

Environmental Stress Cracking of Poly(3-hydroxybutyrate) Under Contact with Sodium Hydroxide

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Received: April 7, 2014; Revised: March 9, 2015

Environmental stress cracking (ESC) is one of the most important causes of polymer premature failure, occurring when a combination of mechanical load and an aggressive fluid is applied. The phenomenon is well known by polymer producers and product designers but its mechanisms are not very well understood. Although the ESC effects of many commercial polymers are well known, this type of failure in biopolymers were not studied yet. In the current work, the stress cracking behaviour of poly(3-hydroxybutyrate) (PHB) with 4,0 and 6,2% of hydroxyvalerate (HV) was investigated in injection-moulded bars under contact with sodium hydroxide (NaOH) solutions. The experiments were conducted using two different types of stress arrangements: (i) an ordinary tensile testing and (ii) a relaxation experiment. In both situations the injection-moulded bars were exposed to the NaOH solution and some testing conditions were varied, like the cross-head speed of the tensile test and the maximum load of the relaxation arrangement. The results showed that NaOH acted as a strong stress cracking agent for PHB, causing surface cracking and reducing significantly the mechanical properties. Catastrophic failure with an extensive surface damage was also observed by photographed and scanning electron microscopy (SEM) images. The magnitude of the effects increased with decreasing crosshead speed and increasing loading level.

Keywords: PHB, stress cracking, mechanical properties, failure

1. Introduction

Most polymer products are made from non-renewable resources like oil-based chemicals. In recent years, polymers made from natural products are gaining increasing interest in several areas, including biomedical, packing, agricultural and conventional consumer products. Among these polymers, poly(3-hydroxybutyrate) (PHB), a semicrystalline thermoplastic, biodegradable and biocompatible (nontoxic) resin, is a promising material. PHB is obtained from renewable resources (mainly sugar cane) by biotechnological processes of low environmental impact. Ongoing research, intended on establishing its properties, extending its applications, and optimizing its processing conditions is reported in the literature¹⁻⁶.

During their lifetime, polymer products may be subjected to aggressive environments, like high temperature, ultraviolet radiation and certain chemicals, with consequences like the deterioration of mechanical properties and/or poor surface appearance. The investigation of the nature of these damages is of great importance to reduce failure probability and hence to design products with extended lifetime^{7,8}. The reduction of polymer properties by the action of an active chemical agent under simultaneous stress is a phenomenon defined as environmental stress cracking (ESC)⁹.

ESC is one of the main reasons for shortening the lifetime of polymers, accounting for about 25% of the failures¹⁰, where the formation of surface crazes and cracks result in lower properties. The magnitude of the damage caused by ESC is related to size and distribution of the crazes and cracks formed, together with their capacity for energy absorption, and with the dissolution of the active agent in the polymer (or polymeric compound)¹¹. Even though the effects of stress cracking on polymers is known for many decades^{12,13}, very few investigations are reported in the scientific literature. One of the authors of this paper has some contribution in this field, with works on the combined effect of stress cracking and chemical degradation of poly(ethylene terephthalate) (PET)^{14,15}, poly(methyl meta acrylate) (PMMA)^{16,17}, polycarbonate (PC)¹⁸ and polystyrene (PS)¹⁹.

To the best of the authors knowledge, no work was done on the investigation of ESC behavior of PHB. This is considered to be an important gap in this field due to increasing importance of this polymer in, for example, medical prosthesis. In this application the product may be subjected to body fluids and mechanical loads that might cause ESC. For example, when using PHB implants in cats, failure was reported at very low levels of stresses²⁰, but the relation to ESC was not considered by the authors.

This work is concerned with the environmental stress cracking behaviour of PHB in contact with an aqueous

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solution of sodium hydroxide (NaOH) 3M (12%) acting as an aggressive agent. The effect of NaOH in ESC mechanisms were studied by tensile experiments under different arrangements. Thermal properties and crystallinity were determined by differential scanning calorimetry (DSC) whereas the effects on surface cracking, and fractography of injection molded bars were investigated by macrophotography and scanning electron microscopy (SEM) analyses.

2. Experimental

Two grades of PHB were used, namely (i) FE-141, with 3-hydroxyvalerate (3HV) content 4.0%, MFR = 23-25 dg/min (ASTM D 1238, 190 °C/2.16 kg), hereinafter called PHB-1; and (ii) FE-112, with 3HV content 6.2%, MFR = 30-33 dg/min, called PHB-2. Both resins have a density of 1.2 g/cm³ (ASTM D 729) and were supplied by PHB Industrial S/A (Brazil). Analytical grade of sodium hydroxide (NaOH) was used as stress cracking agent in concentration of 3M (12g/100 mL). The chemical structure of 3HB and 3HV structural units are given in Figure 1.

Type I (ASTM D 638) tensile test bars were produced in a Romi 130 injection molding machine, operating with a barrel temperature ranging between 150-190 °C and the mold at 20 °C. Mechanical properties under tension (modulus, strength, deformation at break) were measured at room temperature (23 °C) with an EMIC DL2000 universal testing machine with load cell of 5 kN; tests were performed with crosshead speeds ranging between 0.1 and 5.0 mm/min. In addition, a tensile relaxation test was conducted, in which a load (from 231 N to 1099 N) was pre-applied and its decay monitored as a function of time for up to 20 minutes. In both cases, tensile and relaxation conditions, the fluid was applied on the surface of the samples during testing, following a procedure described elsewhere¹⁵. After testing, the fracture and molded surfaces were photographed with an Olympus 10 MP digital camera and by scanning electron microscopy using a Shimadzu SSX 550 Superscan equipment. Fractured surfaces were sputtered with gold prior to SEM inspection to avoid charging.

Thermal properties and degree of crystallinity were determined using a differential scanning calorimeter DSC Q20 TA Instruments, with ~5 mg samples, at constant heating rate of 10 °C/min, from 0 °C to 200 °C under nitrogen flux of 50 mL/min. From DSC scans two melting endotherms were observed, and melting temperature of peak I (lower endothermic peak temperature) and peak II (higher endothermic peak temperature), (T_{pI}) and (T_{pII}), were determined, as well as latent heat of melting, ΔH_m^o and crystallinity degree. The crystallinity degree was computed from the melting peak latent heat as:

$$X_c = \frac{\Delta H_m}{\Delta H_m^o} \quad (1a)$$

where:

$$\Delta H_m = \frac{\int_{t_1}^{t_2} |J(t) - J_0(t)| dt}{m_s} \quad (1b)$$

where $J(t)$ is the heat flow (W/g) between the sample and the surroundings, $J_0(t)$ is suitable virtual baseline during the event, t_1 and t_2 are the initial and final times of the event, m_s is mass of the sample (mg), and ΔH_m^o is the latent heat of fusion of the 100% crystalline polymer. For PHB: $\Delta H_m^o = 146 \text{ J/g}$.^[13]

3. Results and Discussion

3.1. Differential scanning calorimetry (DSC) measurements

It is very well known that morphology and crystallinity have a great influence on polymer performance²¹. To assess the effect of HV content on crystallinity, thin films were removed from the moulded surfaces and tested by DSC. Since PHB is a high crystallinity polymer, well defined melting peaks were observed with double melting for both types of PHB, as shown in Figure 2. Complex melting peaks were observed for both materials with the main ones occurring in the range 142–179 °C and 137–176 °C for PHB-1 and PHB-2, respectively. Multiple melting peaks are commonly observed in many semicrystalline polymers, including polyesters such as poly(ethylene terephthalate) (PET)²² and poly(trimethylene terephthalate) (PMT)²³, polyethers such as poly(ether ether ketone) (PEEK)²⁴, and polyolefins such as polypropylene (PP)²⁵. Multiple melting peaks may be attributed to the melting of crystals of different sizes and perfection. Specifically, small and less perfect crystals melt at lower temperature relative to the larger and more perfect ones. Multiple peaks may be also attributed to the existence of different crystal modifications, or to melting/recrystallization processes occurring during the DSC scan^{26,27}. The degree of crystallinity calculated according to Equation 1 was 49.8% and 47.0% for PHB-1 and PHB-2, respectively. It is known that high crystallinity is related to a compact and dense phase; it is also known that hydroxyvalerate units (HV) inserted within PHB chains tend to decrease its crystallinity²⁸. Table 1 summarizes the results obtained from DSC thermograms.

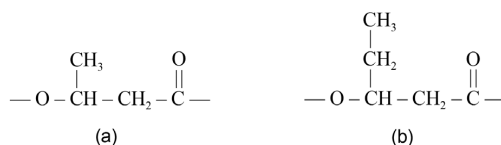


Figure 1. Structural units of 3-hydroxybutyrate 3HB (a) and 3-hydroxyvalerate 3HV (b). Commercial PHB's used in the present work are random copolymers of 3HB and 3HV.

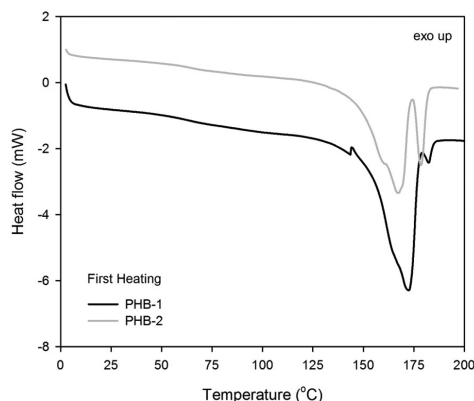


Figure 2. DSC scans of PHB-1 and PHB-2 during heating at 10 °C/min.

3.2. Stress cracking under tensile testing

Figure 3 shows stress-strain plots for PHB-1 unexposed and exposed to the NaOH solutions, with crosshead speeds ranging between 0.1 and 5.0 mm/min. Even in the absence of NaOH, PHB failed in a fragile way due to the combination of high crystallinity and high glass transition temperature. Figure 3b shows a strong effect of the crosshead speed when NaOH solutions are applied during tensile testing. The lower the crosshead speed, the longer is the contact of the aggressive solution with the polymer surface, increasing the effects of stress cracking. This caused in a great reduction in both tensile strength and maximum elongation and, therefore, showed that NaOH is a strong stress cracking agent to PHB. Even a brief exposure to NaOH during the

Table 1. Melting parameters of PHB-1 and PHB-2 determined during heating at 10 °C/min.

Parameter	PHB-1	PHB-2
Melting range (°C)	125.9 – 182.6	118.3 – 171.9
$(T_p)_I$ (°C)	166.0	153.8
$(T_p)_{II}$ (°C)	172.5	167.6
ΔH_M (J/g)	101.2	87.8
X_C (%)	69.3	60.1

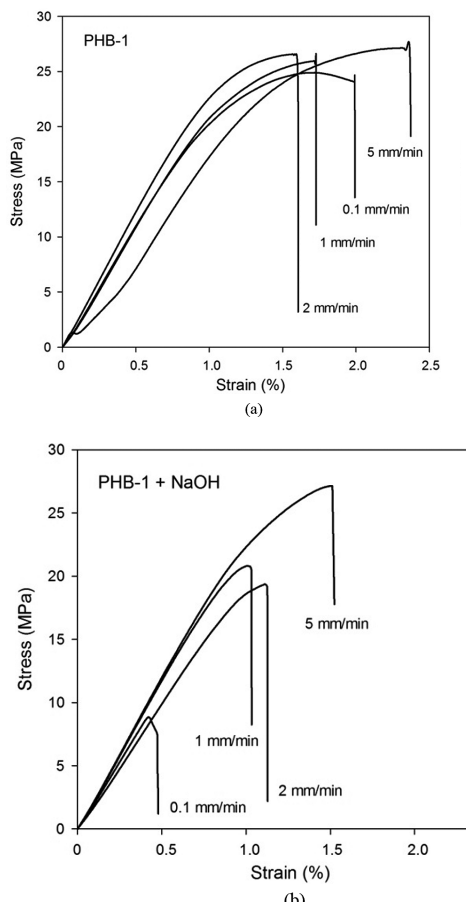


Figure 3. Stress-strain curves of PHB tested under several crosshead speeds (indicated) with specimens unexposed (a) and exposed (b) to the alkaline solution.

test resulted in a remarkable effect on the stress-strain behavior. This chemical has already shown to attack PET¹⁴.

The final results of tensile modulus, tensile strength, and deformation at break of PHB-1 and PHB-2, unexposed and exposed to NaOH are summarized in Table 2. Firstly, an increase in tensile strength with increasing crosshead speed for the unexposed bars is evident, and this is due to viscoelastic effects²⁹. Exposure to NaOH did not affect the elastic modulus significantly, meaning that the solution did not cause plasticization in an extent to soften the bulk of polymer structure. The most acceptable theory of stress cracking mechanism considers that the action of the fluid is restricted to sites of high stress concentration without widespread plasticization¹⁰. The remarkable effect of NaOH was seen in the ultimate properties, tensile strength and maximum elongation, which reduced by 30% and 40% respectively when compared to the unexposed samples. The effect was stronger at low crosshead speeds, when reduction of these properties of 60 and 70% was observed. We suggest that stress and exposure times to the aggressive agent promoted formation of crazes, cracking and, possibly, breakage of molecular chains¹⁴.

3.3. Analysis of macroscopic images

The surface of PHB sample bars, tested at several crosshead speeds, unexposed and exposed to NaOH, were analyzed in photographic images. Figure 4 shows unexposed and NaOH exposed PHB-1 bars after tensile testing at 2 mm/min. In Figure 4a some micro-fissures on the shell region of the bar are observed. This is the region most susceptible to the occurrence of ESC due to stress concentration effects. During ordinary tensile testing, micro-fissures or cracks can be originated by chain stretching and slipping of the crystal planes³⁰. When NaOH solution is applied during testing, the effects of stress cracking appear as crazes and cracks at the sample surface as a result of the physical and/or chemical attack^{8,31,32}. The presence of tiny crazes in a brittle polymer may be a way to absorb energy before fracture, acting as toughening agent³³. This was not the case here, since the tensile properties, including maximum elongation, were reduced in contact with the active fluid. Instead, the crazes and cracks act as stress risers, causing a deterioration in mechanical properties. Figure 4b shows the macrophotography of PHB-1 exposed to NaOH, which acted aggressively and led to the formation of deeper micro-fissures and cracks.

In Figure 4c the formation of a greater number of deeper crazes is observed when lower crosshead speeds are used, which coincides with lower mechanical properties (Table 2). The slower the crosshead speed, the longer is the time that the sample remains under the stress, favoring the surface damage. When this type of specimen was tested under NaOH solution much more cracks are noted (Figure 4d), including the formation of deeper cracks, unable to absorb a high amount of energy before failure and thus causing a more brittle fracture. According to Bernier & Kambour¹², when the ESC 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 are observed. Similar tendencies were observed before by one of the authors of this work^{14,15,17}.

Figure 5 shows images of PHB-2 exposed to NaOH and tested at 1.0 mm/min (Figure 5a) and at 0.1 mm/min (Figure 5b). It is clear that cracking is notably more severe when the sample is tested at 0.1 mm/min when compared to the one tested at 1.0 mm/min, following the same trend showed in Figure 4. The pattern of surface cracks, however, are different between the two types of PBH's. It is not clear the reasons why these two polymer behave differently,

but the stiffer chemical structure of the valerate units in PBH-2 may be a reason.

In the present work similar values of the crystallinity of PHB-1 and PHB-2 were obtained (see Table 1). However, it is possible that changes of the inner structure were caused by the addition of valerate units, which lead to a more open or irregular structure in PHB-2, as a result of the ethyl side group of the valerate compared to the methyl group of the butyrate (different polarities and energy status).

Table 2. Mechanical properties of PHB unexposed and exposed to NaOH 3M.

Mechanical Property	Crosshead Speed (mm/min)	PHB-1	PHB-1 + NaOH	PHB-2	PHB-2 + NaOH
Tensile	0.1	2393 ± 142	2114 ± 115	2478 ± 29	2332 ± 137
Modulus (MPa)	1.0	2294 ± 29	2447 ± 41	2224 ± 71	2379 ± 252
	2.0	2436 ± 94	2243 ± 270	2179 ± 4	2172 ± 134
	5.0	2195 ± 96	2106 ± 23	1959 ± 21	2139 ± 251
	0.1	24.51 ± 0.54	8.32 ± 0.74	20.03 ± 0.46	7.80 ± 0.93
Tensile Strength (MPa)	1.0	25.35 ± 0.85	19.37 ± 2.05	22.77 ± 0.44	18.14 ± 0.41
	2.0	26.50 ± 0.12	19.33 ± 0.06	21.79 ± 0.08	20.61 ± 0.71
	5.0	27.18 ± 0.02	24.67 ± 0.38	27.23 ± 0.21	21.08 ± 2.27
	0.1	1.76 ± 0.32	0.47 ± 0.01	0.95 ± 0.00	0.43 ± 0.00
Deformation at Break (%)	1.0	1.68 ± 0.06	0.97 ± 0.08	1.47 ± 0.19	0.90 ± 0.05
	2.0	1.57 ± 0.00	1.10 ± 0.03	1.39 ± 0.14	1.09 ± 0.12
	5.0	2.25 ± 0.18	1.85 ± 0.12	1.65 ± 0.04	1.15 ± 0.05

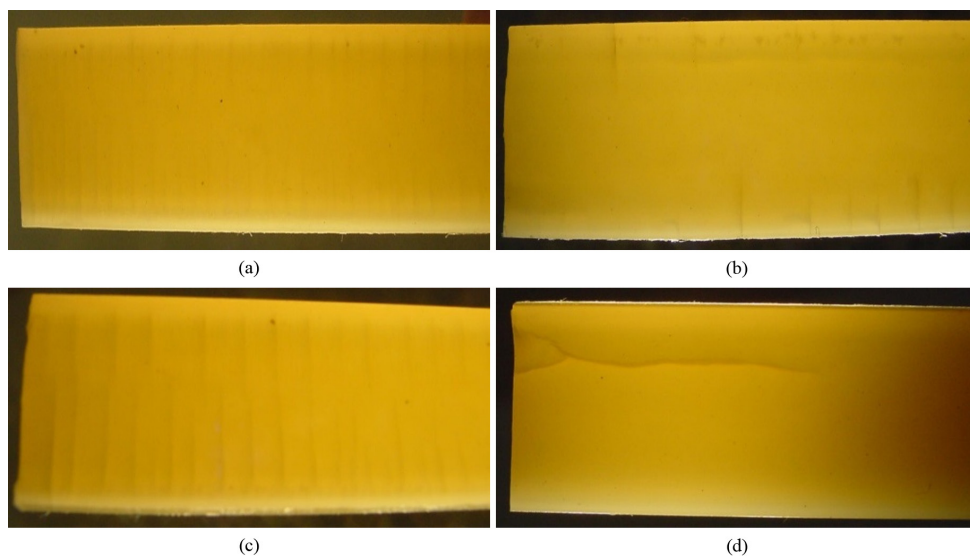


Figure 4. Macrophotographic images of the surface of PHB-1 samples after tensile testing: (a) unexposed to NaOH at 2 mm/min, (b) exposed to NaOH at 2 mm/min, (c) unexposed to NaOH at 0.1 mm/min, (d) exposed to NaOH at 0.1 mm/min.

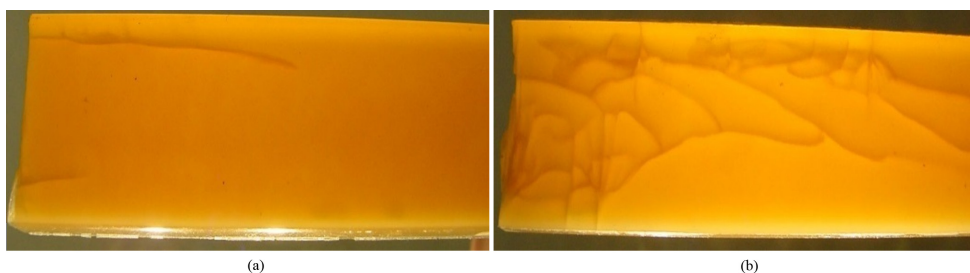


Figure 5. Macrophotographic images of the surface of PHB-2 samples after tensile testing, (a) exposed to NaOH at 1.0 mm/min, (b) exposed to NaOH at 0.1 mm/min.

3.4. Stress cracking under stress relaxation

In this experiment, test bars of PHB-1 and PHB-2 were preloaded to 25%, 50% and 75% of the maximum stress measured in the standard tensile tests, and the machine stopped at a constant deformation. During time, the stress relaxation takes place, which is a typical effect of the viscoelastic behavior of polymers²⁹. During this procedure, NaOH was applied to the bar surface and the decay of load was monitored with time up to a maximum of 20 minutes. Typical results are given in Figures 6 and 7 as plots of load vs. time. It was observed that both PHB-1 and PHB-2 not exposed to NaOH withstand the stress without fracturing during the pre-established 20 minutes. The decay in load was similar in both polymers and was more intense when higher initial loads were applied. When the experiment was conducted with the bars exposed to NaOH the decrease in the load was significantly higher and, very important, in many samples the experiment did not reach the end of the exposure time of 20 minutes since the bar fractured before that. From these curves, the relaxation rate was determined as the ratio between the decay of load and the exposure time (20 minutes or until fracture). Table 3 shows the effect of the preloads on the relaxation rate of PHB-1 and PHB-2. There is an increase in the relaxation rate with the initial load for all the systems investigated.

All samples tested under stress relaxation and in contact with NaOH failed before the end of the defined exposure time of 20 minutes. The effect of the preload on the time of failure is shown in Figure 8. The higher the preload the more rapid the sample breaks. The effect is more intense with PHB-2, indicating that, under these conditions, this grade is more susceptible to the stress cracking effect under the contact with NaOH solutions.

Aggressive external environment reduces the time that the material can withstand high stresses without failure. The formation of surface crazes and cracks is the most visible effect of stress cracking that result in fracture during

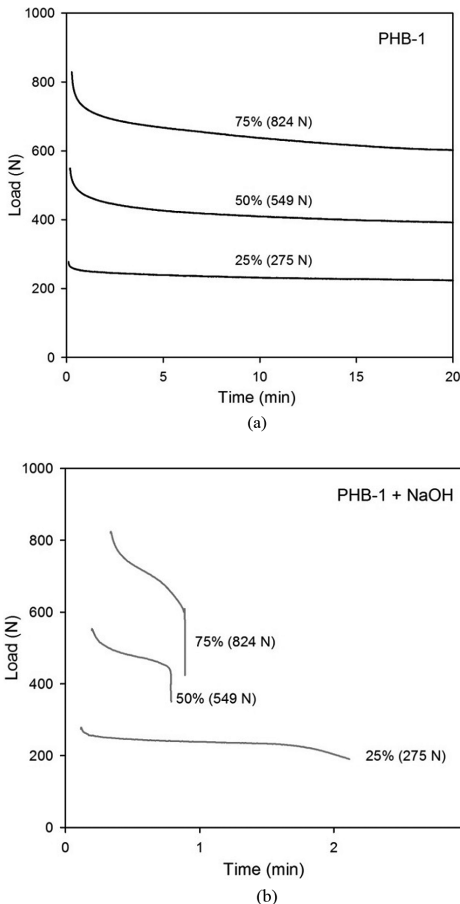


Figure 6. Stress relaxation curves for PHB-1 samples tested without (a) and with (b) NaOH.

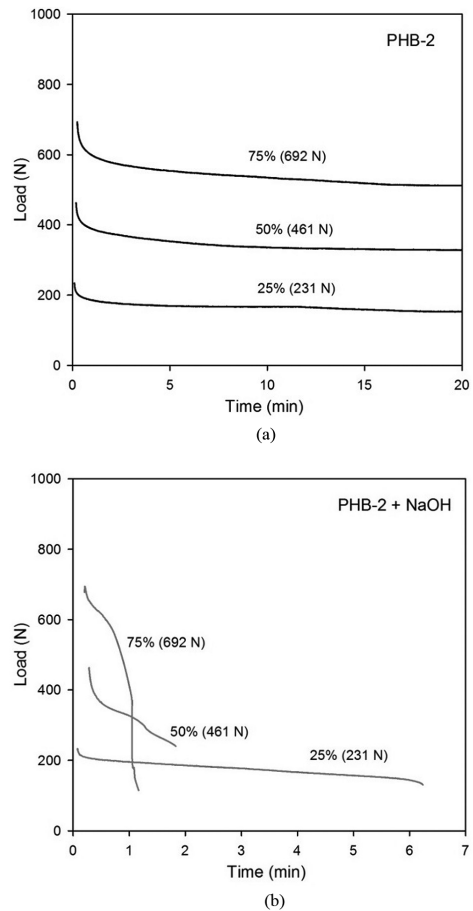


Figure 7. Stress relaxation curves for PHB-2 samples tested without (a) and with (b) NaOH.

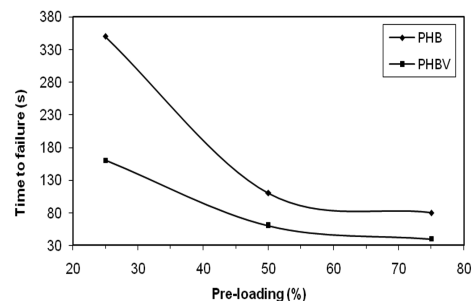


Figure 8. Time to failure of PHB-1 and PHB-2 as a function of pre-loading.

stress relaxation experiments. Breaking of linkages of tie molecules, dislocation and slips of crystalline planes, are also possible factors that may lead to the formation of open (less dense) structures that may facilitate the access of NaOH to the inner layers of PHB. This condition could promote local plasticizing and lead to craze initiation, growing and, ultimately, to fracture. Since ESC depends on the diffusion of the chemical agent into the polymer structure, the rate of fluid absorption is a critical parameter affecting the rate of craze initiation and extension. The faster the chemical agent is absorbed, more rapidly the polymer will be subjected to crazing and subsequent failure¹⁰. In a previous work³⁴ PHB-2 was observed to absorb higher quantities of NaOH than PHB-1.

Figures 9 and 10 show images of the surface of test specimens subjected to stress cracking during stress relaxation tests. The appearance of surface damage is evident, which become more visible and intense as load increases, which also leads to shorter times until fracture. The magnitude of these defects is more intense in PHB-2 than in PHB-1, following results shown before (Figures 4 and 5).

Hydrolysis reactions may occur between the water (H₂O) present in NaOH 3M solution and the ester group (COO) of PHB, releasing reaction products containing acid and alcohol groups. The hydrolysis is a chemical degradation reaction very common in polyesters like PET and polycarbonate³⁵ and is of major importance in defining their lifetime. Since the hydrolysis rate increases

significantly with increasing temperature³⁶, and this work were performed at ambient temperature (23 °C), hydrolytic reactions may be a contributing factor, but probably not the decisive one, for the failure of exposed samples. This, however, is not discharged since it took place with PET in contact with NaOH solutions¹⁴.

Localized plasticizing effects certainly take place in samples exposed to the NaOH solution and is associated to the main reason for ESC deterioration. NaOH diffuses into the polymer structure in sites where stress raisers are present and initially promote the formation of a gel (solubilization), which facilitates the formation of a swollen structure and allows cracks and crazes to develop easily, by breaking chemical bonds in the macromolecular chains and tie molecules (disentanglement) leading to plasticization. The imposition of an external load contributes to plasticizing by facilitating the formation of voids and pores and hence the diffusion of NaOH.

Saponification reactions between NaOH and PHB-1 or PHB-2 occur primarily on the surface. The ion OH⁻ of the NaOH reacts with the carbonyl carbon of the PHB, which is positively polarized, leading to the formation of alcohol and sodium salt. The reaction is irreversible and promotes the polymer degradation. In the existence of pores on the samples shell, the entrance of OH⁻ is facilitated and promotes the breaking bonds of inner layers leading to degradation and decreasing the mechanical strength of PHB.

Table 3. Relaxation rate under several preloads of PHB-1 and PHB-2 samples unexposed and exposed to NaOH.

Preload (N)	Relaxation Rate (N/s)		Preload (N)	Relaxation Rate (N/s)	
	PHB-1	PHB-1 + NaOH		PHB-2	PHB-2 + NaOH
275 (25%*)	0.047 ± 0.005	0.530 ± 0.160	231 (25%*)	0.061 ± 0.007	0.292 ± 0.035
549 (50%*)	0.117 ± 0.021	3.198 ± 0.537	461 (50%*)	0.111 ± 0.002	2.082 ± 0.103
824 (75%*)	0.191 ± 0.009	8.738 ± 1.760	692 (75%*)	0.144 ± 0.008	8.581 ± 1.140

(*) Corresponding percentages of the the breaking stress during tensile experiment of the unexposed sample.

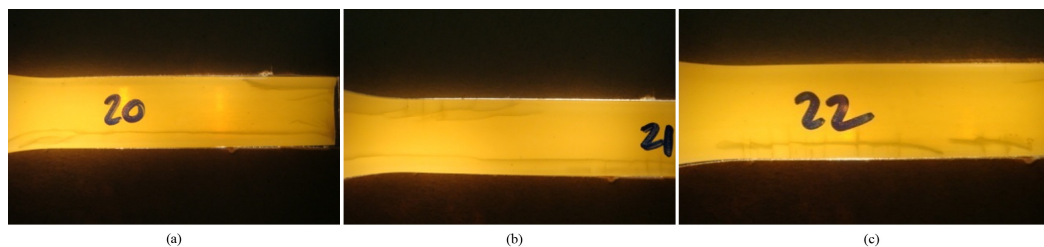


Figure 9. Macrophotographic images of sample surfaces of PHB-1 after tensile testing at 2 mm/min exposed to NaOH, preloads: (a) 275N, (b) 549N, (c) 824N.

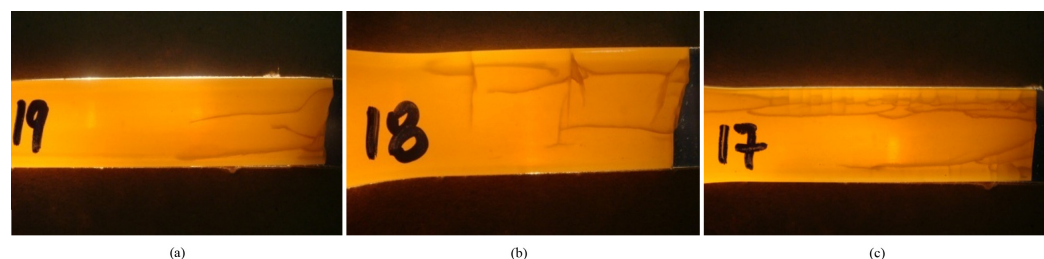


Figure 10. Macrophotographic images of sample surfaces of PHB-2 after tensile testing at 2 mm/min exposed to NaOH, preloads: (a) 231N, (b) 461N, (c) 692N.

3.5. Scanning electron microscopy (SEM)

The fracture surfaces of PHB-1 bars broken under tensile testing are shown in Figure 11 for samples tested under a strain rate of 0.1 mm/min. The images (a), (c) and (e) correspond to the upper border, middle and lower border, respectively, of PHB-1 bar not exposed to NaOH whereas the images (b), (d) and (f) are the corresponding areas of the sample tested under contact to NaOH solution. In general, unexposed samples showed a typical behavior of a fragile material, which is consistent with the mechanical behavior (Figure 3), and not many rough zones. Rough areas are related to ductile behaviour (with energy consumption before fracture) and smooth areas to brittleness (without energy consumption before fracture). Several mirror zones are evident, indicating that fracture initiation occurred from more than one spot. Cracks and void (indicated by arrows) are also seen. Porosity may be related to the existence of internal defects (pre-existing and originated during processing), which are places of stress concentration. In Figure 11b a large area with whitening characteristic is prominent, and is related to the ESC, which causes crazing that alter optical properties due to light scattering by the voids. Even though the stress cracking is a surface phenomenon, the propagation of crazes and cracks took place into the sample interior. Higher magnification images of the samples in Figure 11 are given in Figure 12, showing in better detail features like voids, mirror zones and rough areas. Figure 13 presents SEM images of PHB-1 fractured bar after stress cracking under stress relaxation tests and

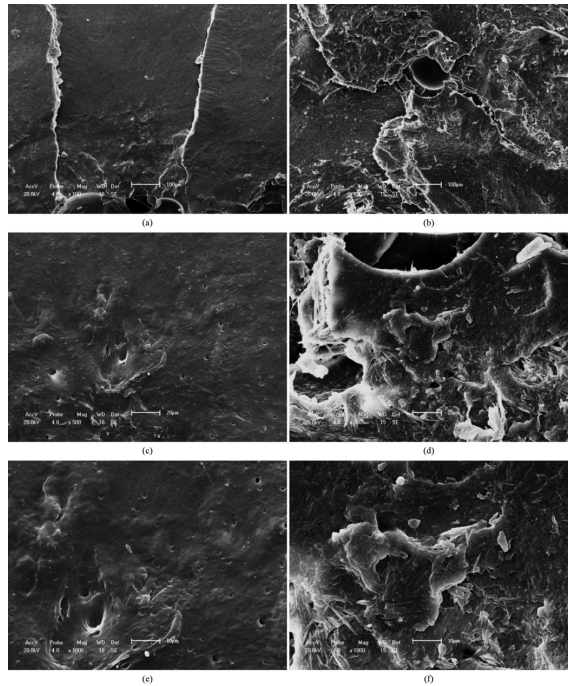


Figure 12. Scanning electron microscopy of fractured surface of PHB-1 bars, during stress *versus* strain tests at 0.1 mm/min. Images (a), (c), (e) of unexposed bars, images (b), (d), (f) of bars exposed to NaOH. Images (a) and (b): low magnification; images (c) and (d): intermediate magnification; images (e) and (f): high magnification.

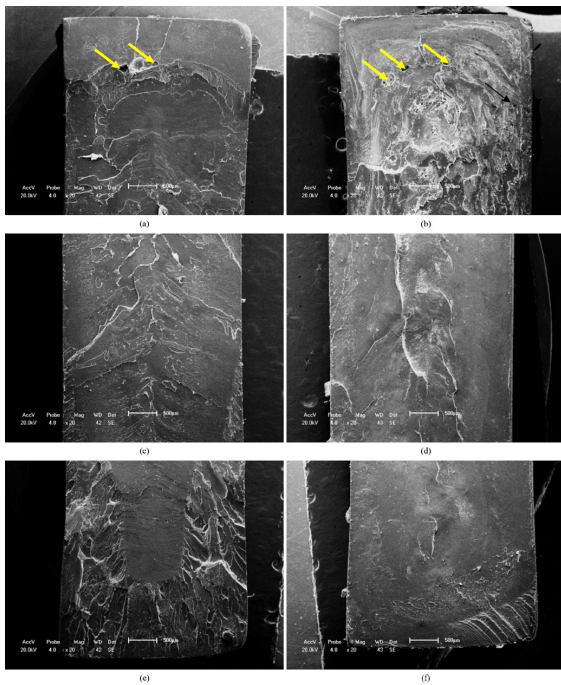


Figure 11. Scanning electron microscopy of fractured surface of PHB-1 bars, during stress *versus* strain tests at 0.1 mm/min. Images (a), (c), (e): upper border, middle and lower border, respectively, of unexposed bars. Images (b), (d), (f): upper border, middle and lower border, respectively, of bars exposed to NaOH.

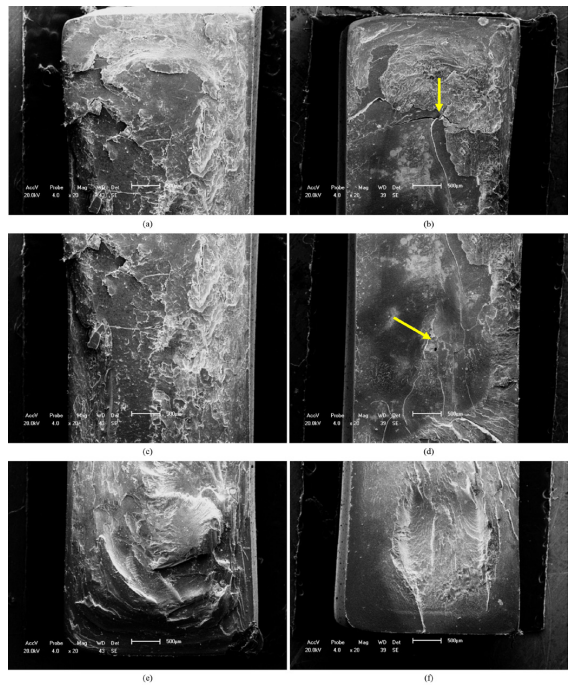


Figure 13. Scanning electron microscopy of PHB-1 fractured bar surface exposed to NaOH, during stress relaxation tests. Images (a), (c), (e): upper border, middle and lower border of the bar, respectively, with applied load of 275 N. Images (b), (d), (f): upper border, middle and lower border of the bar, respectively, with applied load of 824 N.

exposed to NaOH during the experiment. The images of Figure 13a, c and e correspond to the upper border, middle and lower border, respectively, of the PHB-1 fractured bar under the effect of 275 N as preload; whereas (b), (d) and (f) the corresponding images of a sample tested under a load of 824 N. The images for the test with 275 N show a larger amount of whitened areas compared to one tested at 824 N, indicating a more intensive crazing effect. Under a higher load, smoother areas were observed, suggesting that high initial stresses lead to catastrophic failure by brittle fracture. It seems that craze and crack propagation is more likely to take place when lower levels of stress are applied whereas catastrophic failure is more probable when the experiment is done under a higher load. In images (b) and (d) of Figure 13 cracks and porosities inside the bar are noted (indicated by arrows), which may be regarded as start sites of rupture.

4. Conclusions

This work investigated the environmental stress cracking (ESC) of injected samples bars of two PHBV samples with HV content of 4.0% and 6.2%, respectively. NaOH solution 3M was used as the active fluid. The tensile mechanical behavior of these polymers was examined using crosshead

speeds ranging from 0.1 mm/min to 5.0 mm/min. During the stress relaxation tests preloads were used corresponding to 25%, 50%, and 75% of the maximum load obtained during the standard tensile tests. Results showed that the effect of the aggressive agent NaOH was remarkable and all experiments carried out with the bars exposed to NaOH 3M presented inferior properties when compared to the unexposed ones. Action of NaOH on surface layers of PHB, together with the application of mechanical load, resulted in the formation of microfissures, cracks and crazes, leading to the catastrophic failure. We also analyzed the effect of ESC in PHB unexposed and exposed to NaOH 3M applying fatigue tests, the results will be presented in the forthcoming paper.

Acknowledgements

The authors wish to thank Prof. Agnelli (UFSCar, São Carlos, SP, Brazil) for molding the test samples. PHB Industrial SA (Brazil) for the PHB resins. The authors are also grateful to the *Conselho Nacional de Desenvolvimento Científico e Tecnológico* (CNPq/Brazil) and *Fundação de Amparo à Ciência e Tecnologia do Estado de Pernambuco* (FACEPE/Brazil) for financial support.

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