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The ESC behaviour of a toughened PMMA after exposure to gamma radiation

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Abstract This work is a sequence of a previous one where we investigated the influence of gamma radiation dose on environmental stress cracking (ESC) of a conventional poly(methyl methacrylate) (PMMA) (Sousa et al. Polym Degrad Stab 92:1465, 2007). In that work, we observed that low doses of gamma radiation intensified the ESC effects, but on higher doses the gamma radiation effect was predominant over the stress cracking. The present work describes a similar study, but using a toughened PMMA (t-PMMA). The polymer was submitted to gamma radiation doses up to 100 kGy, and then tested to ESC susceptibility through tensile and relaxation tests. Two different types of active fluids were used: ethanol (an aggressive one) and ethylene glycol (a moderate liquid stress cracking agent), based on absorption results. A synergistic effect between ESC and radiation degradation was noted, with a substantial decay in mechanical properties when these two effects were present. The ethanol action caused dendritic pattern formation in the fracture surfaces of t-PMMA, as revealed by scanning electron microscopy.

Introduction

The polymeric materials have to be carefully designed and processed to withstand the harsh conditions of use and hence to have a maximum lifetime. Procedures like better controlled synthesis, proper design and processing and the use of adequate additives are constantly being considered as appropriate ways to achieve the success with both commodity and engineering polymers [1, 2]. The exposure environment is one of the main concerns related to the lifetime of polymers. In most situations, the complexity of the various environment elements makes the degradation mechanisms and, therefore, the prediction of effects a really difficult task.

Among the various causes for polymer failure the environmental stress cracking (ESC) continues to be a preferred area of investigation because there is still lack of information on the understanding of the mechanisms involved in this type of phenomenon. Besides, a high percentage of failure of polymer products is related to ESC [3, 4]. ESC may take place in moulded products when a certain combination of aggressive fluid and a mechanical stress is acting upon the material. This results in surface crazes or cracks that eventually lead to a catastrophic fracture. Even ductile polymers like acrylonitrile butadiene styrene copolymer (ABS) and polycarbonate can suffer from stress cracking [5, 6]. Several different methods of experimental investigation have been used to evaluate stress cracking degradation, most of them based on traditional procedures [4], which have been recently added by some new ones, like electronic microscopy techniques and others [5, 7, 8].

The combined action of stress cracking and other source of degradation have been investigated in detail by some of the present authors. In general, we have shown that a previously degraded polymer is more susceptible to the stress cracking effects. This was shown in several situations, like the photodegradation of polystyrene [9], high-impact polystyrene (HIPS) [10] and polycarbonate [11], as

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well as in the degradation by gamma radiation of PMMA [7]. This is still an area that requires further investigations since the mechanisms involved in the determination of potential effects of degradation and stress cracking are not fully understood yet. Indeed, the theme has a very practical appeal for the high possibility of a previously degraded product come into contact with an aggressive fluid. This work, therefore, is an extension of the previous ones, bringing new results on the effects of stress cracking in products that had been previously exposed to γ-radiation. In this time a toughened grade of PMMA (t-PMMA) was exposed to different doses of gamma radiation and ESC susceptibility in two different liquids was evaluated. In a toughened polymer the deformation mechanism, and therefore the failure mode, is rather different from the neat polymer, giving more insights on the stress cracking failure.

Experimental

The t-PMMA was supplied by Resarbrás (Brazil) as tensile test bars (ASTM D-638), with thickness of approximately 3 mm. The t-PMMA is a blend based on 10% of PMMA (01DHLEP grade) and 90% an acrylic/elastomer copolymer (01DHEC grade). The samples were obtained by injection moulding, processed using a temperature profile of 190–205 °C (barrel) and 35 °C (mould).

The specimens were irradiated in IPEN-CNEN/Brazil using a gammacell ^{60}Co source of gamma irradiation with an applied dose rate of 3.01 kGy/h. The applied doses were 25, 50 and 100 kGy. All tests done with irradiated samples were also done with non-irradiated ones for comparison.

The molar mass variation due to gamma radiation was monitored by viscometry tests using an Ostwald viscometer, at 25 ± 0.1 °C, with chloroform as a solvent. For each dose the intrinsic viscosity was obtained by extrapolating the linear fitting of reduced viscosities measured in four different concentrations to zero concentration [7]. The comparison parameter used here was the intrinsic viscosity because of the unavailability of Mark-Houwink constants of the blend for molar mass determination.

Tests of liquid absorption were done by immersing the tensile bars in the environments and then weighting them periodically using a balance with a precision of 0.1 mg. The liquid excess on samples surfaces was removed before measuring using an absorbent tissue.

The stress cracking resistance was evaluated through tensile and relaxation using a Lloyd LR10 K tensile-testing machine in a constant temperature room set at 23 °C. The tensile tests were done using different crosshead speeds: 1, 10 and 100 mm/min. In relaxation tests, the pre-load used was 400 N (equivalent to 18.6 MPa). For both tests the liquids used were analytical grades of ethanol and ethylene glycol. The methodology was the same of the previous work [9].

The fracture surfaces of samples after tensile tests were inspected by scanning electron microscopy (SEM) with a Jeol JSM-6360 equipment after the specimens were sputtered with gold to avoid charging problems.

Results

The stress/strain behaviour of t-PMMA is different from the conventional PMMA (Fig. 1), with higher elongation and lower tensile strength and modulus. The mechanism of toughening involves firstly the cavitation of the rubber particle embedded in the polymer matrix due the stressing and then the either the shear yielding or volumetric crazing takes place, leading to an extensive deformation up to fracture [12, 13]. The toughening mechanism is based on the stress concentration close to the rubber particles. This creates several fronts of crazing/shear yielding that result in a higher ultimate deformation and, hence, a higher toughness [14].

t-PMMA degradation by gamma radiation

The molar mass, here represented by intrinsic viscosity, reduced with increasing gamma radiation dose, as shown in Fig. 2, following the same trend observed with PMMA, as a consequence of the predominance of chain scission reactions [7, 15]. The rubbery phase in t-PMMA could have resulted in a different type of behaviour, like crosslinks formation, but this was not observed. The chemical similarity between the PMMA and the t-PMMA might have results in a similar type of behaviour. The decay in intrinsic viscosity of Fig. 2 is relatively small with a

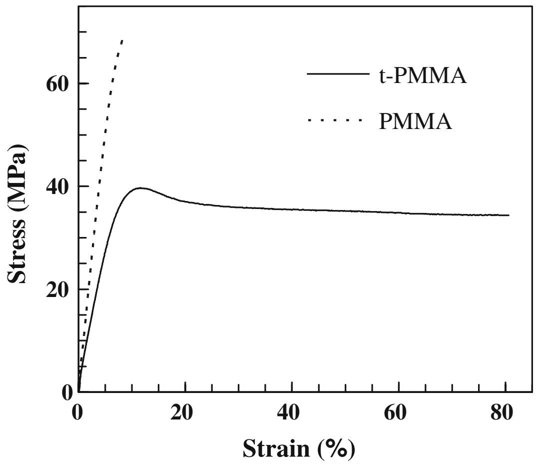

Fig. 1 Stress/strain curves of t-PMMA and PMMA

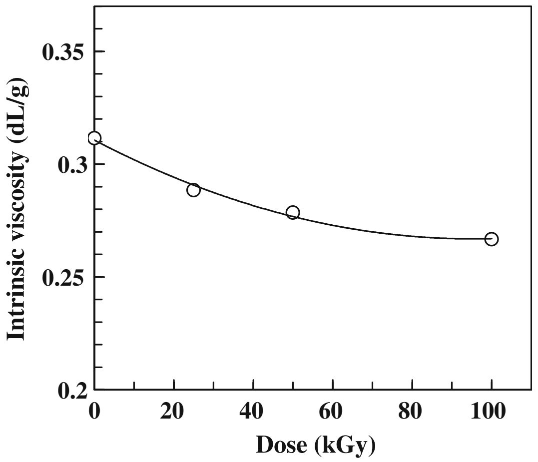

Fig. 2 Intrinsic viscosity of t-PMMA as a function of γ-radiation dose

maximum difference of less than 15% in relation to the unexposed polymer.

Another evidence of radiation action is the yellowing of t-PMMA with increasing dose (see Fig. 12 later on in this article), which can be due the others degradation mechanisms, like the formation of conjugate double bonds or trapped free radicals. Lin and Lee [15] showed that when gamma irradiated PMMA was heated or exposed to a solvent the original sample colour was recovered, and this was argued to be due radical recombination.

Liquid absorption

Ethanol

The results for ethanol absorption by t-PMMA are shown in Fig. 3. The rate of liquid uptake increased with the radiation dose in a similar fashion to what was observed with PMMA using the same liquid and environment conditions [9], with over 30% of weight gain after 90 h. This type of behaviour is a result of a high affinity between the polymer and the liquid. In addition, it is also shown in Fig. 3 that γ-irradiated t-PMMA had higher levels of weight gain, and this might have an influence in the stress cracking behaviour since a higher absorption is an indicative of a better affinity between the polymer and the fluid. Actually, liquid absorption experiments are largely used as a complementary indication of ESC susceptibility [6, 16, 17].

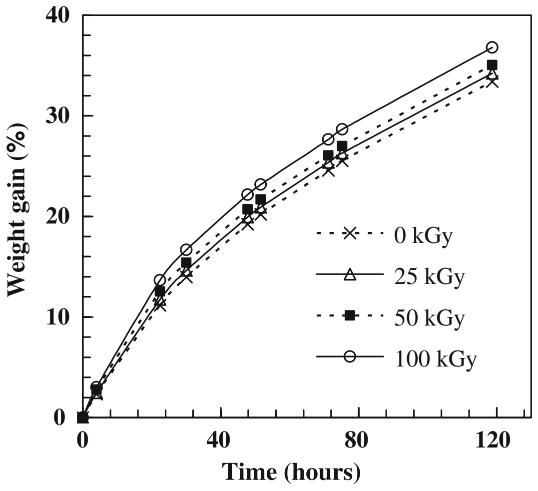

Fig. 3 Ethanol absorption as a function of immersion time for samples exposed to different gamma radiation doses

Ethylene glycol

The results for ethylene glycol absorption are shown in Fig. 4. Different from the behaviour with ethanol, there was no mass gain during the test. The curves registered a slight mass reduction followed by the stabilization after 400 h. Arnold [17] obtained similar results with PMMA under ethylene glycol and attributed the initial mass loss to the extraction of some mobile components from PMMA. The inability of liquid absorption was also related to the relatively high molecular size and chemical dissimilarity in relation to the polymer.

ESC of irradiated t-PMMA under tensile tests

The experiments shown in this section were conducted under three different cross-head speeds: 100, 10 and 1 mm/min. Besides the viscoelastic effect, these conditions allowed different contact times between the polymer and the active fluid. Most of the results will be shown for maximum elongation, since this was the most sensitive property to the effects of stress cracking and gamma irradiation. In some instances, a large decay in tensile strength was also noted. The Young's modulus, however, had practically

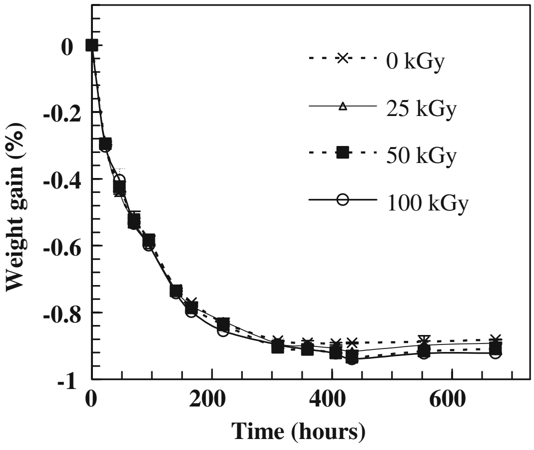

Fig. 4 Ethylene glycol absorption versus immersion time for samples exposed to different gamma radiation doses

no change with γ-exposure and stress cracking, a similar result obtained with PMMA under the same conditions [7].

Figure 5a shows the data of maximum elongation of irradiated t-PMMA under the various environments: without liquid (atmospheric conditions), ethanol and ethylene glycol. This was done with a crosshead speed of 100 min/min. The elongation at break showed just a slight variation with the increasing doses when tests were done without liquid. This was due to a relatively small change in molar mass by degradation, as shown by the results of intrinsic viscosity of Fig. 2). When tensile testing was conducted in the presence of ethanol or ethylene glycol a large reduction in this property was observed. For the unexposed material, the maximum elongation was reduced from 68% (without liquid) to 19% and 40% under ethanol and ethylene glycol, respectively. This later observation suggests that a synergist effect occurred when two sources of polymer deterioration, namely stress cracking and gamma radiation, are present. For a better visualization of this combined effect, the relative property was plotted as a function of radiation dose and the results are given in Fig. 5b. This confirms that there was no influence of the gamma radiation dose on tests done without liquid, whereas the results with the simultaneous liquid application the relative elongation decreased with the rising dose and the effects are more severe when ethanol was used. In comparison to the experiments reported in the previous article with PMMA [7], the results shown here indicate a higher tolerance to gamma radiation dose of t-PMMA in comparison to PMMA when tests were done without liquid.

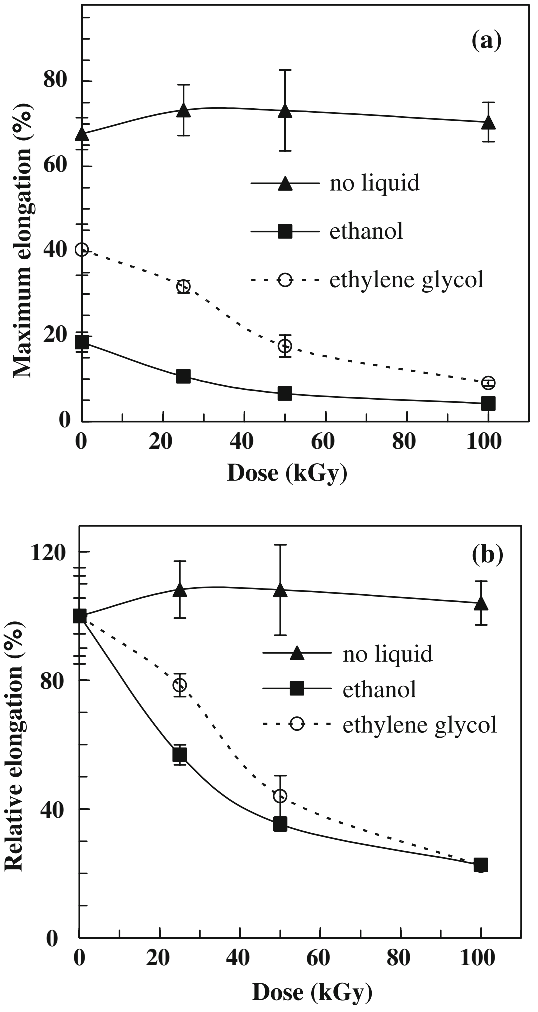

Fig. 5 Maximum elongation (**a**) and relative elongation (**b**) as a function of radiation dose, for three different environments: without liquid, ethanol and ethylene glycol. The strain rate applied during test was 100 mm/min

The stress–strain curves of t-PMMA done under different environments are useful to understand the results obtained (Fig. 6). Figure 6a compares the unexposed sample with the one exposed to a dose of 100 kGy, tested without liquid, where there is an almost perfect overlap of the two curves. Figure 6b shows the curves for the polymer tested under ethylene glycol where the continuous decrease of the strain at break with increasing radiation dose is noted. It is also observed that samples exposed to 100 kGy had also a reduction in tensile strength and no yielding. The curves of tensile tests done under ethanol are similar to those obtained under ethylene glycol but the higher aggressivity of the liquid reduced the yielding and tensile strength for all γ-exposed samples (Fig. 6c).

The results obtained using a strain rate of 10 mm/min for the various types of exposure conditions are given in Fig. 7a. Similar to what was observed with the higher crosshead speed (Fig. 6), there was no influence of the gamma radiation dose on rupture strain data when the experiments were done without liquid. When the tests were conducted under the presence of ethanol, a high deterioration in mechanical properties was observed (Figs. 7a and 8). The effect is clearer on plotting the relative data (Fig. 7b), where the synergy between ESC and radiation on reducing the mechanical integrity is clearly observed. Figure 8 also shows a large reduction in tensile strength for this testing condition.

When the lowest strain rate was used (1 mm/min) a different type of behaviour was observed for the polymer tested without liquid, with a decrease of the maximum elongation with increasing doses (Fig. 9a). For the unexposed sample the maximum elongation was higher than those obtained with higher crosshead speeds, which is expected due to relaxation effects [18]. The reduction in elongation with dose, that did not occurred with other strain rates, may be associated with a sensitivity of damage caused by γ-degradation at this low strain rate. Alternatively, the slight reduction in molecular sizes by gamma degradation (Fig. 2) reduced the concentration of entanglements, which

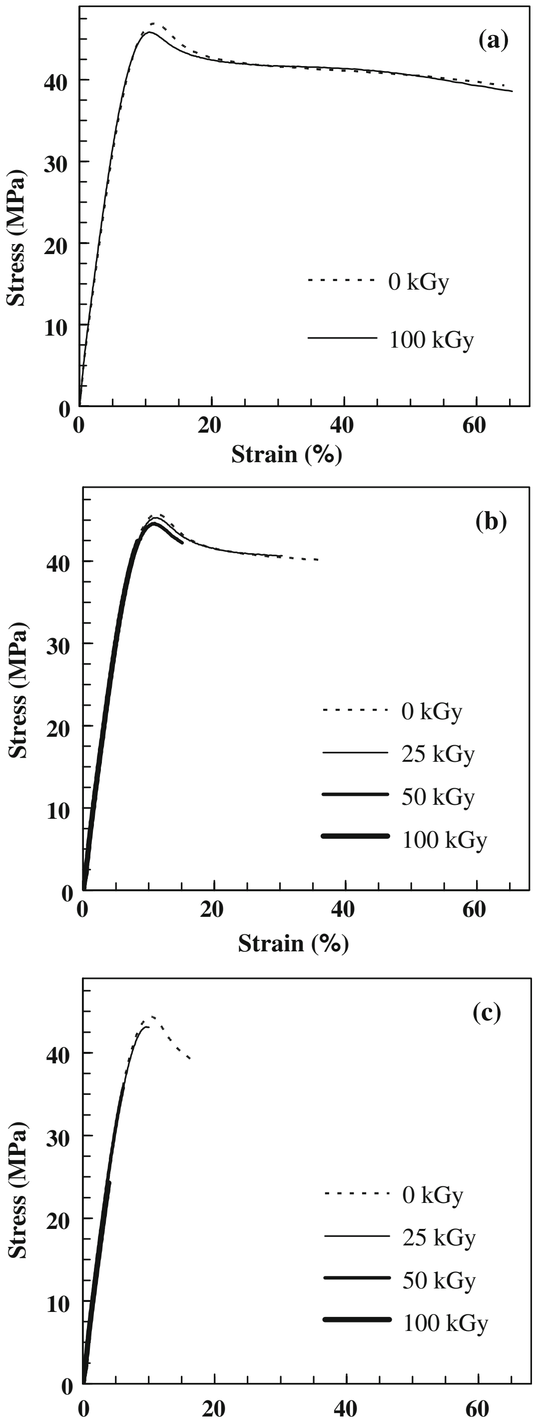

Fig. 6 Stress–strain media curves at 100 mm/min **a** without liquid **b** under ethylene glycol **c** under ethanol

are a major responsible for polymer deformation. At low strain rates, the large deformation of these entanglements eventually leads to crack formation and the catastrophic failure. Under high strain rates the deformation of these entanglements are not as high to be sensitivity to the concentration of entanglements.

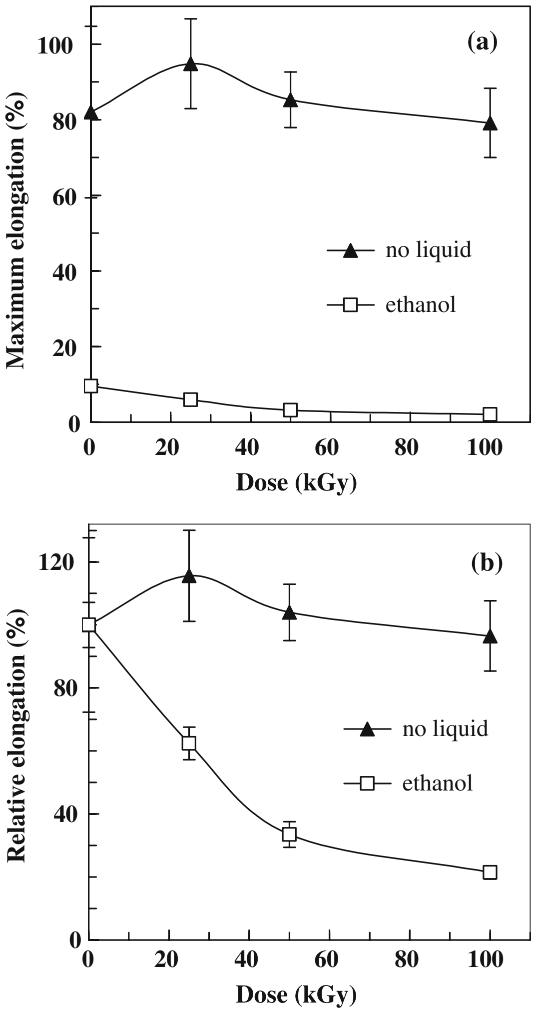

Fig. 7 Maximum elongation (**a**) and relative elongation (**b**) as a function of radiation dose, for two different environments: without liquid and ethanol. The strain rate was 10 mm/min

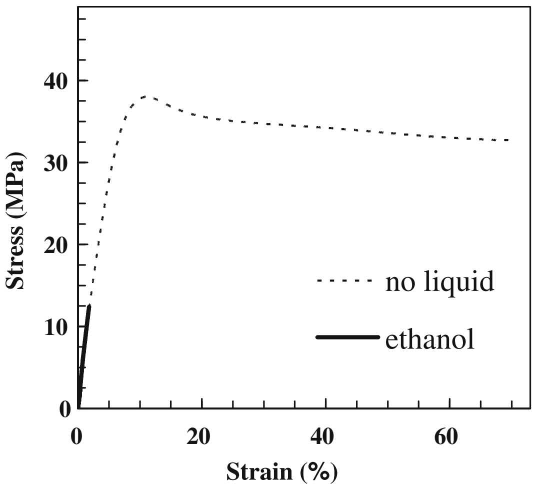

Fig. 8 Stress–strain media curves of 100 kGy irradiated t-PMMA at 10 mm/min showing the strain localization caused by ethanol

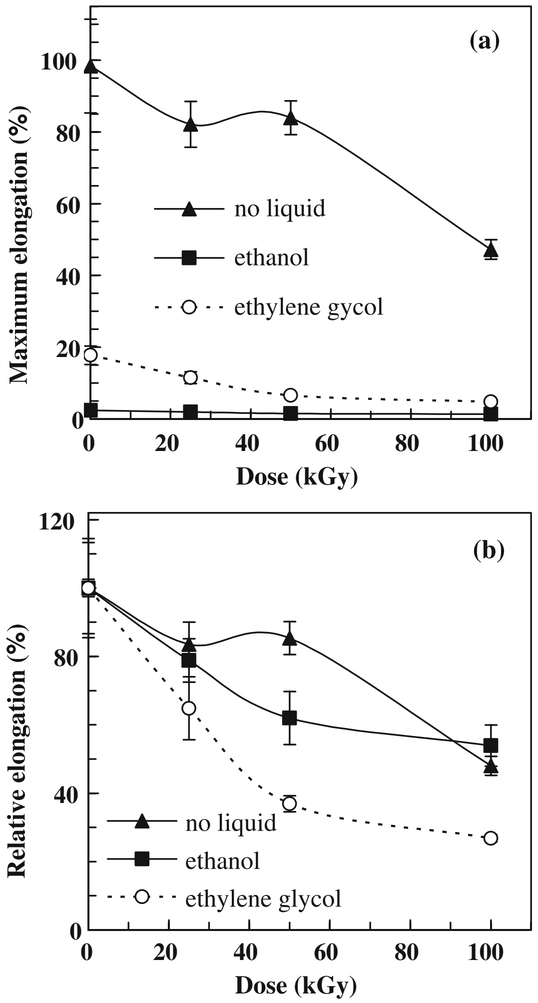

Fig. 9 Maximum elongation (**a**) and relative elongation (**b**) as a function of radiation dose, for different environments. The strain rate was 1 mm/min

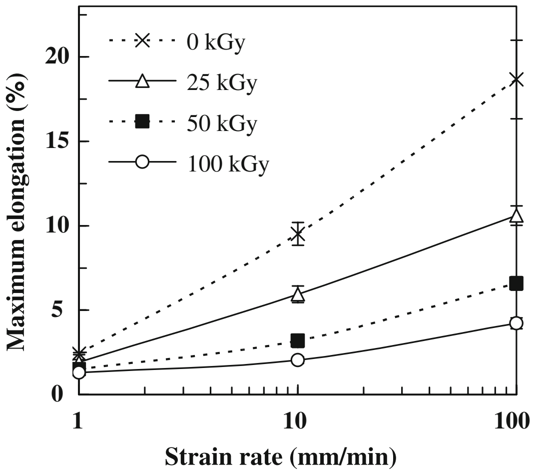

Fig. 10 Maximum elongation of t-PMMA tensile-tested under the presence of ethanol for various strain rates

When the tests were done with the contact with active fluids, there appears to follow the same trend of those conducted with higher crosshead speeds. Here again, the exposure to ethanol was to most detrimental to mechanical properties. The longest contact time between the liquid and polymer in this test condition promotes a drastic ESC effect to the polymer, especially when ethanol was applied to the surface of t-PMMA. When data are plotted as relative values (Fig. 9b) a proportional larger reduction in maximum elongation is observed when a previously γ-exposed polymer is tested under the presence of ethylene glycol. This reveals the predominant ESC effect on tests done with ethanol at this strain rate that overcomes the degrading effect of gamma irradiation. This predominance is showed more clearly on Fig. 10. When tests were done under higher strain rates the property was very dependent on the applied dose, whereas tests conducted at 1 mm/min, the maximum elongation was virtually independent on the γ-radiation dose. Note also in Fig. 10 that the maximum elongation of t-PMMA in contact with ethanol increased with increasing strain rate. This trend is the opposite of what is normally observed in polymers, where, due to viscoelastic effects, the elongation decreases with increasing strain rate [14]. The presence of the active fluid in the current experiments changes this type of behaviour since the stress cracking effects take place on the surface of the samples and these effects are much more effective when more time is available (i.e. at lower strain rates). A similar behaviour was observed before by the authors [7, 9].

Another type of tensile experiment conducted in the present work was ESC exposure under a fixed elongation. When the specimen is in this condition, a stress relaxation phenomenon takes place, which is monitored as a function of time. In previous work done with polystyrene, polycarbonate and PMMA [7, 9, 11], the authors showed that the magnitude of stress relaxation could be an indication of tendency to the stress cracking. In the current work the measurement of stress relaxation did not show much sensitivity to the stress cracking agent, perhaps because the toughened PMMA, due to a rubbery phase, already shows high levels of stress relaxation. The same happened with high impact polystyrene, which also contains a rubbery phase [10]. On the other hand, the specimens exposed to ethanol under a constant deformation fractured during exposure. The time to fracture was measured and some results are given in Fig. 11 for samples that had been previously exposed to the gamma radiation. The time to fracture for a non-exposed sample was 39 s and reduced progressively with increasing radiation dose. Since the γ-irradiated samples without contact with ethanol did not fracture under this test (up to 10 min of testing), the results shown in Fig. 11 confirm that the combined action of

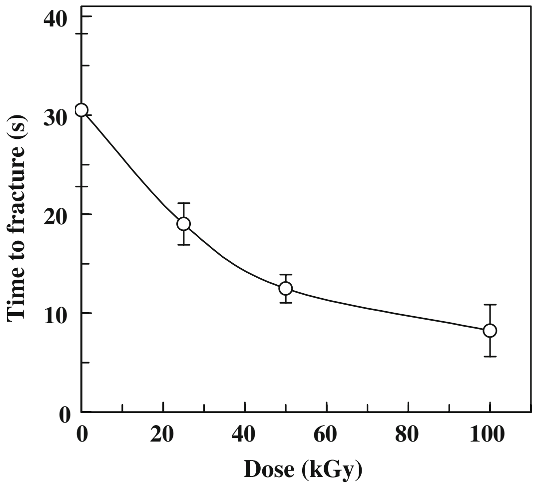

Fig. 11 Fracture time of t-PMMA under an elongation of 3.3% (after applying a stress of 18.6 MPa) and exposed to ethanol

γ-radiation and a stress cracking agent is highly harmful to the polymer under investigation.

Visual effects of gamma irradiation and stress cracking

Without liquid

The inspection of samples after tensile tests helps to explain some mechanisms occurred during the stress application [17]. Firstly, by comparing the undeformed with the deformed sample without liquid exposure, it is noted that the sample changed from transparent to totally opaque after tensile tests (Fig. 12a, c). This suggests the occurrence of intensive plastic yielding deformation due the toughness mechanism induced by shear bands and cavitations around the rubbery phase particles, commonly denominated stress whitening [12]. The stress whitening was also observed with the irradiated samples tested without liquid (Fig. 12d) which is consistent with the tensile tests results that showed intensive deformation even for the irradiated one. Note also in Fig. 12c the intense yellowing caused by gamma radiation.

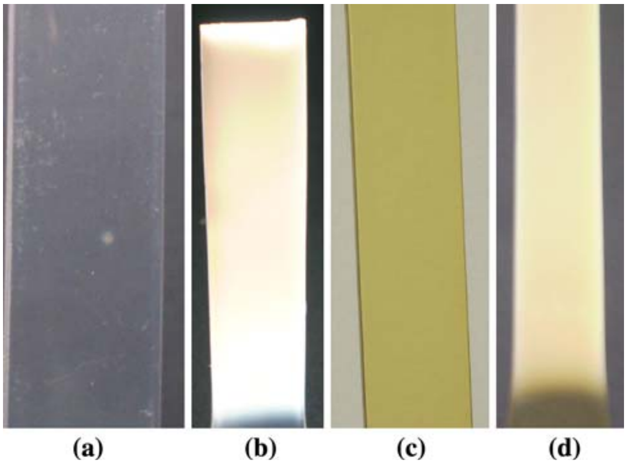

Fig. 12 Visual aspects of the tensile samples without a stress cracking agent. **a** unexposed, before tensile-testing; **b** unexposed, after testing at 100 mm/min; **c** 100 kGy γ-irradiated, before tensile-testing; **d** 100 kGy γ-irradiated, after tensile-testing at 100 mm/min

Under ethylene glycol

The samples tested with ethylene glycol showed dependence with the radiation dose and the strain rate, as observed at tensile tests results. Figure 13 shows that under the lower strain rate (1 mm/min) some surface crazes are formed, leading to some stress whitening. On rising dose the samples developed some yellowing but the stress whitening effect was much less evident, which can be associated to the higher fragility. The crazing effects are not as extensive as that shown in Fig. 12, leading to the interpretation that ethylene glycol reduced the existing toughening mechanism of the t-PMMA, resulting in polymer brittleness (as also seen by the mechanical properties shown before). At the same time, this type of liquid contact may nucleate new crazes by the stress cracking effect (regardless the presence of rubber particles in the polymer) [17]. These crazes formed during ESC are generally spaced, as those observed by the authors with polystyrene [9]. Figure 13 shows that this was not the case in the combination of t-PMMA and ethylene glycol, with the sample been practically free of visible crazes.

For the tests done with a crosshead speed of 100 mm/min under ethylene glycol, the unexposed sample showed stress whitening (Fig. 14), comparable to the samples tested without liquid. This is probably due to the relatively short contact time to give much influence on the toughening of t-PMMA. However, for the γ-degraded samples, the opacity reduced with dose, indicating an increasing influence of

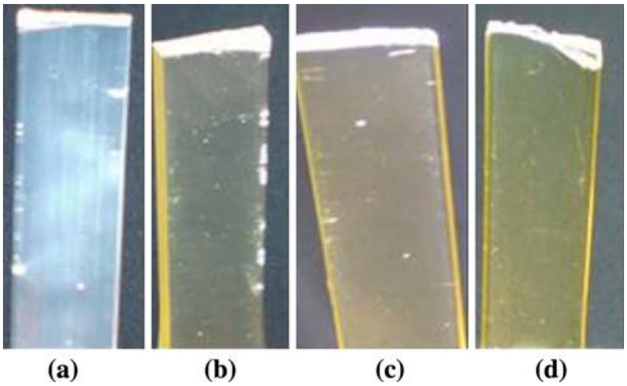

Fig. 13 Tensile-tested samples under ethylene glycol at 1 mm/min. **a** unexposed; **b** 25 kGy; **c** 50 kGy; **d** 100 kGy

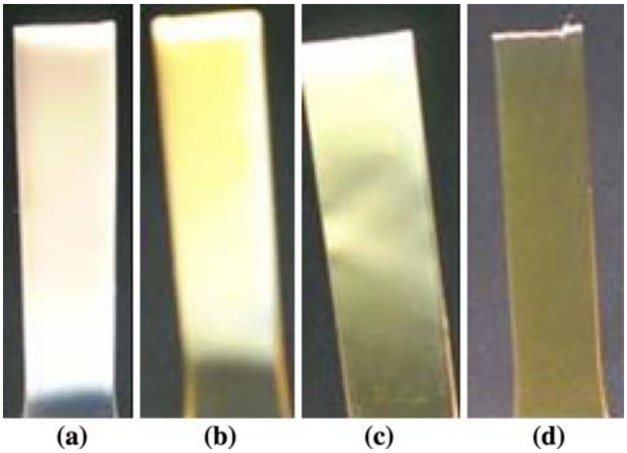

Fig. 14 Tensile-tested samples under ethylene glycol at 100 mm/min. **a** unexposed; **b** 25 kGy; **c** 50 kGy; **d** 100 kGy

the stress cracking. Again, this observation indicates that previously the degraded polymer is more susceptible to the stress cracking effect. Comparing to the results at 1 mm/min strain rate under ethylene glycol, the samples showed more stress whitening, in agreement with the tensile results.

Under ethanol

The tensile tests under ethanol at the higher strain rate (100 mm/min) indicated that only the unexposed sample exhibited some yielding (Fig. 6c). On visual observation of the tested samples (Fig. 15a) there are both zones of shear bands and surface crazes, which is in agreement with the tensile tests. In comparison with the tests done under ethylene glycol (Fig. 14a) and without liquid (Fig. 12b), the stress whitening effect is less evident due to the stronger action of ethanol as a stress cracking agent. With rising doses, the specimens showed just some surface cracks and crazes and, again, this indicates a reduction in the toughening mechanism in the presence of the active fluid. On 25 kGy exposure (at 100 mm/min) an intensive tiny crazing on ethanol applied surface is noted (Fig. 15b). On rising dose the number of visible crazes increased, indicating a major susceptibility to the catastrophic failure (Fig. 15c, d).

Under the more drastic ESC condition (at a crosshead speed of 1 mm/min) the effects observed using the other strain rate are intensified, with much reduction in stress whitening, even for the unexposed sample (Fig. 16). On this sample there are few and spaced surface crazes, but they are relatively large. By rising doses the crazes get fewer and smaller. With irradiated samples the critical size for crack propagation is reduced and, therefore, fracture occurs very rapid when compared to the unexposed polymer.

Surface topography from tensile-tested samples

t-PMMA tested without liquid

The fracture surface of unexposed t-PMMA in Fig. 17a indicates that the fracture started from the flat region of the surface edge and propagated into the interior. Since the maximum elongation was very high for this sample (Fig. 9a), the flat region may have been formed by tearing. The features of the propagation region like roughness, irregularities and fibrous aspect can be associated with the toughness exhibited by this material [19]. When the sample was γ-exposed for 100 kGy and then tensile-tested, some differences in the fracture surface was seen (Fig. 17b). A mirror region is clearly detected near the edge, indicating the starting of the fracture process. The interior regions are relatively featureless in relation to unexposed one with

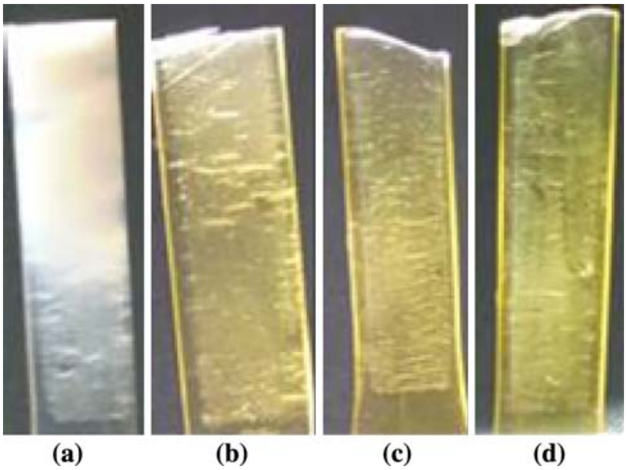

Fig. 15 Tensile-tested samples under ethanol at 100 mm/min. **a** unexposed; **b** 25 kGy; **c** 50 kGy; **d** 100 kGy

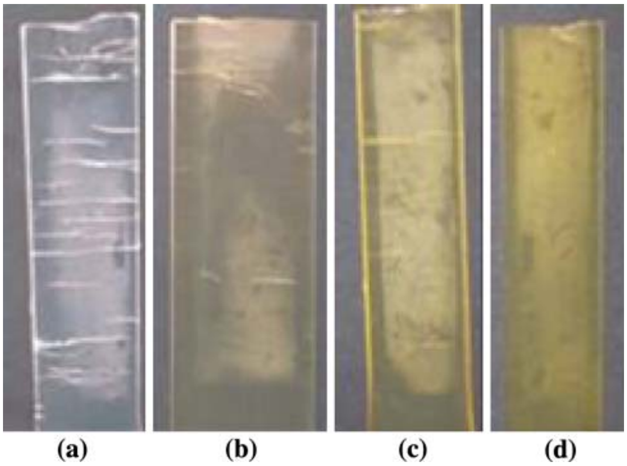

Fig. 16 Tensile-tested samples under ethanol at 1 mm/min. **a** unexposed; **b** 25 kGy; **c** 50 kGy; **d** 100 kGy

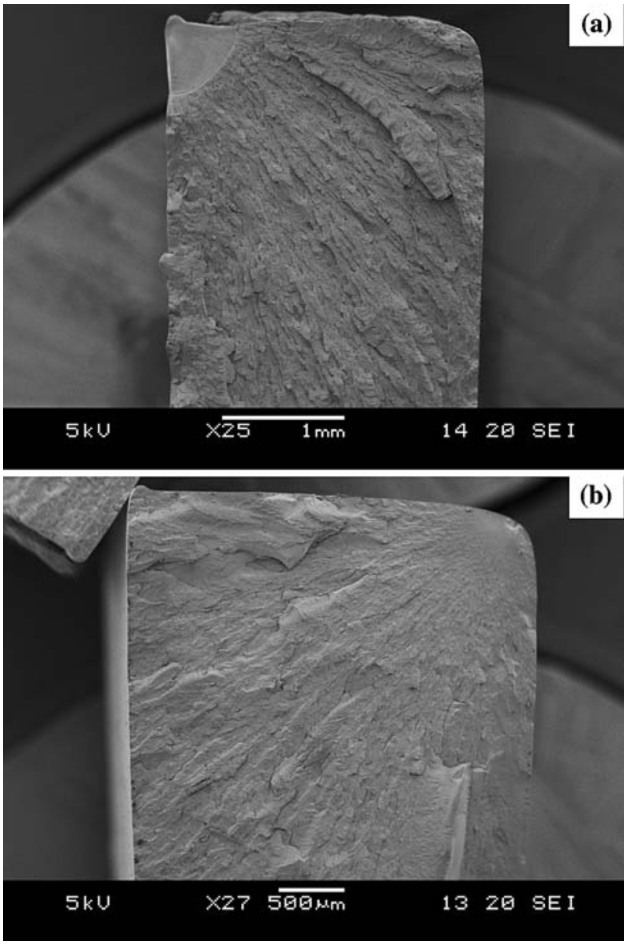

Fig. 17 Fracture surfaces of t-PMMA samples tensile-tested without liquid at 1 mm/min. **a** unexposed; **b** 100 kGy

some fracture marks. It is possible that the reduction in molecular sizes by radiation (Fig. 2) reduced the possibilities of shear yielding, a mechanism that promotes ductility.

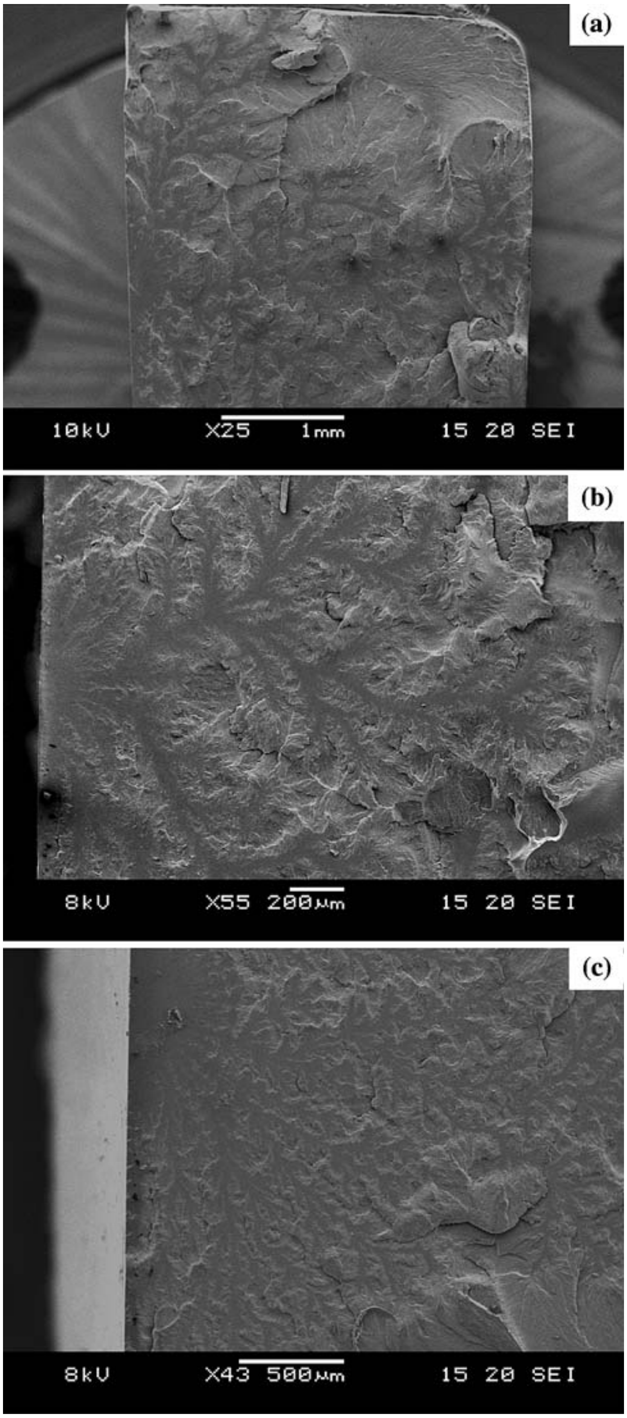

Fig. 18 Fracture surfaces of t-PMMA samples tensile-tested under ethanol at 1 mm/min. **a** unexposed; **b** 25 kGy; **c** 50 kGy

t-PMMA tested with ethanol

The drastic effect on mechanical properties caused by ethanol, especially at lower strain rates can be also observed on fracture surfaces of the samples (Fig. 18). Figure 18a shows a fracture surface image from unexposed t-PMMA after tensile-testing under ethanol. The surface presents low roughness in comparison those tested without liquid. The fracture nucleated from a craze formed on surface where ethanol was applied during tensile-testing. A dendritic pattern propagating from the surface to body interior is observed, similar to the one that occurred with PMMA under ethanol [7]. The branches have high length extending through the thickness of the sample. The pattern resembles the water treeing, a degradation mechanism that happens with insulation electric cables, commonly seen with polyethylene, under water vapour. This mechanism is normally explained by the absorption of water vapour by preferred ways, like porous regions, motivated by high electrical potential [20]. Water treeing is explained by the synergism between the high electrical tension and the liquid absorption under the polymer. Meyer and Filippini [21] argued that water treeing may be considered as an

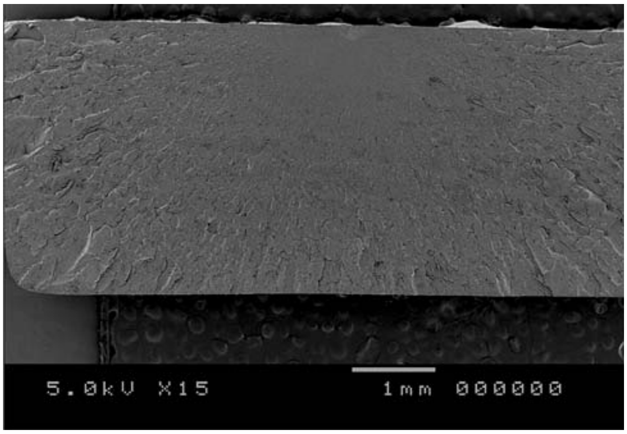

Fig. 19 Fracture surface of 50 kGy γ-exposure t-PMMA sample tensile-tested under ethylene glycol at 1 mm/min

ESC mechanism, in which the electrical voltage induces mechanical stress and, acting under water vapour, such patterns are formed. A similar situation may have happen here when a combination of mechanical stress and active fluid is present. In this work the dendritic pattern was observed only when an ESC situation is present.

Figure 18b refers to 25 kGy gamma radiation exposure, tested under the same conditions of liquid and crosshead speed. The aspects of the surface are similar to the unexposed one, with smoothness in the channels and some localized plastic deformation around them. The intensification of fragility with rising radiation dose can be seen in the sample exposed at 50 kGy (Fig. 18c). The dendritic behaviour gets denser, and the fracture surface is smoother, which can be attributed to the synergistic effect between the radiation and liquid on the failure of the polymer.

Figure 19 shows the fracture surface of a 50 kGy γ-exposed sample after tensile-tested at 1 mm/min in the presence of ethylene glycol. The general aspect is very typical of a fragile material. The fracture initiated from the side where the liquid was applied and propagated on a drastic way into the interior. This is consistent with the results of mechanical properties, where in these conditions a large reduction in maximum elongation was noted (Fig. 9a). However, the action of ethylene glycol in the fracture surface was different to what was observed with ethanol, without the dendritic pattern. This is in agreement with the lower aggressivity of this liquid, according the mechanical tests results.

Conclusion

This work showed new results about the influence of gamma radiation on stress cracking resistance by using a toughened polymer (t-PMMA). It was possible to observe a major number of deformation mechanisms by combining radiation doses, ESC agents and different strain rate tests. The gamma radiation caused some reduction in the polymer molar mass which accelerated the stress cracking. All tests conducted here showed that ethanol was a more aggressive agent to t-PMMA than ethylene glycol. Despite of being less aggressive and no significant absorption of the last one by t-PMMA, it caused severe ESC. With the action of stress cracking, the polymer changed from highly ductile with intense stress whitening, to a fragile behaviour. The analysis of the fracture surfaces revealed that the ESC action caused by ethanol in t-PMMA was similar to the one observed with PMMA in a previous work, with dendritic pattern formed on fracture surface.

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References

1. Navarro RF, d'Almeida JRM, Rabello MS (2007) J Mater Sci 42:2167. doi:10.1007/s10853-006-1387-7
2. Rabello MS, White JR (1996) Polym Comp 17:691
3. Brostow W, Corneliussen H (1986) Failure of plastics. Hanser, Munich
4. Wright DC (1996) Environmental stress cracking of plastics. Rapra, Shawbury
5. Kawaguchi T, Nishimura H (2003) Polym Eng Sci 43:419
6. Al-Saidi LF, Mortensen K, Almdal K (2003) Polym Degrad Stab 82:451
7. Sousa AR, Araujo ES, Carvalho AL, Rabello MS, White JR (2007) Polym Degrad Stab 92:1465
8. Kjellander CK, Nielsen TB, Kingshott P, Ghanbari-Siahkali A, Hansen CM, Almdal K (2008) Polym Degrad Stab 93:1486
9. Sousa AR, Amorim KL, Medeiros ES, Melo TJA, Rabello MS (2006) Polym Degrad Stab 91:1504
10. Timoteo GAV, Fechine GJM, Rabello MS (2007) Macromol Symp 258:162
11. Timoteo GAV, Fechine GJM, Rabello MS (2008) Polym Eng Sci 48:2003
12. Rabello MS (2000) Aditivação de Polímeros. Artliber Editora, São Paulo
13. Biwa S, Ito N, Ohno N (2001) Mech Mater 33:717
14. Argon AS, Cohen N (2003) Polymer 44:6013
15. Lin CB, Lee S (1992) J Appl Polym Sci 44:2213
16. Bernier GA, Kambour RP (1968) Macromolecules 1:393
17. Arnold JC (1998) J Mater Sci 33:5193. doi:10.1023/A:1004431920449
18. Sperling LH (1986) Introduction to physical polymer science. Wiley, New York
19. Suarez JCM, Blasi RSDE (2003) Polym Degrad Stab 82:221
20. Ciuprina F, Teissedre G, Filippini JC (2001) Polymer 42:7841
21. Meyer CT, Filippini JC (1979) Polymer 20:1186