\Delta J''_M$(GIM36), and $\Delta J''_M$(GIM58) are lower than J''(PMMA) (Fig. 6b). It is worth pointing out that this feature is the opposite of that we observed in the low temperature range. A simple reason accounts for this behaviour: when the temperature increases at a given frequency, sub-T_g motions of the MMA units in PMMA homopolymer shift from an isolated to a cooperative character, implying some coupling of the main-chain conformational changes over a certain spacial scale, as shown by n.m.r. [19]. As in the case of maleimide copolymers, presence in the chain of rather rigid glutarimide units makes these cooperative motions less likely to occur and, as a consequence, diminishes the relevant damping.

In the case of the glutarimide-rich copolymers considered in the high temperature part of the secondary relaxation (0°C–100°C), positive values of $\Delta J''_G$(GIMx) are found, as illustrated in Fig. 6a on the example of GIM 76. Thus, GIM units are now able to promote some damping. Possible explanations might be that the increase in temperature is accompanied by the gradual development of either mechanically-active isolated motions of the GIM units as the result of fluctuations in their neighbouring, or cooperative motions involving both GIM and MMA units. A more reliable alternative is that the GIM units are involved in GIM–GIM type cooperative motions along the GIM sequences. The latter hypothesis is supported by several observations. Firstly, as can be seen in Table 3, the probabilty to find a GIM–GIM–GIM triad is much greater in GIM 76 than in all the other copolymers; in contrast, the probability to find a triad involving GIM–MMA linkages does not vary very much when copolymer composition is modified. Secondly, the gap existing between $\Delta J''_G$(GIM76) and $\Delta J''_G$(GIM21) is quite large (Fig. 6a). And finally, it is worth observing in Fig. 6a that the upper temperature for which $\Delta J''_G$(GIMx) keeps a positive value increases markedly with increasing glutarimide amount.

It is also interesting to compare the sub-T_g loss compliance behaviour of a GIM copolymer of intermediate glutarimide amount with that of a MIM copolymer of similar composition. Owing to the data available in both series, the comparison was achieved by considering GIM21 and revisiting the literature data relative to CMIM15 [18]. For this purpose, it is sufficient to collate the temperature dependence of J''(GIM21) and J''(CMIM15) with that of J''(PMMA), normalized to the actual amount of MMA units in the copolymer, namely $0.79 \times J''$(PMMA) and $0.85 \times J''$(PMMA), respectively. Fig. 7a just corroborates our above findings on GIM 21: the damping of this material is greater than that of PMMA at low temperature, in the region of the isolated MMA motions, and weaker at higher temperature, in the region of the cooperative sub-T_g motions. More interesting is the inspection of Fig. 7b, relative to CMIM15. The compliance analysis of the data

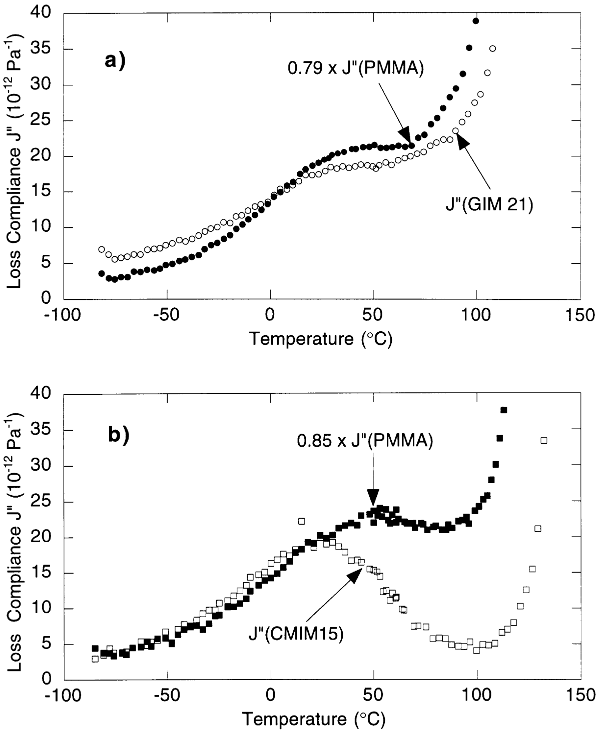

Fig. 7. Comparison of the loss compliance behaviour of MMA-*co*-GIM and MMA-*co*-cyclohexyl MIM copolymers in the secondary relaxation region: plot (a), J''(GIM21) (open circles); and 0.79 × J''(PMMA) (filled circles) versus temperature; and plot (b), J''(CMIM15) (open squares) and 0.85 × J''(PMMA) (filled squares) versus temperature.

is in excellent agreement with the earlier analysis based on E'' data [18]: low amounts of CMIM units are sufficient to hinder the MMA cooperative motions and decouple completely the β and α relaxation processes. Fig. 7b does not provide any indication that the presence of the maleimide ring might make easier the MMA isolated motions: indeed, the traces of J''(CMIM15) and of 0.85 × J''(PMMA) are identical within the experimental error in the low temperature region. This is the first feature which differentiates the effect of the maleimide unit from that of the glutarimide unit in this intermediate composition range. Direct comparison of Fig. 7a and b reveals a second peculiarity of the maleimide unit: its capacity to decouple the β and α relaxation processes is much greater than that of the glutarimide unit. These two differences can be explained by the differences of rigidity of the MIM and GIM units, as already pointed out in the previous paragraph for accounting for the observed differences in T_g behaviour.

Summarizing, our description of the mechanically active motions involved in the β relaxation of the materials under study is based on the occurrence at low temperature of isolated motions of the MMA units which are favoured by the neighbouring of GIM units, and then, at higher temperature, on the possible occurrence of cooperative motions, either along the MMA sequences at low glutarimide amount of the copolymers, or along the GIM sequences at high enough glutarimide amount; in the intermediate composition range, the cooperative motions are assumed to be impeded at the time scale of the experiments, in the same way as previously shown in the case of the maleimide copolymers, but less efficiently.

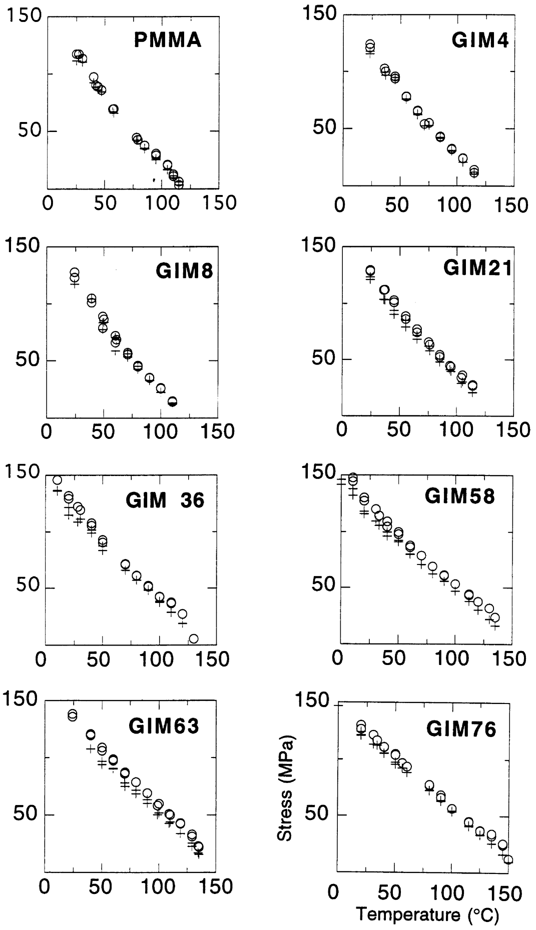

Fig. 8. Yield stress (circles) and plastic flow stress (crosses) versus temperature (strain rate: 2 × 10^{-3} s^{-1}) for PMMA and the various GIM copolymers.

3.2. Analysis of the plastic behaviour

This study is based on the inspection of the stress–strain curves obtained at a strain rate of 2 × 10^{-3} s^{-1}. As usual, these curves (not shown) exhibit an elastic behaviour at low deformation, then an anelastic (non linear) behaviour before the yield point, σ_y, which is observed at deformations depending on temperature in the range 0.04–0.09, and finally a possible strain softening, *SA*, before the plastic flow, characterized by the stress σ_{pf} which is observed at deformations systematically smaller than 0.15. Because the levels of deformation are quite small, engineering stresses and strains are considered, as a first approximation, instead of the true stresses and true strains. The experimental values of σ_y and σ_{pf}, determined at various temperatures for the different GIM copolymers under study, are graphically given in Fig. 8. Analysis of these data will result from the consideration of: (1) the temperature dependences of σ_y and

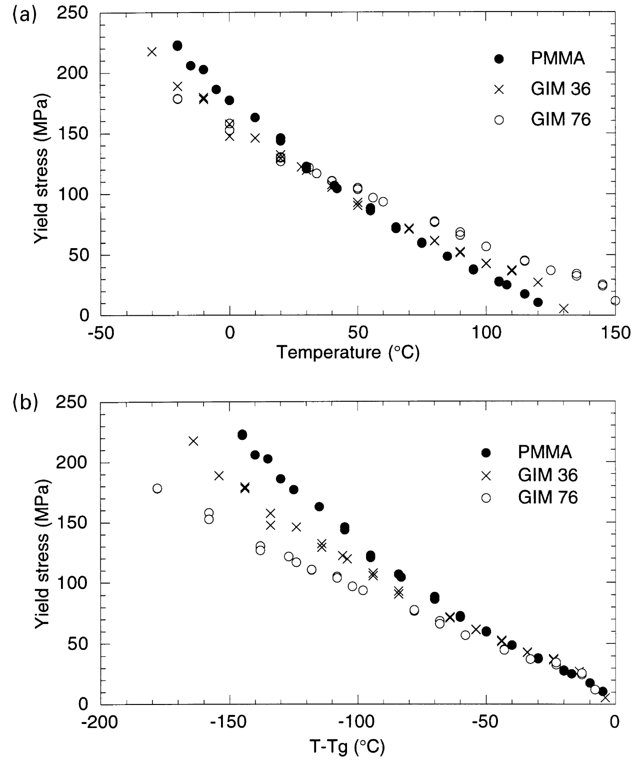

Fig. 9. Yield stress of PMMA, GIM36 and GIM76 versus temperature (plot a) and versus ($T - T_g$) (plot b).

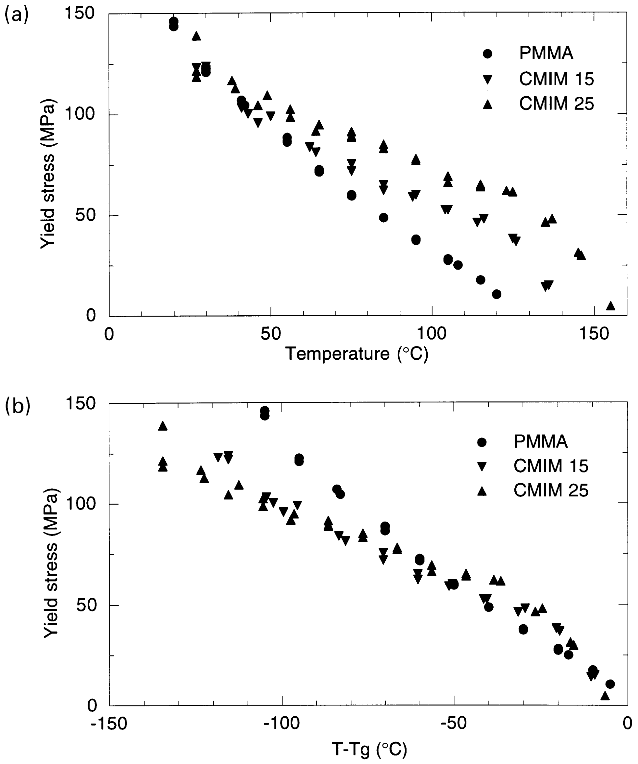

Fig. 10. Yield stress of PMMA, CMIM15 and CMIM25 versus temperature (plot a); and versus ($T - T_g$) (plot b).

σ_{pf}; and (2) the values of strain softening amplitude $SA = \sigma_y - \sigma_{pf}$ as a function of the glutarimide comonomer amount.

For sake of clarity, Fig. 9a concentrates on the plots of σ_y versus temperature for the two extreme and one intermediate compositions, namely PMMA, GIM36, and GIM76. The three curves intersect around room temperature, meaning that σ_y increases with increasing GIM amount at high temperatures and, in the other hand, decreases with increasing GIM amount at low temperatures. Whereas the latter statement is probably undisputable, the former result seems to be mainly a consequence of the differences in glass transition temperature of the materials under consideration. As shown in Fig. 9b, indeed, this conclusion is no longer validated, except very close to T_g, when plotting σ_y as a function of ($T - T_g$). Comparison of these trends with those already reported for the maleimide copolymers [18] and replotted in Fig. 10 is instructive. Although the general behaviour is similar, the comonomer effect is enhanced in the CMIM series, especially at temperatures approaching T_g.

A classical argument to try to justify the sensitivity to comonomer nature and amount of the σ_y observed at low temperatures would be to consider the Young's modulus values, E, and to assume that the higher the modulus, the larger the σ_y value is. From a qualitative viewpoint, the yield stresses (Fig. 9b and Fig. 10b) rank in the same order as the moduli (Table 4) in both GIM and CMIM series. By the way, a crude explanation for the observed decrease of modulus with increasing comonomer content can be given. The cyclic structure of the MMA comonomer (GIM and CMIM as well) may restrict the packing of the MMA units: indeed, the MMA ester functions are known to be oriented perpendicular to the main-chain segments [25] whereas the comonomer cycles tend to adopt a position in the main-chain plane. Quantitatively, if the values of σ_y are governed by the modulus only, then identical values of σ_y/E should be

Table 4
Young's moduli of PMMA and selected copolymers in the low temperature range

Material	Young's modulus (MPa)		
	at $T - T_g = -100$°C	at $T - T_g = -120$°C	at $T - T_g = -140$°C
PMMA	3170	3650	4000
GIM36	3120	3400	3650
GIM76	2980	3230	3460
CMIM15	2480	2750	2960
CMIM25	2200	2500	2750

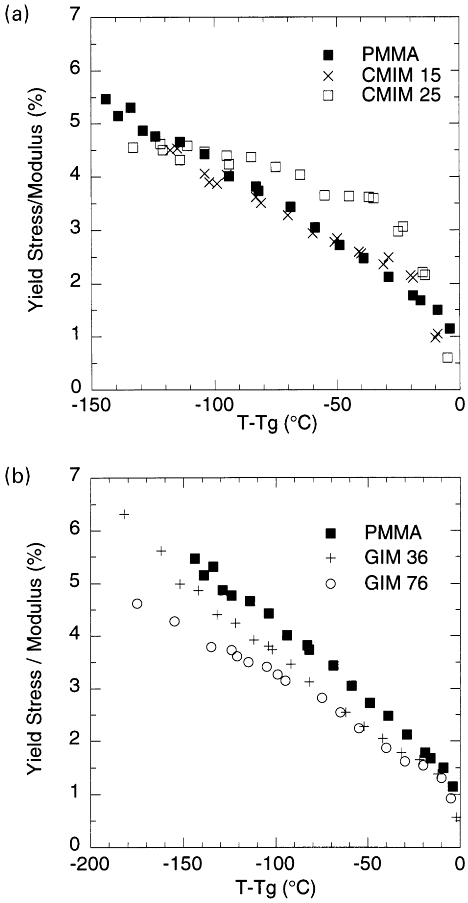

Fig. 11. Ratio of yield stress over Young's modulus versus ($T - T_g$): plot (a) PMMA, CMIM15 and CMIM25; and plot (b) PMMA, GIM36 and GIM76.

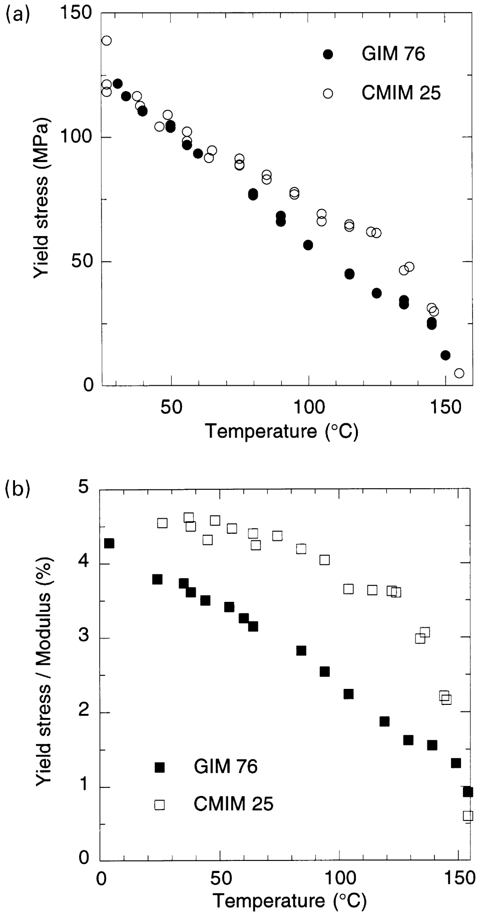

Fig. 12. Comparison of the yield behaviour of GIM76 and CMIM25: plot (a) yield stress versus temperature; and plot (b) ratio of yield stress over Young's modulus versus temperature.

expected whatever the material under consideration. Such situation is encountered for the CMIM series at sufficiently low temperatures (Fig. 11a).

By contrast, it is not observed for the GIM copolymers: over a broad temperature range, one finds (Fig. 11b): σ_y/E (PMMA) $>$ σ_y/E (GIM36) $>$ σ_y/E (GIM76). This just means that the influence of molecular mobility is stronger on yield stress than on modulus when increasing the GIM amount. As pointed out in our previous paper [18], this observation suggests that motion cooperativity is still present along the main-chain: it would involve GIM and MMA units in the case of GIM 36, and mainly GIM units in the case of GIM 76. In addition, the plots of σ_y/E versus ($T - T_g$) are quite linear for both GIM76 and PMMA, in agreement with the fact that the involved cooperative β motions may be regarded as α precursors.

At the end of this discussion of the σ_y values, one might wonder whether our conclusions are affected by the choice, to some extent arbitrary, of ($T - T_g$) as the comparison scale in Fig. 9b, Fig. 10b and Fig. 11. With this respect, inspection of the yield stress behaviour of GIM76 and CMIM25 (Fig. 12) is interesting since these two systems exhibit quite similar values of T_α (1.2 Hz) (158°C and 160°C, respectively) and, therefore, can be compared directly without any curve shift. As a validation of the use of the ($T - T_g$) scale, comparisons made from Fig. 9b, Fig. 10b and Fig. 11 in one hand and from Fig. 12 in the other hand lead to the same conclusion, namely higher σ_y values for CMIM than for GIM.

Analysis of the plastic flow stress values is simpler than that of the yield stress values. As recalled previously [18], the large scale cooperative motions, which are at the origin of the mechanically-induced plastic flow, are identical to those responsible for the thermally-induced glass transition phenomenon. This conclusion holds whatever the temperature of the mechanical test is. Therefore, the profiles of σ_{pf} versus ($T - T_g$) are linear, within the experimental error, over a very broad temperature range, and that, whatever the nature of the comonomer, either GIM (Fig. 13a) or CMIM (Fig. 13b). In these figures, the differences in amplitude of σ_{pf} which are observed among the materials could, at least qualitatively, be assigned to the same differences in chain packing as discussed above for explaining the σ_y behaviour at low temperature.

Variations of the strain softening amplitude, *SA*, as a function of comonomer amount and temperature are just the resultant of the effects on σ_y and σ_{pf}. Missing the

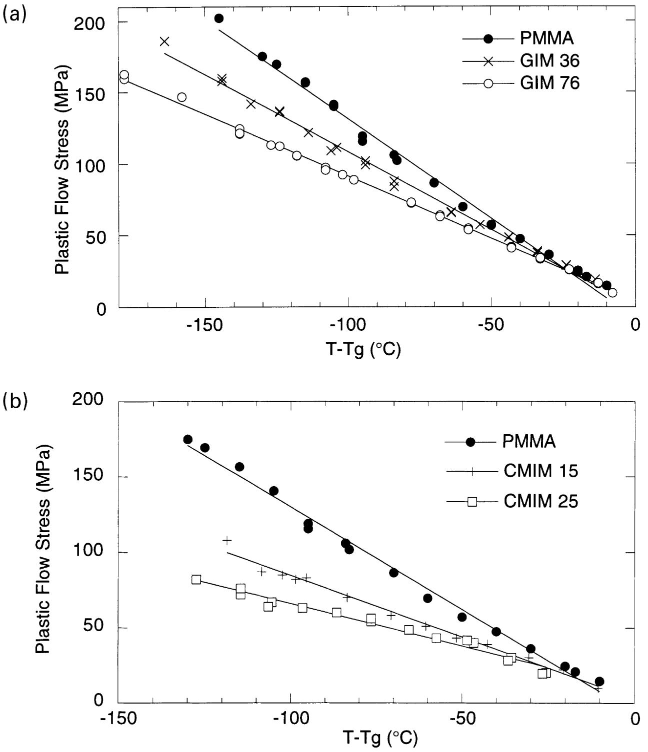

Fig. 13. Plastic flow stress versus ($T - T_g$): plot (a) PMMA, GIM36 and GIM76; and plot (b) PMMA, CMIM15 and CMIM25.

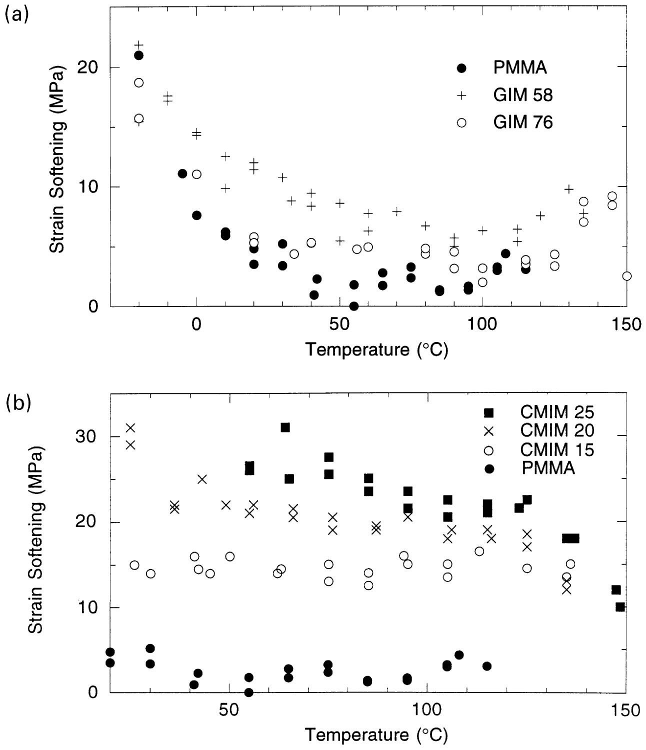

Fig. 14. Strain softening amplitude versus temperature: plot (a) PMMA, GIM58 and GIM76; and plot (b) PMMA, CMIM15, CMIM20 and CMIM25.

temperature region close to T_g, which may be sensitive to physical aging effects, the profiles of *SA* as a function of temperature in the GIM series exhibit two separate regions (Fig. 14a): (1) at low temperature, *SA* increases with decreasing temperature; and (2) at higher temperatures (but well below T_g), *SA* remains constant within the experimental error and takes the value so-called SA_0. Qualitatively, these features are identical to those previously reported for the MIM series [18] and recalled in Fig. 14b. The main difference between Fig. 14a and b is that the strain softening is weaker in the glutarimide series than in the maleimide series. The same conclusion holds for the SA_0 values (Fig. 15). In addition, Fig. 15 shows that SA_0 increases monotonically over the restricted range of maleimide compositions available, whereas it passes through a maximum for a certain glutarimide amount.

This set of data supports the idea, proposed in our previous publication [18], that strain softening amplitude would tend to vanish when the molecular motions which are involved at the yield point are quite similar to those responsible for the flow process, i.e. when we are dealing with cooperative β motions precursors of the α process. This situation is actually expected to occur in pure PMMA and GIM76. On the other hand, strain softening is detected as long as the α motions are decoupled from the β motions. This situation, unambiguously observed in the MIM series, is supposed to hold also in the GIM series (GIM21 to GIM58). The effect would be much less marked than in the MIM series just because the decoupling power of the glutarimide units is less than that of the maleimide rings.

In conclusion, all the above measurements, as well as the earlier data relative to the maleimide-*co*-methylmethacrylate copolymers, are consistent with the idea that the condition for strain softening to be negligible in this series of vinylic polymers would be that the molecular motions involved in the high-temperature side of the secondary relaxation region are precursors of the α relaxation processes. This means, for the MMA copolymers under

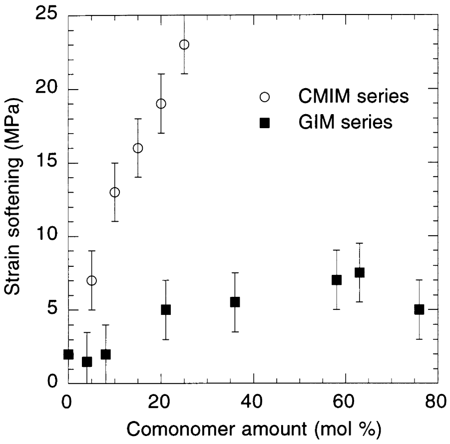

Fig. 15. Plateau value of strain softening, SA_0, versus copolymer composition in GIM and CMIM series.

consideration, that the high temperature β main-chain motions do exhibit the same cooperative character as the α transition motions, however, restricted over a shorter spatial scale.

This approach can also be confronted with benefit to the previously published results on the deformation micromechanisms in GIM copolymers [16]. It turns out that in addition to the entanglement density, which is considered to be a fixed parameter in this series of materials, changes in the yielding behaviour influence the competition between shear deformation and crazing in thin films. Crazing clearly dominates at compositions for which the α-β motion coupling is dramatically reduced. On the other hand, shear microdeformation zones are unambiguously detected in pure PMMA and GIM-rich materials, for which cooperative β motions were evidenced. It will be shown in a companion study, to be presented in a forthcoming publication [21,22], that the mobility behaviour has also a clear repercussion on the macroscopic fracture behaviour of the materials. A pending question is to know whether these findings are also suitable for non-vinylic polymeric materials: this is the subject of other studies, which are currently in progress in our laboratory.

Acknowledgements

This research was supported by Elf-Atochem, France. We especially acknowledge this company for its interest in this study and for the PhD grant gratefully given to one of us (L.T.). Thanks are also due to the ‘Groupe Français des Polymères’ which awarded its ‘Prix de Thèse 1996’ to L.T. for a contribution which is presented here in part.

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