

Stress Cracking and Chemical Degradation of Poly(ethylene terephthalate) in NaOH Aqueous Solutions

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ABSTRACT: Stress cracking is one of the most frequent causes of premature failure of polymers, affecting also engineering polymers like PET. In this work, the stress cracking behavior of injection moulded PET was investigated using sodium hydroxide (NaOH) aqueous solutions in various concentrations as active fluids. The application of mechanical load to the sample bars was done in a tensile testing machine, using the ordinary tensile test and also a relaxation procedure. The results showed that all NaOH

solutions were aggressive stress cracking agents for PET, reducing mechanical properties and causing catastrophic failure with a significant surface damage. The occurrence of hydrolysis reactions was also observed when NaOH solutions were applied in combination with tensile loads, causing a reduction in molar mass of PET molecules. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3089–3101, 2010

Key words: PET; stress cracking; degradation

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a widely used thermoplastic polymer that, in many applications, may have contact with chemical compounds that cause environmental stress cracking (ESC). ESC is one of the main reasons for premature failure of polymers, occurring when a simultaneous action of mechanical stress and a chemical active compound takes place on the product.¹ Surface crazes and cracks are usually formed, resulting in lower mechanical properties.^{2,3} The exact mechanism to explain stress cracking is not fully established yet, but it is believed that the active fluid act locally, causing plasticization that, together with the mechanical stress, allow molecular displacement and the formation of crazes.^{4,5} This action, therefore, depends on the level of the interaction between the polymer and the fluid. A comprehensive investigation on the type of chemicals that cause stress cracking in polymers was conducted by Hansen and co-workers.^{6–8} They showed that the most effective fluids that act as ESC agents have a level of interaction with the polymer that is intermediate between a good solvent and a non solvent. Several types of ordinary compounds were shown to cause stress cracking, including: paints, adhesives, cleaning prod-

ucts, lubricants, food components, and even polymer additives.⁹

Whereas the meaning of stress cracking is clearly very different from dissolution, it is common to mix up its meaning with chemical attack. Both ESC and chemical attack phenomena may cause surface cracks and fragility and, therefore, a visual inspection is not sufficient to differentiate them. One may consider that the main difference between chemical attack and stress cracking would be the occurrence (or not) of chemical reaction, as ESC has been related to a purely physical phenomenon, whereas chemical attack to the occurrence of chemical reaction between the polymer and the fluid, causing in some cases molecular degradation.^{10,11} However, some authors considered that the stress cracking agent may also cause chemical attack to the polymer.^{12–14} In this respect, we understand that the difference between the two phenomena is not the occurrence of chemical reactions but the presence or not of a mechanical stress. Under stress, the formation of surface cracks caused by the presence of an active fluid is named stress cracking, even if chemical reactions take place. On the other hand, if chemical reactions occur without mechanical stress, this can be defined as chemical attack.

Although the effects of stress cracking are widely known by designers and manufactures since many decades ago, this is not a subject of many reports in the literature and few new publications are available every year. One of the present authors is contributing to this theme with some recent work on the combined effect of stress cracking and chemical degradation of polymers.^{15–20} As far as PET is concerned, the amount of scientific work is much lower

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when compared with other types of polymers like polystyrene and polycarbonate. As an important engineering thermoplastic, PET products may be in contact with an aggressive fluid and mechanical stress in service. Therefore, the investigation of ESC behavior of this polymer is of much practical interest and some work was done throughout years.^{12–14,21–23}

However, the identification of the most critical stress cracking agents for PET as well as the description of the failure mechanisms still need further attention. In the case of the action of sodium hydroxide solution on PET, there is not a consensus whether the phenomenon is stress cracking, chemical attack, or both occurring simultaneously. The main objective of this work is to contribute to a better understanding of the stress cracking behavior of PET under the presence of sodium hydroxide aqueous solutions. Different concentrations of NaOH were used as stress cracking agent and the effects on mechanical properties, surface cracking and fractography of injection moulded bars of PET were investigated.

EXPERIMENTAL

The PET grade used was Cleartuf Turbo (M&G/Brazil), with an intrinsic viscosity of 0.8 dL/g. Type I (ASTM D-638) tensile test bars were produced in a Fluidmec H3040 injection molding machine operating with the barrel at 300°C and the mold at 15°C. Aqueous solutions of sodium hydroxide (NaOH) were used as stress cracking agents with concentrations ranging from 0.05 to 5M.

The ESC resistance was evaluated by means of mechanical testing using a Lloyd LR10k tensile testing machine in a constant temperature room set at 22°C. The bars were kept at the test temperature for a minimum of 24 h before testing. Two testing procedures were used: (i) an ordinary tensile testing, using crosshead speeds of 2 and 5 mm/min; (ii) a tensile relaxation testing, in which a load (ranging from 1000 to 1900 N) was applied and the decay in load was monitored as a function of time. In both situations, the fluid was applied to the sample surface during testing, following a previous procedure.¹⁵ After mechanical testing, the fracture and molded surfaces were analyzed by macrophotography and by scanning electron microscopy. The latter was done in a Shimadzu SSX 550 Superscan equipment, after sputtering a gold layer to avoid charging.

In selected samples, the determination of NaOH solution absorption by the polymer was done by weighting the sample after several soaking times (precision of 0.1mg). After this procedure, the specimens were inspected by optical microscopy using a Labomed equipment operating in transmission.

The determination of molar mass of PET before and after stress cracking exposure was conducted by

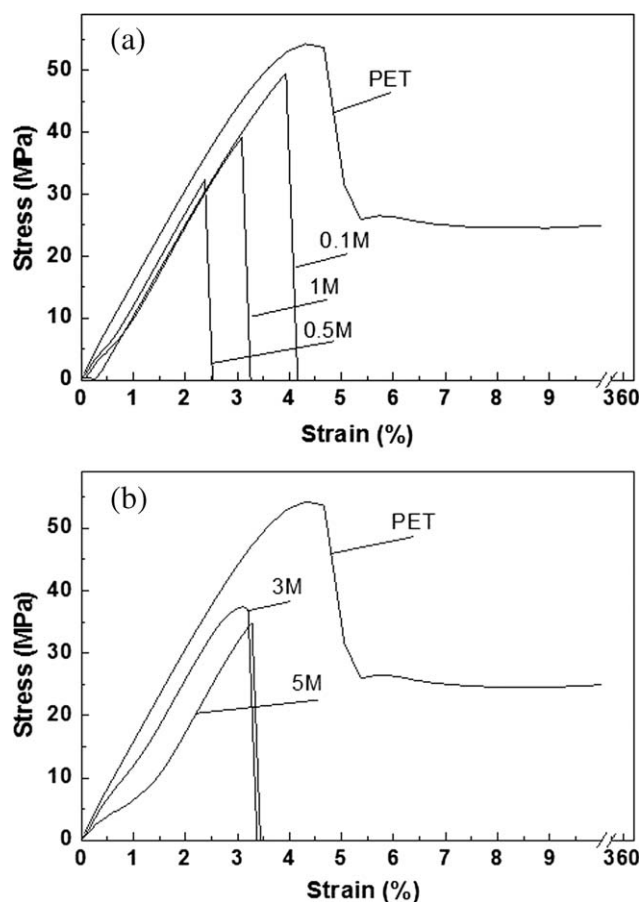


Figure 1 Selected stress-strain curves of PET samples tested under the presence of several NaOH solutions. The concentrations of the solutions are indicated near the curves. Crosshead speed: 5 mm/min.

intrinsic viscosity measurements using a solution of 0.50% of PET in a 60/40 phenol/1,1,2,2-tetrachloroethane mixture. An Ubbelohde U 4944 2KRK ($\varnothing = 0.75$ mm) glass capillary viscometer was used, following ASTM D 4603. The intrinsic viscosity ($[\eta]$) was calculated and the weight-average molar mass (M_w) was determined with the following equation²⁴:

$$M_w = \sqrt[0.68]{\frac{[\eta]}{4.68 \times 10^{-4}}} \quad (1)$$

RESULTS AND DISCUSSION

Stress cracking under tensile testing

The behavior of PET under a condition of ESC was evaluated with different concentrations of sodium hydroxide aqueous solutions, ranging from 0.05 to 5M.

The first set of experiments were ordinary stress-strain tests using a strain rate of 5 mm/min and the results are given in Figure 1, plotted in different graphs for data clarity. The unexposed PET showed

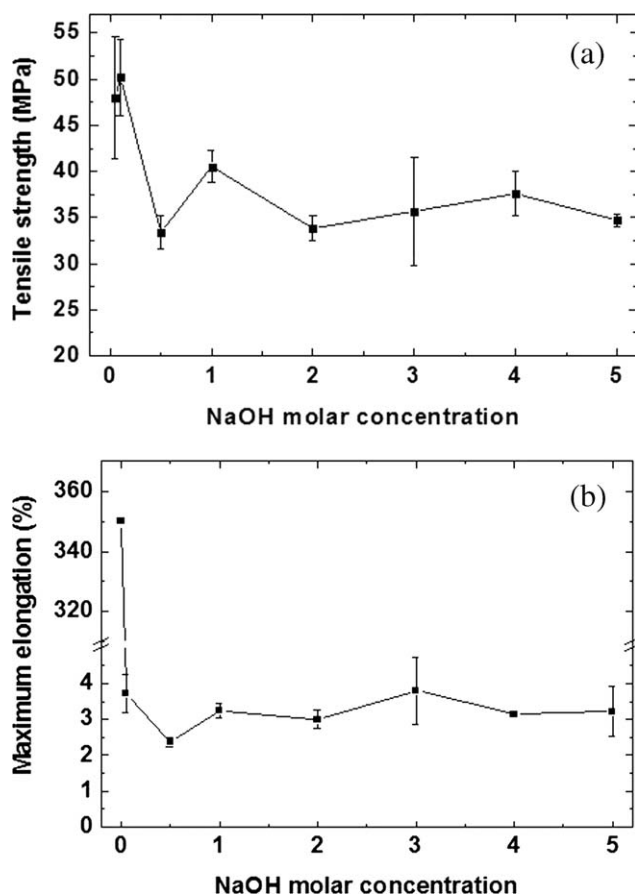


Figure 2 Tensile properties of PET samples in contact with several NaOH solutions. Crosshead speed: 5 mm/min.

a very ductile behavior, with a high value of maximum elongation. Actually, the deformed sample bars reached the machine limit of displacement without breaking. On the other hand, when the specimens were tested under the presence of NaOH solutions, they failed in a brittle way, with much lower elongation. The ultimate mechanical properties are shown in Figure 2. Besides the reduction in maximum elongation, the tensile strength also decreased significantly under the presence of NaOH solutions, even with concentrations as low as 0.05M. The reduction in mechanical properties, however, was not systematic in relation to NaOH concentration and some oscillation was observed. It seems that the solution with a concentration of 0.5M caused the highest decrease in tensile properties, but the values obtained with higher concentrations were within experimental variation. As the ESC behavior is closely related to the interaction between the aggressive fluid and the polymer,⁸ it is possible that 0.5M of NaOH was the critical concentration to cause ESC in PET. Higher concentrations of NaOH caused a higher instability in mechanical behavior. This observation is somewhat comparable to the work done by Moskala,¹² who showed that the crack

growth rate in PET was higher when solutions with lower concentrations of NaOH were used as stress cracking agents.

Figure 3 shows the surface appearance of selected samples after tensile tests under contact with NaOH solutions. For NaOH concentrations lower than 1M no visible crazes or cracks were noted [Fig. 3(a)], but these samples had significant reduction in tensile properties [Fig. 1(a)]. According to Bernie and Kambour,²⁵ when the ESC fluid is highly aggressive there is a tendency to form just one crack on the specimen surface that propagates very fast into the interior and no other surface crazes were observed. This was also noted in a previous work of PMMA stress cracking developed by one of the authors.²⁰ With 1M and 3M solutions other cracks starts to appear [Fig. 3(b,c)] and the growth of one of them caused the catastrophic failure. The sample exposed to the 5M solution showed a different pattern of cracks [Fig. 3(d)], with small ones in some spots and also very large cracks, extending almost throughout the specimen thickness. This heterogeneity in surface damage may be related to local discontinuities within the product, such as variations in molecular orientation, crystallinity, internal defects, etc. In other words, the test bar could have regions more vulnerable to stress cracking than others. A relation between the internal structure and the pattern of surface cracking was discussed before by one the authors in a investigation of polypropylene photodegradation.^{26,27} These studies showed that the cracks were formed along flow lines generated during processing. A similar type of dependence on the internal structure may also have occurred in this study, as the stress cracking takes place in regions with higher stress concentration²⁸ and/or in regions with a lower density of entanglements. Note that the samples exposed to the solutions of 1 and 3M [Fig. 3(b,c)] also have heterogeneities in surface cracking.

An additional study was conducted with the same type of samples tensile tested using a crosshead speed of 2 mm/min. With a lower strain rate the contact time between the stressed polymer and the active fluid is higher, increasing the stress cracking effects.^{20,29} For this set of experiments, NaOH concentrations of 0.1, 0.5, 1, 2, and 3M were used and stress-strain curves for 1M NaOH concentration are given in Figure 4 in comparison with tests done with the higher strain rate. Both tensile strength and maximum elongation were reduced with reducing strain rate but the shape of the curves was not very different, suggesting that the deformation and failure mechanisms were similar. The ultimate properties for the whole series of concentrations are shown in Figure 5. The data obtained with 2 mm/min were more consistent, indicating that less unstable conditions were observed under this strain rate. Up to a

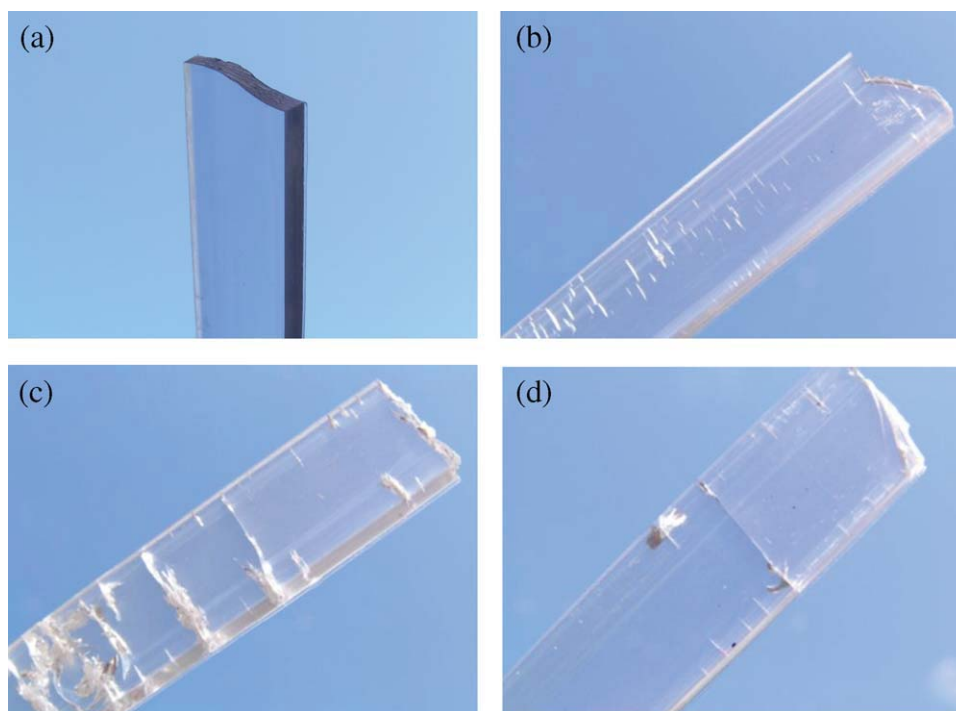


Figure 3 Macrophotography images of sample surfaces after tensile testing at 5 mm/min under the presence NaOH solutions: (a) 0.5M, (b) 1M, (c) 3M, and (d) 5M. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

concentration of 0.5M no difference in relation to the strain rate was noted, but with higher concentrations of NaOH in the solutions the effects were clearly more significant when tested at 2 mm/min. This was due to a more prolonged exposure time, allowing more liquid diffusion into the sample. The pattern of surface cracks were different in comparison with those observed in samples tested under the higher crosshead speed (see Fig. 6). At 2 mm/min less cracks were formed, leading to a higher stress concentration effect and, hence, to lower mechanical properties. This trend was also observed before by Arnold.³⁰

The fracture surfaces of selected samples after tensile testing at 2 and 5 mm/min under contact with NaOH solutions were inspected by scanning electron microscopy and the images are given in Figure 7. Figures 7(a–c) show general views of samples exposed to 0.05M and 3M, the latter tested using two crosshead speeds. The arrows on the pictures indicate the starting location of the fracture which, in all cases, was at the side in contact with the ESC agent. The other Figures [7(d–f)] show the corresponding images under higher magnification. The features in both Figures 7(a,b) suggest a rapid crack propagation process, but there are some differences between the two samples. In the one in contact with the 3M solution the fracture started apparently from a small spot [smooth region in the bottom of Fig. 7(b)] next to the surface that were in contact with

the solution. On other hand, the sample in contact with the 0.05M solution [Fig. 7(a)] showed a larger mirror zone, typical of a lower crack propagation process that started on the upper right corner and propagated to the opposite side forming a concave shape from right to left. Comparing the two images [Fig. 7(a,b)] one can note a much rougher aspect of the sample exposed to the 0.05M solution. The roughness of the fracture surface is associated with the intersection of advancing cracks coming from different planes, and it is the source of energy

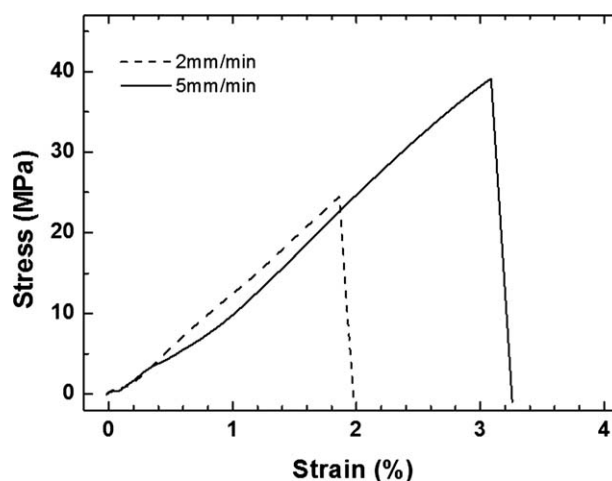


Figure 4 Stress–strain curves of PET tested at two cross-head speeds under the presence of 1M NaOH solution.

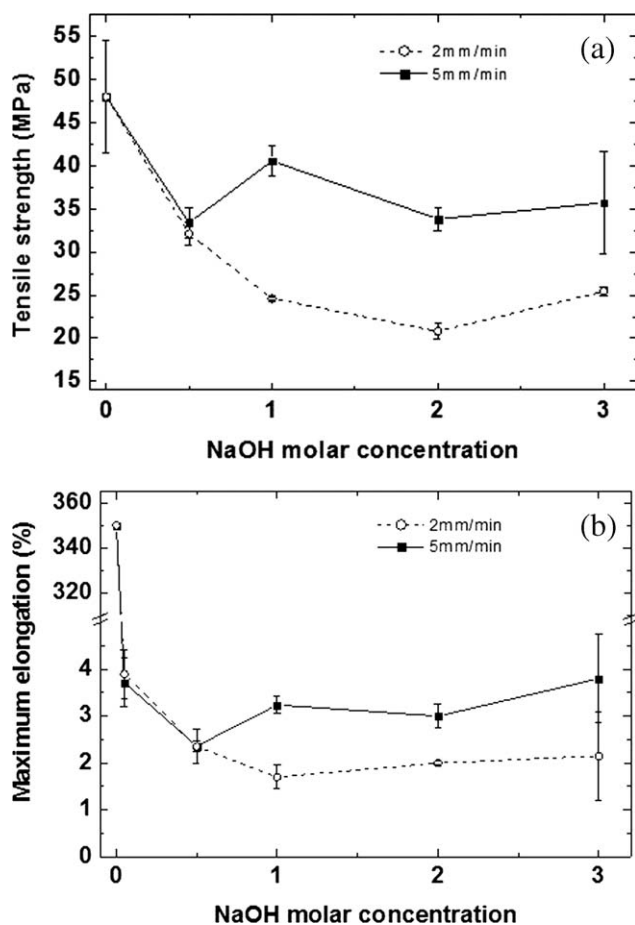


Figure 5 Ultimate mechanical properties of PET tested under the presence of NaOH solutions using crosshead speeds of 2 and 5 mm/min.

absorption during testing.³¹ This observation is consistent with the results of mechanical properties (Fig. 5), in which the samples exposed to solutions with a lower concentration of NaOH had less deterioration in tensile properties. When the specimen of Figure 7(a) was observed under higher magnification, several crack propagation fronts are noted. This characteristic indicates that the cracks generated at the bar surface were not strong enough to propagate steadily throughout the sample. The cracks probably were arrested when propagating into the undamaged material and broke up into several parallel cracks. In Figure 7(e), which is a higher magnification of Figure 7(b), an unusual fibrillar feature that resembles needles is seen. This type of pattern was not observed in the sample exposed to the 0.05M solution and might be the result of an extensive plasticization within the sample and/or a consequence of degradation reactions (see later).

The effect of crosshead speed during tensile testing on the fracture surface of the samples exposed to 3M is observed by comparing Figure 7(b,c). For the sample tested at 2 mm/min [Fig. 7(c)], the fracture started also from the side in contact with the

stress cracking agent, but the mirror region is clearly much larger in comparison with the one tested with a higher speed [Fig. 7(b)]. This difference follows the tensile results (Fig. 5) and is a consequence of a longer contact time with the active fluid during testing. Under higher magnification [Fig. 7(f)], the “needle-like” pattern is much more evident for the specimen tested at 2 mm/min, indicating a higher plasticizing effect. This effect, however, did not avoid a reduction in tensile strength that was more dependent on the crack initiation process at the specimen surface and manifested by a larger mirror zone.

Stress cracking under stress relaxation

For this set of experiments, the sample bar was stressed using the tensile testing machine to a target load and the NaOH solution was applied over the sample. During the exposure the load decay was monitored, as shown in Figure 8 for selected conditions. The larger stress decrease in the presence of the aggressive fluid when compared with the neat polymer was due to the plasticizing effect, making

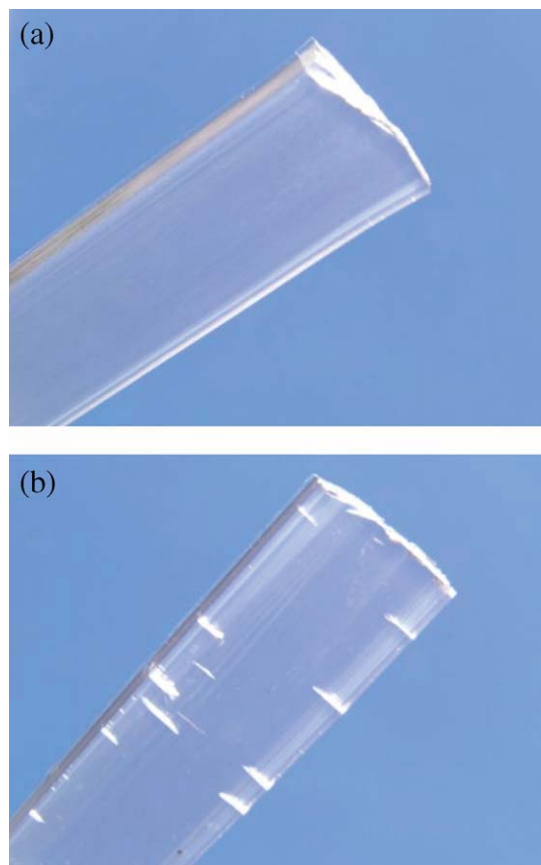


Figure 6 Macrophotography images of sample surfaces after tensile testing at 2 mm/min under the presence of NaOH solutions: (a) 1M, (b) 3M. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

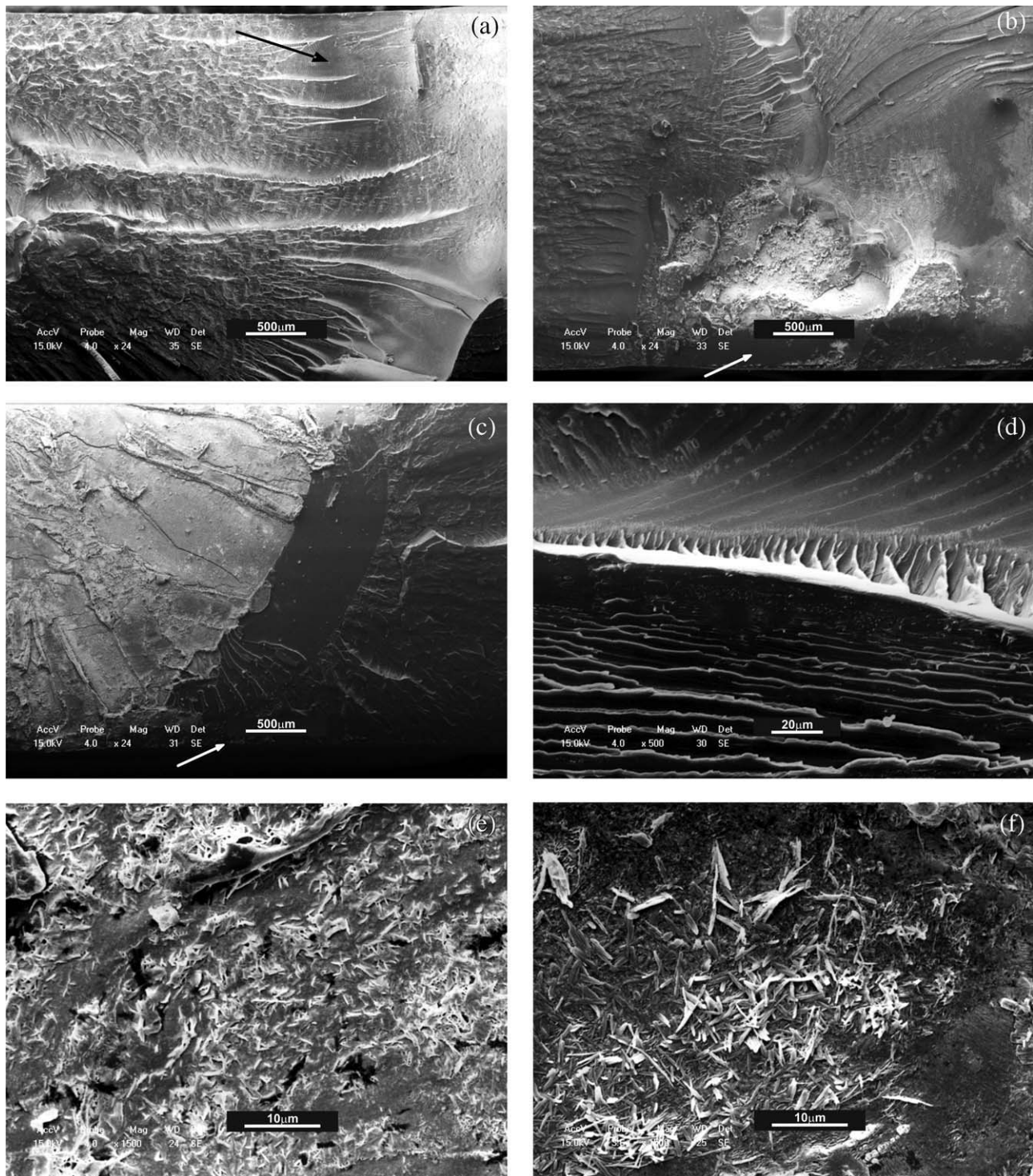


Figure 7 Scanning electron microscopy images of the fracture surface of PET bars viewed under two magnifications. NaOH solution concentration and testing speeds are indicated. The arrows show the side in contact with the ESC agent which coincides with the fracture initiation site.

this test one of the most valuable to evaluate the stress cracking behavior.^{15,32} The samples tested without the aggressive fluid did not break during the experiment, but all the others, even the ones under contact with low NaOH concentrations, fractured during exposure. In these cases, the exposure

times until fracture were less than 25 s. Surface cracks lying perpendicular to the stress direction were formed in all samples, and the quantity and depth of these cracks varied with the applied load and NaOH concentration (Fig. 9). Bars exposed to 1M solutions had few and deep cracks when a load

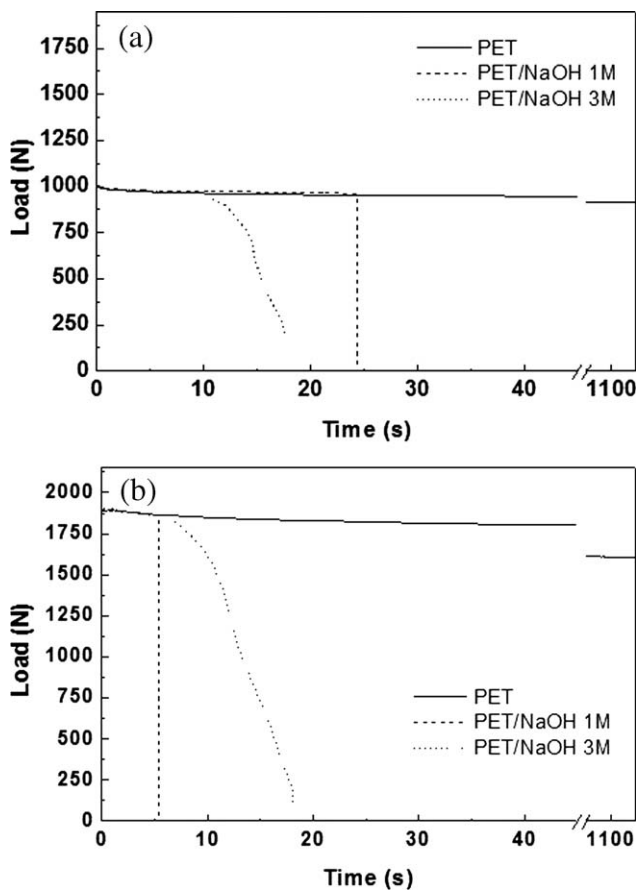


Figure 8 Stress relaxation curves for PET samples tested without and with NaOH solutions using loads of (a) 1000 N and (b) 1900 N.

of 1000 N was applied [Fig. 9(a)]. For higher loads, the cracks were more abundant and shallower [Fig. 9(b)]. When the 3M solution was used, the cracks were much more intense in comparison with the 1M solution. In this case (3M solution), both the quantity and depth of cracks increased with the applied load [Fig. 9(c,d)]. Figure 9(d) shows the most deteriorated sample, with cracks spreading throughout the thickness direction and reaching the opposite (nonexposed) side.

Figure 8 also shows that the shapes of the curves load vs. time were different according to the concentrations of NaOH. The load dropped rapidly with samples exposed to 1M solution, whereas the ones exposed to 3M the stress relaxation curves had a certain sinuosity, showing a time lag between the deviation from the pure PET curve and the final fracture. This behavior may be related to the pattern of surface cracks (Fig. 9). The samples exposed to 1M had few fissures that, due to stress concentration effects, reached critical conditions to propagate catastrophically. On the other hand, the great number of cracks formed on the sample exposed to the 3M solution caused a kind of stress distribution effect, in opposition to stress concentration in few cracks. This is somewhat similar to what was observed when polymers were cracked under ultraviolet radiation, in which, depending on the intensity of surface damage, the cracks could delay the catastrophic fracture.^{26,33} In the case shown in Figure 8, the fracture process of 3M exposed samples might have occurred

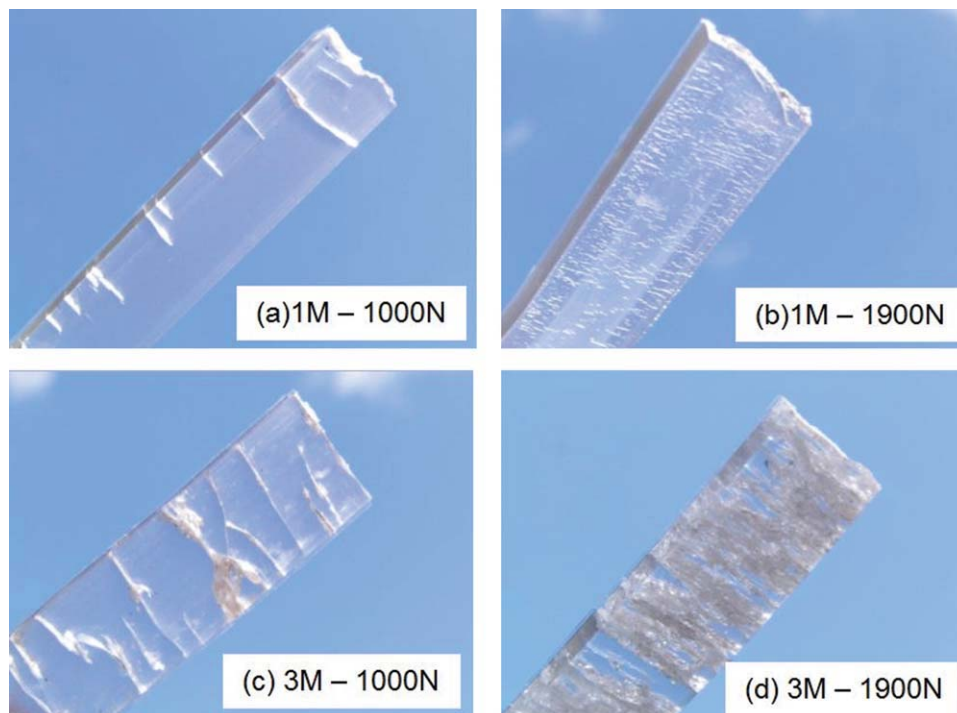


Figure 9 Macrophotography images of sample bars fractured during stress relaxation testing under the presence of NaOH solutions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

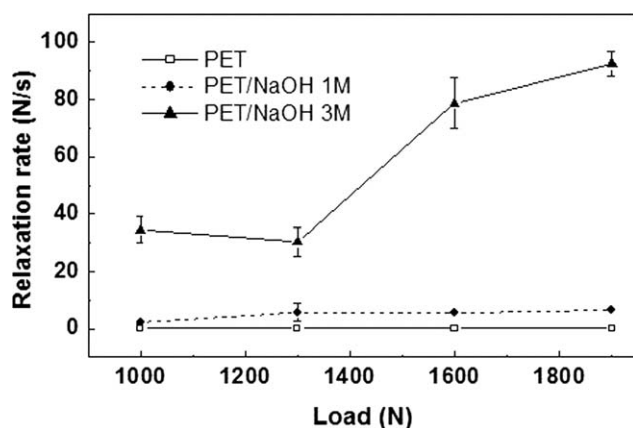


Figure 10 Effect of initial load on the relaxation rate of unexposed PET and under the presence of NaOH solutions.

in several steps until the final failure. Another explanation for this step-like behavior would be an excessive plasticizing effect, causing material softening that led to a fracture in different stages.

From the stress relaxation curves like those shown in Figure 8, the rate of relaxation was calculated as described before¹⁵ and the results are given in Figure 10 as a function of the applied load. The relaxation rate increased with increasing load, possibly due to the higher diffusion of liquid caused by the molecular displacement during testing. The rate of stress relaxation of PET in air was very low, between 0.1 and 0.25 N/s, and increased considerably under the presence of 1M NaOH solution, reaching 6 N/s. However, the most intense effect was obtained with the 3M solution, when a relaxation rate over 90 N/s was observed. This is consistent with the presence of surface cracks on the samples, which were more intense when higher loads were applied [Fig. 9(d)].

During stress relaxation experiments, some samples broke before the test was over and a drop to zero on the load vs. time curve was observed (Fig. 8). The values of time to fracture were collected and the results are compiled in Table I. For samples exposed to 1M NaOH solutions, the fracture time decreased progressively with increasing load, indicating that even though the fissures seem to be superficial [Fig. 9(b)], their effects were strong enough to reduce the resistance of this polymer to stress cracking. In practical terms, if a PET component is exposed to this type of solution and equivalent stress, the failure may occur in a few seconds. For example, if a product is exposed to 1M NaOH solution and a stress of 25 MPa (equivalent to a load of 1000 N in the case of these tensile test bars), the failure will occur in less than 25 s, even though the tensile strength of this grade of (unexposed) PET is about 50 MPa. This fact is remarkable and has a huge implication to the design of PET products. The

knowledge of this type of behavior is totally important to prevent premature failure of components in service.

Table I also shows that when PET was exposed to 3M solutions, the time to failure decreased with increasing load up to 1300 N. For loads higher than 1300 N, an increase in time to failure with increasing load was observed. This occurred despite the fact that under higher loads the surface deterioration was higher than under lower loads (Fig. 9). For loads higher than 1300 N, the samples took longer to failure in contact with the more concentrated solutions (see Table I) even though the bars had more surface damage (Fig. 9) and higher stress relaxation rates (Fig. 10). This seems to be inconsistent, but in a constant strain condition, the propagation of cracks is very dependent on the stress concentration effects. If only few cracks are present, they cause high stress concentration that lead to a critical condition to crack displacement and eventually to the final fracture. If a sample contains more cracks, a distribution of stress among the various defects takes place, causing a delay on the final fracture. This is similar to what happens when toughening agents are added to fragile polymers.³⁴ A somewhat similar case was observed in studies of photodegradation of polypropylene, developed by one of the authors,^{26,35} in which prolonged exposures were shown to increase the tensile strength in comparison with intermediate exposures. A possible explanation given for that type of behavior, valid also in the current study, was that the large number of surface cracks could mutually interact, causing unloading and hence reducing the stress concentration. An inverse correlation between the stress cracking effects in PET and the time to failure was also observed by Zhou.²²

Another issue to be considered in this study is the possibility of hydrolytical chemical reactions in PET molecules during exposure to NaOH solutions. This type of solution is used in industry to clean PET flakes for recycling proposes³⁶ or even for chemical recycling of this polymer.^{37,38} In both cases, however, the treatment requires long times and/or elevated temperatures, and these conditions were not

TABLE I
Time to Failure of Pet Samples During Stress Relaxation Experiments Under Different Loads and NaOH Concentrations

Load (N)	Time to failure (s)		
	Unexposed PET	PET NaOH 1M	PET NaOH 3M
1000	>1200 ^a	24	18
1300	>1200 ^a	18	12
1600	>1200 ^a	8	14
1900	>1200 ^a	6	18

^a The samples did not break during the experiment.

TABLE II
Weight-Average Molar Mass of PET in Contact with NaOH Solutions in the Presence and Absence of External Loads

Load (N)	M_w	
	NaOH 1M	NaOH 3M
1000	14,700 ± 80	18,000 ± 70
1900	21,700 ± 150	32,800 ± 160
Without stress	–	46,300 ± 460

The M_w for unexposed PET was 44,600 ± 260.

used in this investigation. To find out whether or not chemical reactions actually took place, selected samples were used for viscometry analyses, and the results are displayed in Table II. A significant decrease in molar mass was observed as a consequence of the contact between PET and NaOH solution during the ESC experiments. This is a characteristic of chemical degradation and it is remarkable that it happened in a very short contact time—less than 25 seconds. Another study done by Barbosa³⁶ in the same laboratory showed that recycled PET treated for 10 min with 1M NaOH solution had a molar mass reduction of 15%, whereas in this study the reduction was 67% in less than 25 s (under a load of 1000 N).

The determination of the molar mass of PET in contact with NaOH solution and without external stress was also done to clarify if degradation also occurred in the short contact time just due to the NaOH solution. A 3M solution was spread over the sample for 25 s (the maximum contact time to failure during stress relaxation experiments, as shown in Table I). The value obtained (Table II) was very similar to the one for unexposed PET, confirming that the short contact time of the NaOH solution with the polymer was not, alone, sufficient to cause chemical reactions. The presence of external load was necessary to cause both stress cracking and hydrolysis.

Certainly, the ESC experiment caused scission of PET chains and a possibility to be considered is the influence of the external load. In pioneering work about the influence of mechanical load on the kinetics of chemical degradation of polymers, Zhurkov et al.³⁹ observed that oxidation rate r was accelerated under the presence of external stresses and proposed that this dependence follows an Arrhenius-type equation:

$$r = A \exp \left[\frac{-(\Delta G - B\sigma)}{kT} \right] \quad (2)$$

where ΔG is the free energy barrier, B the activation volume, k the Boltzmann constant, and T the temperature. According to this equation, the applied stress reduces the energetic term for chemical reaction, favoring the degradation. A similar type of

phenomenon might have occurred here, resulting in chain scissions in PET molecules during the ESC experiments. This possibility was considered also by Morrison et al.,¹⁴ who observed that PET bottles had a higher tendency to premature failure in contact with sodium bicarbonate solutions. These authors, however, did not measure the molar mass of the polymer to confirm their hypothesis.

The data in Table II indicate, however, that the reduction of PET molar mass was lower when higher values of load were applied. This trend was also observed in studies of polymer oxidative degradation,⁴⁰ and it was attributed to the effects of molecular orientation under higher stresses, reducing the oxygen diffusion into the sample. Similar effect may have happened here, with the diffusion of NaOH solution being lower when PET was exposed to higher loads. Another result that draws attention in Table II is that the chemical degradation was more effective when less concentrated solutions were used. It seems that

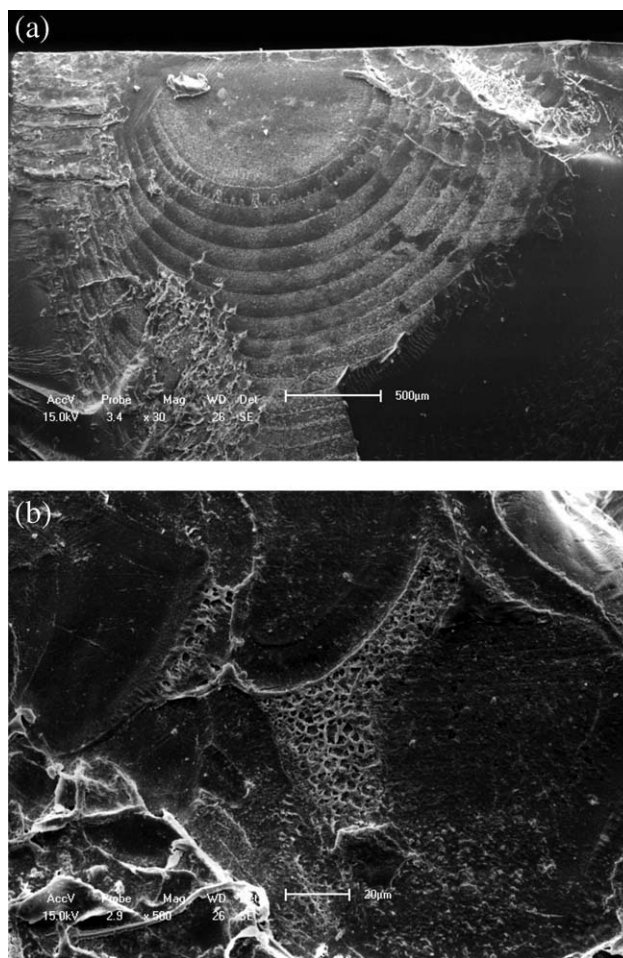


Figure 11 Scanning electron microscopy of the fracture surface of a PET sample broken during stress relaxation test at 1000 N and under the presence of 1M NaOH solution. (a) Low magnification; (b) higher magnification of the circular arcs of (a). The arrow indicates the crazed region.

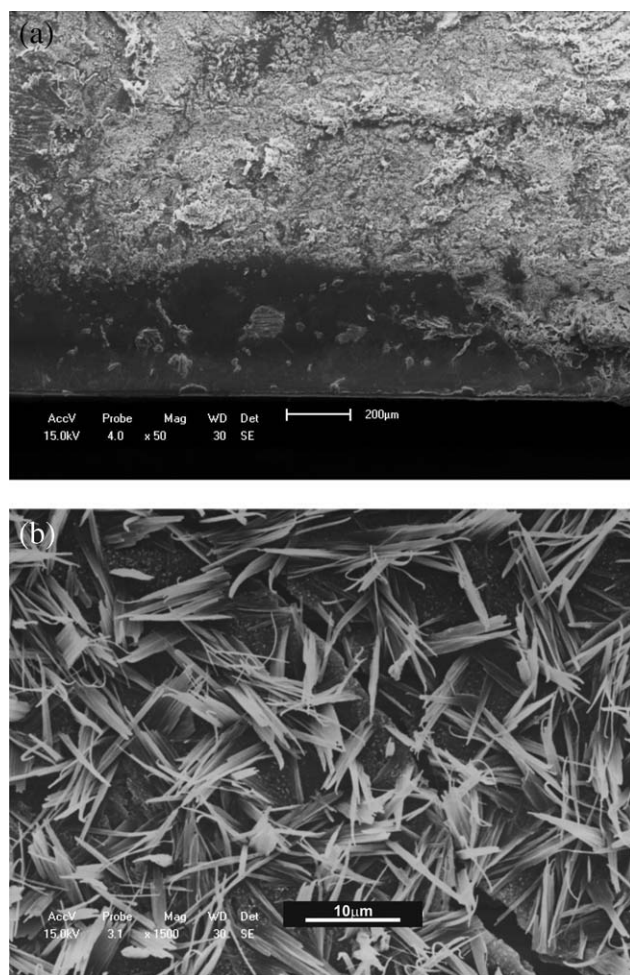


Figure 12 Scanning electron microscopy of the fracture surface of a PET sample broken during stress relaxation test at 1000 N and under the presence of 3M NaOH solution. (a) Low magnification; (b) higher magnification of the central area of (a).

the synergistic effect of hydrolysis and mechanical stress was more significant with the 1M solutions. The high number of surface cracks in samples exposed to 3M NaOH solutions (Fig. 9) suggest that with this NaOH concentration the level in interaction with PET enhanced the stress cracking effects even though the chemical degradation was not at its maximum. In other words, with this NaOH concentration, ESC was the predominant effect.

The results shown in Table II also explain the lower fracture time observed in experiments done under high loads (Table I). It is well known that the higher the molecular size, the more resistant to stress cracking the polymer is.¹ The reason for this trend is that a product with smaller molecules has a lower concentration of entanglements, which are load bearing components to withstand the harsh condition of the stress cracking attack. If the molar mass is reduced during the experiment, as observed here (Table II), it is reasonable to accept that the con-

centration of entanglements is also reduced, with direct consequences to the stress cracking behavior.

The fracture surfaces of the test bars broken during stress relaxation experiments are displayed in Figures 11–13. Figure 11(a) shows the fracture surface of a sample broken during the contact with the 1M solution and under a load of 1000 N. The mirror zone, where the fracture probably started, is clearly seen at the top of the surface, which coincides with the side where the ESC fluid was applied. The pattern resembles the failure by fatigue loadings, with ring-like features emanating from the centre of the mirror zone. The large area involved with this feature indicates a high level of fragility, which is consistent with the mechanical behavior (Table I). A higher magnification of an internal area of this fracture surface is shown in Figure 11(b). Porous structures similar to crazes were observed [indicated by an arrow in Fig. 11(b)], which is typical of failure caused by ESC.¹⁵ At the bottom left of Figure 11(b), one can see a fibrillar structure caused by extensive drawing. This type of feature was more intense in the sample exposed to 3M NaOH solution [Fig. 12(b)] and resembles needles [similar to the ones shown in Fig. 7(f)], where, apparently, the fibrils were not fully developed. The fracture of the fibrils into needles may be a result of the reduction of molecular size during exposure, inhibiting full stretching of the molecules. Under lower magnification [Fig. 12(a)], the fracture surface showed extensive white regions, which could be a consequence of a larger plasticized area in the specimen. The mirror zone of Figure 12(a) (lower part) showed spots of material within the fragile region, which will be considered below.

The fracture surface of the sample exposed to 3M NaOH solution under a load of 1900 N is displayed in Figure 13. Under low magnification [Fig. 13(a)], the variety of features is evident, with smooth regions intercalated with rough ones, indicating that the whole fracture process took place in several different steps, prolonging the final failure. A higher magnification image of the interphase between the smooth and rough regions is shown in Figure 13(b), where molecular stretching is seen on the left hand side. This molecular stretching may be due to the localized plasticization that caused molecular softening, leading to extensive deformation. In Figure 13(c), a higher magnification image of the smooth region of Figure 13(a) is displayed. Similar to Figure 12(a), there are small spots of material within this region. This type of feature was observed only in samples tested under the stress relaxation condition and with this NaOH concentration (3M). We do not know the reason for this feature, but it is possible that the molecular scissions caused by the presence of NaOH solutions (Table II) released molecule

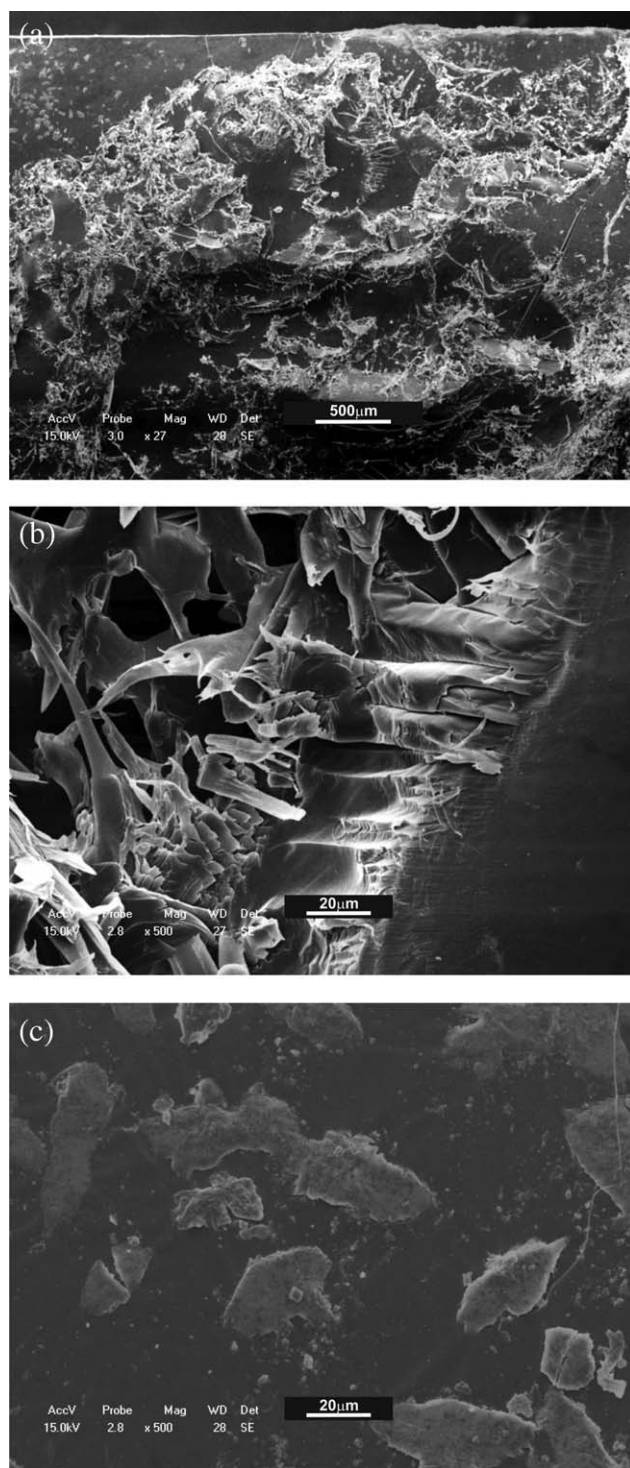


Figure 13 Scanning electron microscopy of the fracture surface of a PET sample broken during stress relaxation test at 1900 N and under the presence of 3M NaOH solution. (a) Low magnification; (b) detail of the interphase between the smooth and rough zones; (c) higher magnification of the smooth region, showing spots of material.

segments at entanglements that, together with the plasticizing effect of the solution, were able to crystallize during testing. This is similar to what occurs during photodegradation of polymers,⁴¹ which is

called chemi-crystallization and was also reported during hydrolysis of PET.⁴² When crystallization occurs from the solid state, which is common with PET, this is named cold crystallization and a whitening effect is observed on the product.⁴³

Absorption experiments

When a polymer is in contact with a fluid, several types of effects may take place, including mass gain, mass loss, or dissolution. The mass gain happens when the fluid diffuses into the bulk of the polymer, whereas mass loss is usually related to extraction of compounds like additives and oligomers or to degradation. In an attempt to gain more information regarding the interaction between the NaOH solutions and PET, absorption experiments were conducted for periods of up to 65 days, and the results are displayed in Figure 14.

At the very beginning of the experiment, a mass gain of 0.053% and 0.036% were observed when test bars were immersed in the 1M and 3M NaOH solutions, respectively. As the mass gain is closely related to the interaction between the fluid and the polymer,³⁰ the 1M solution was more effective to interact with PET and, therefore, to cause stress cracking as was actually observed (Table I). However, this small gain in mass was detected only during the first day of experiment. After that, the samples started to lose mass continuously, resulting in mass reductions after 65 days of 4.5% and 14.2% for the 1M and 3M solutions, respectively. The magnitude of these numbers suggests that the NaOH solutions were not only extracting low molar mass compounds but also degrading the polymer, as already observed in Table II. The higher effect caused by the 3M solution in prolonged exposures indicates that in this condition the most important effect was chemical degradation, whereas in short exposure times and in the presence of mechanical stresses, the stress cracking was predominant.

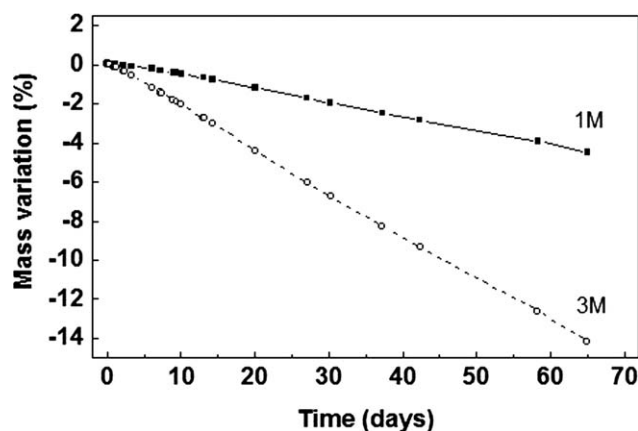


Figure 14 Mass variation of PET in NaOH solutions.

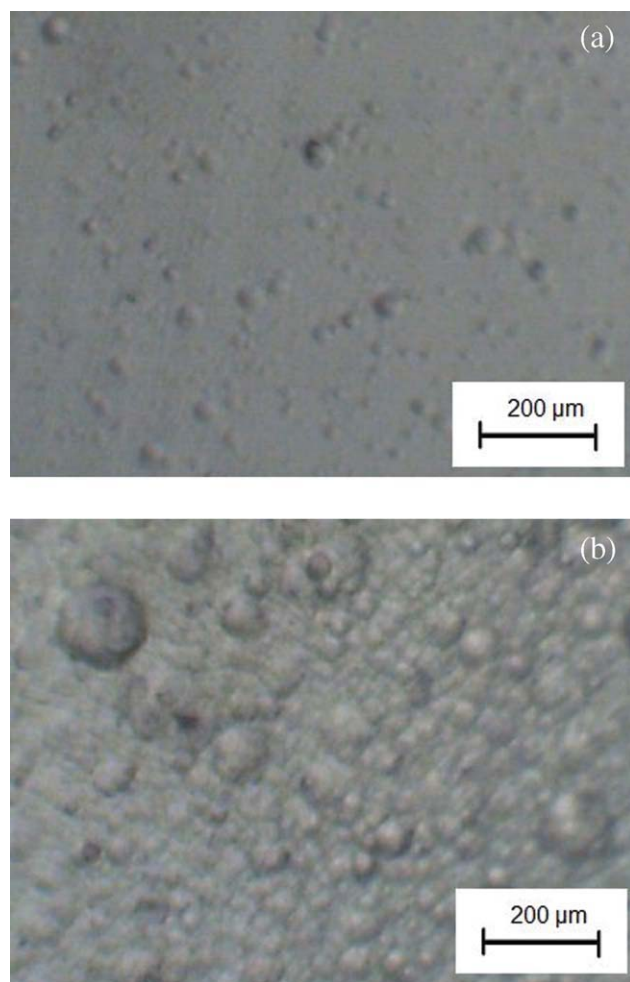


Figure 15 Optical microscopy images of sample bars after 65 days of absorption experiments with NaOH solutions. (a) 1M; (b) 3M. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

After the absorption experiments, the sample exposed to 3M solution was more opaque than the one exposed to 1M. The optical microscopic inspection showed that the opacity was due to porosity within the sample, being more intense in the one exposed to the 3M NaOH solution (Fig. 15), which is in agreement with a higher mass loss (Fig. 14).

CONCLUSIONS

The aim of this work was to investigate the stress cracking behavior of PET under the presence of NaOH aqueous solutions. Injection molded bars were exposed to the stress cracking agent during tensile and relaxation tests and the properties monitored for various NaOH concentrations. The most significant effects were noted with the 3M solution, causing a large deterioration in surface appearance. The simultaneous action of mechanical stress and the contact with NaOH solutions caused hydrolysis in PET molecules, with considerable decrease in

molar mass. This effect was more evident when lower stresses were used. The contact of NaOH solutions with PET in the absence of stress, on the other hand, did not lead to molecular scission reactions. This observation was taken as an evidence that chemical degradation occurs together with stress cracking. The analyses of the fracture surfaces done by scanning electron microscopy showed that for all samples the failure started at the surface in contact with the stress cracking agent. Several different types of features were observed in the fracture surfaces, including, crazes, mirror zones, needles, fibrils and ring-like patterns.

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