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Contribution to Photodegradation Study, Chemical Behaviour of Unsaturated Polyester Resin Under Irradiation

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This survey reports the effect of thermosetting polymer degradation (unsaturated polyester): chemical degradation, under ultraviolet exposure and damage by neutrons irradiation. In order to evaluate the deterioration of present material, some comparative characterizations have been done between standard samples (blank) and damaged ones. Gel permeation chromatography, differential scanning calorimetry, scanning electron microscopy, FTIR spectroscopy are the techniques which have been used. Photomicrography shows the sample surface attack after few minutes in hot water in addition to an immersion of 2 d within a solvent. For this last test, a loss of mass higher than 25 % has been recorded. The FT-IR spectrum of the deteriorated sample surface confirms the damage. A similar phenomenon is observed with UV degradation (the radiance being fixed at 750 w/m^2) the weight loss was 2.25 %. Three identical samples were exposed to a neutron flux 10^{12} n/cm^2.s during 0.5, 1.0 and 1.5 h. Photomicrography obtained by SEM show the polymer damage degree, several reactions seem to be in competition: crosslinking, the chain breaking and oxidation by radicals. In order to assess the rigidity of present thermosetting polymer, the elastic modulus using the ultrasonic methods was determined. A hardness test (Shore D) has also been carried out. The obtained values of the Young's modulus can be interpreted in terms of crosslinking considering the used irradiation level.

Key Words: Unsaturated polyester, Chemical, Neutrons radiation, Degradation.

INTRODUCTION

Development and research activities on systems design processes of polymeric composites are being carried out to optimize its performances, aiming at exceptional features. This objective is attained by a better control of matrix properties. Within the framework of present research, the authors were interested in a matrix constituted by an unsaturated polyester resin. Applications of unsaturated polyester thermosetting resins are numerous in construction sector, in transport, electric spare parts manufactures, consumer goods and anticorrosive materials. The use of these polymeric materials depends considerably on the evolution of their physical and mechanical properties *versus* the time and the medium in which they are set.

Many works have been achieved to study deterioration phenomena of polymeric matrix composites. Liau and Tseng[1] and Monney *et al.*[2] treated the photodegradation of an epoxy composite, Van Den Abeele and his collaborators[3] studied the chemical behaviour of a polyester composite reinforced with glass fibre (PRV) in caustic and sulfuric medium. Ageing process of the PRV used as glazing material has been studied by Blaga[4]. The weathering deterioration of PRV was also subject for researches performed by Startsev and his collaborators[5]. Lucki *et al.*[6] has studied oxidation in surface of an orthophthalic polyester film. In the nuclear field, polymers resistance to radiations is barely known, few works mention polymers radiation interaction, Devanne[7] studied peroxide network radiochemical ageing. In the same context, Chang and Laverne[8] studied the volatile products clearing. Other studies concern the shock resistance effects of plasticizers addition on unsaturated polyesters[9].

The purpose of the present work is assessment of the deterioration and damage of an unsaturated polyesters matrix. The various deterioration tests include a chemical attack, a photodegradation (UV radiation) and a bombardment by neutron radiations (nuclear reactor). In order to value the behaviour of these materials, comparative characterizations were performed between samples (standard and damaged) by optical microscope and SEM observations as well as chromatography analysis by gel permeation (CGP), differential scanning calorimetry (DSC), infrared spectroscopy (FT-IR) and ultrasonic scanning.

EXPERIMENTAL

During the experiments, the same samples compositions have been maintained *e.g.*, 100 g of unsaturated polyester resin + 2 % of (peroxide) hardener + 1 % of accelerator (cobalt acetate). Two kinds of dimensions of the samples have been used *i.e.*, diameter 10 and 20 mm; thickness 4 and 10 mm, respectively. The resin is composed of a solution polymer within styrene. Polymer is resulting from polycondensation reaction of propylene glycol, maleic anhydride and phthalic anhydride. The polymeric solution analysis has been led with an UV-visible spectrophotometer of type Perkin-Elmer (Lambda, UV/visible). It should be noted that prior to this experiment the purity of present product by precipitation test was confirmed. The sample has been submitted to DSC analysis (Mettler type device). Thermogram has been achieved between 20 and 400 °C using a heating speed of 10 °C/min. Chemical deterioration is studied within several mediums, hot water, acetone and saline mist. The duration of samples immersion varies from 5 to 60 d. The exposure of samples to artificial light (xenon) is done in a chamber 'Solarbox 1500' type. The radiance was 750 w/m^2, the parameters keep stationary until experiment ends. Saline mist accelerated corrosion is realized in a pulverization chamber (5 % saline solution), where samples are inclined with an approximate angle of 20° with regard to vertical. The test severity, its high efficiency, its reproducibility allows industrialists to get some precious data regarding quality, control or improvement of their products.

In order to evaluate the material rigidity the Young's modulus has been determined. The measurer 26MG6XT uses the ultrasonic scanning principle[10]. The exposure to a neutrons flux is carried out in the column of the nuclear research reactor of Draria (Algiers). The energetic profile of the incidental fluxes is constituted of fast neutrons ($\Phi_R = 3.10^{12}$ n cm^{-2} s^{-1}, E = 2 Mev) of thermal neutrons ($\Phi_{TH} = 10^{13}$ n cm^{-2} s^{-1}; E = 0.025 ev) and epithermal neutrons ($\Phi_{epi} = 7.10^{11}$ n cm^{-2} s^{-1}; E > 4.9 ev). The received dose flow is 0.4 Kgy.

In aqueous medium and solvent the samples deterioration is evaluated by permeation chromatography (GPC). The equipment is provided of a Rheodyne 7725i injector and a Waters 600E pump operating with a flow of 1 mL/mn. The separation is performed on an HPLC column filled with micro styragel of 105 Å (reticulated polystyrene gel) whose dimensions are L = 30 cm, diameter =7.8 mm. A detector Waters with diodes dampers (barrettes) of 996-photodiode array permits the simultaneous variation of wavelength absorbance as function of time. Data are acquired in a Digital PC computer, provided by a specialized software Millenium. The samples surfaces damage confirmed by infrared spectroscopy using a Fourier transform spectrometer of Perkin-Elmer type spectrum one have been compared. The spectra of standard samples and damaged ones have been compared. Micrographies obtained by optical microscopy (Nikon 500) and SEM (Jeol JSM6360) permit to display and confirm samples surface deterioration.

RESULTS AND DISCUSSION

From the absorption spectrum (Fig. 1), it is assessed the absorbance value with the wavelength of $\lambda = 262$ nm that corresponds to molar absorbance coefficient of styrene ($\varepsilon = 2.19$ cm^{-1} mol^{-1}). The optical path, thickness of the used tank is 1 cm. 10 mg of resin mass is dissolved in 10 mL of THF, which permits to calculate styrene proportion (41 %).

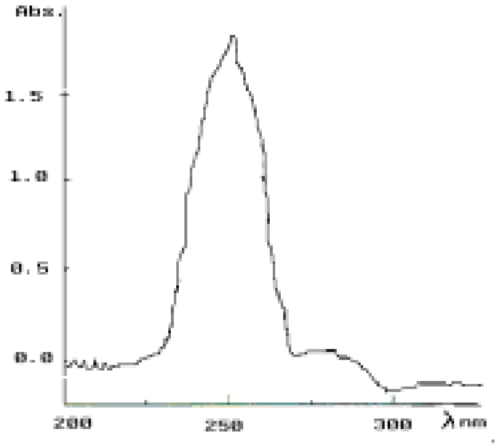


Fig. 1. Absorption spectrum of standard resin sample

Fig. 2 shows the FT-IR spectrum of standard resin sample (non-damaged). The strong absorption bands of 1729, 1286 and 700 cm^{-1} are due to carbonyl and ester ring and vibration of C-O-C rings and aromatic CHS rings.

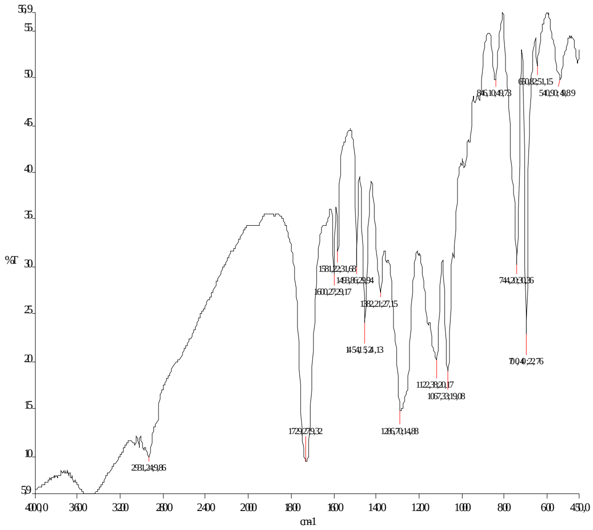


Fig. 2. FT-IR spectrum of standard resin sample (non-damaged)

Fig. 3 shows the scanning calorimetric analysis. It is noted that a transition of the second order at 62 °C as well as an endothermic peak indicating the beginning of the composition (T = 318 °C). The variations of the enthalpy *vs.* the temperature confirm (no crystallization) the amorphous state of the sample.

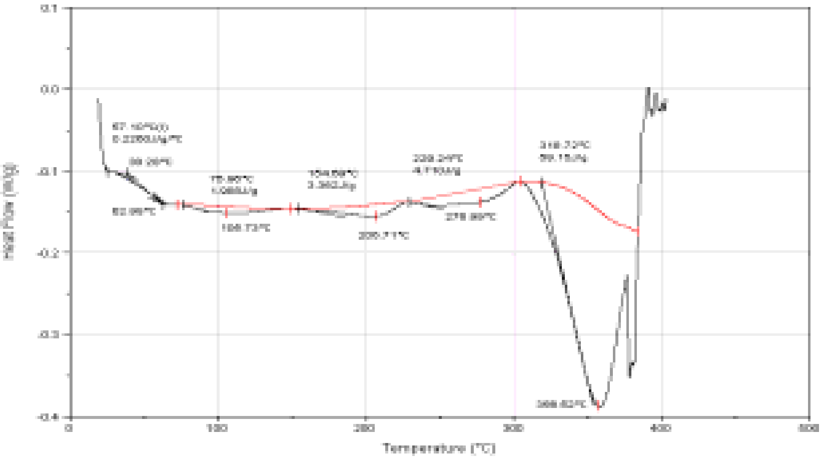
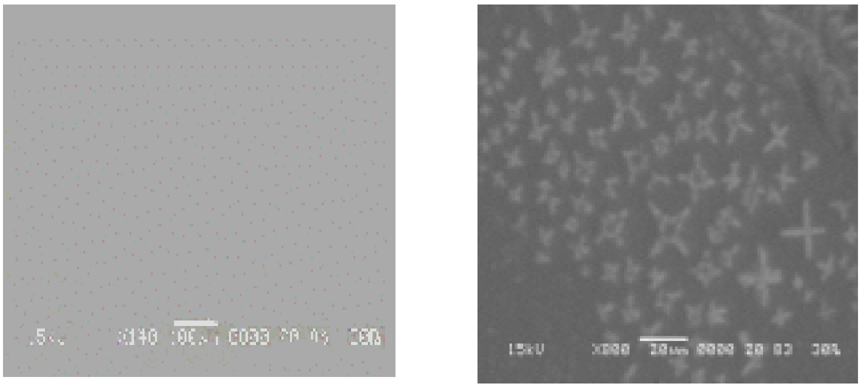


Fig. 3. DSC of the standard sample of polyester unsaturated resin (non-damaged)

The lifetime in real aging (temperature + water) being several tens of years, in order to accelerated agings the temperature is increased. The sample was immersed in hot water (90 °C) during 4 d; surface scaled, fissures, cracks as well as a regular damage are observed on Fig. 4 (SEM).



(a) (b)

Fig. 4. Micrographies (SEM) (a) the sample (standard), (b) after immersion

Ashton[11] reported that the resistance of polyester leaves can be reduced due to the attack of the water of resin in high temperatures. This deterioration is again more marked in a hot water immersion. Results obtained by Dorbe[12] suggested the existence of an osmotic process taking at long term to the formation of blisters and cracks. This situation is caused by a reaction of hydrolysis. Xiao and Shanahan[13] studied the modelling of this phenomenon, reveal the following hypothesis: the scission of chains gives birth down to molecular fragments (low weight) that are eliminated by water that penetrated through flakings. This permits to observe that flakings and scale occur simultaneously. The chromatography analysis, using a UV detector shows the effect of dissolution of some compounds (Fig. 5). This aspect is also confirmed by the acid pH of the final solution (2.5) which initially was 6.5.

In the chemical deterioration test with acetone, it should be noted that the thermosetting sample is not subjected to substantial inflation. However, the leaching of certain compounds has been detected. This result is mentioned by some authors[1]. The obtained micrographics by optical microscopy, reveal a state of surface damage in a non-uniform way. A juxtaposition of cavities resulting from the leaching of certain parts was observed (Fig. 6).

The FTIR spectrum (Fig. 7) of the damaged sample surface confirms the damage. The interpretations give the following observations. A very substantial attenuation of absorption bands to 3000 cm^{-1} that corresponds to methylene rings. Depreciation of absorption band to 1729 cm^{-1} characteristic of ester carbonyl ring.

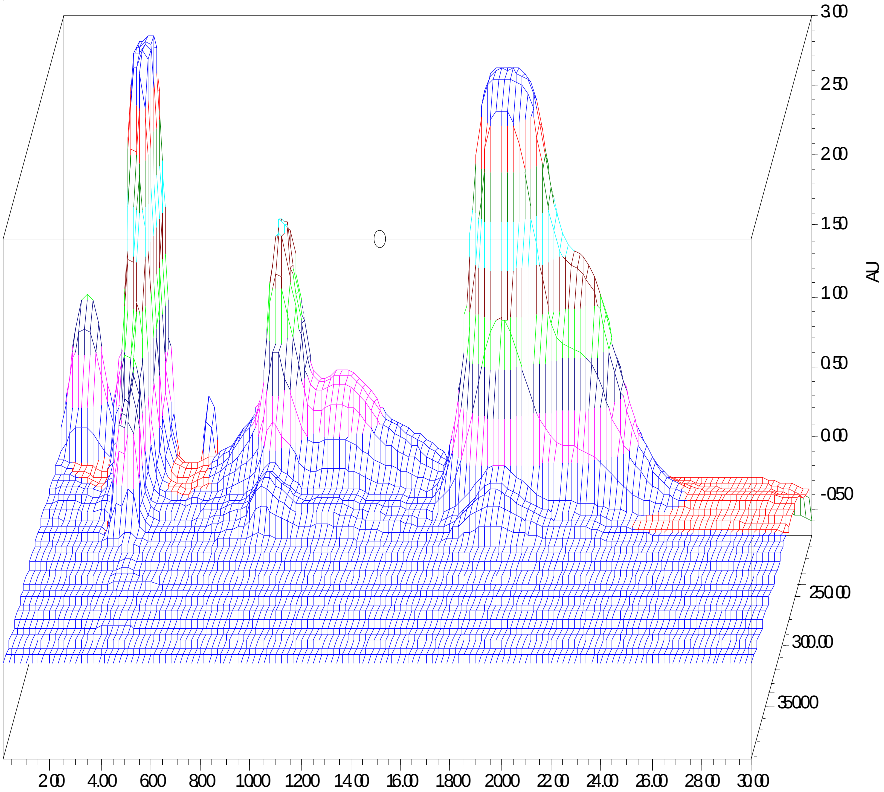


Fig. 5. Qualitative analysis of water by GPC after immersion test

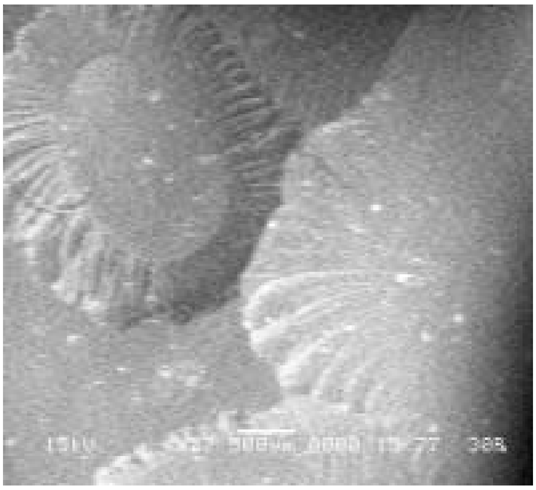


Fig. 6. Micrographic of partially leached sample by acetone

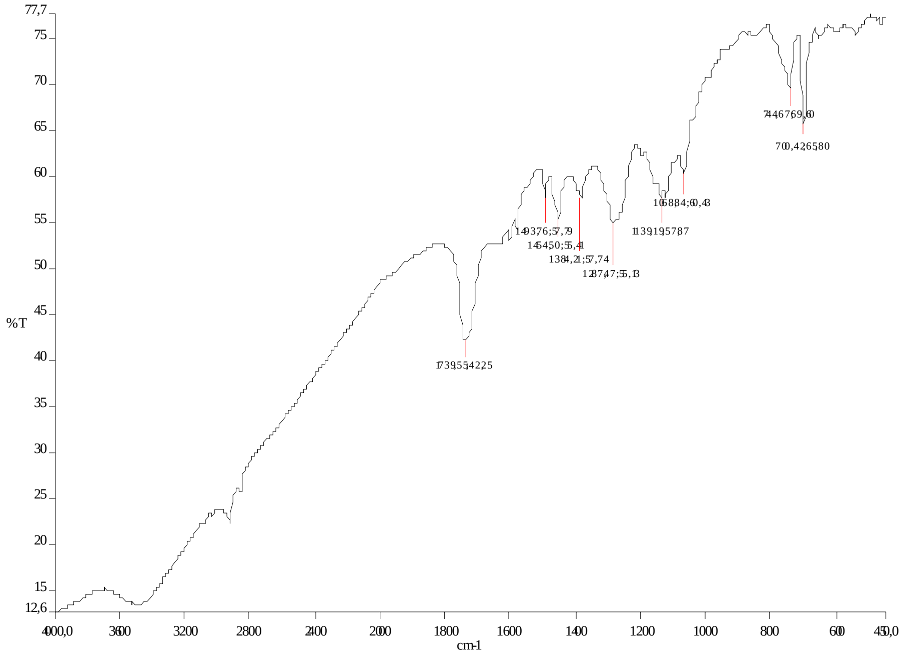


Fig. 7. FTIR spectrum of the damaged resin

The transmission percentage passes from 17 to 55 % for C-O-C group (1286 cm^{-1}). Intense reduction of the absorption band corresponding to -O-O- peroxide group (744 cm^{-1}).

In present case, acetone as an aprotic polar solvent is characterized by two important parameters, a dielectric constant (e) = 20.7 that indicates the capacity of a solvent to separate the charges while the other is dipolar moment (µ) = 2.86. This high degree of (dielectric constant) polarity, shows the electrical charges presence that will interfere to reduce the strength of the solid intermolecular attraction, which is translated by dispersion in the solvent. Otherwise, acetone contains a polar hydrophilic group (carbonyl, C=O) that will increase dissolution. Fig. 8 shows the sample weight evolution *vs.* to the immersion time. The experiment of photodegradation consists in exposing test material. They are irradiated by a powerful energy source whose irradiance was 750 w/m^2.

Fig. 9 shows the sample weight evolution *versus* to the exposure duration. A loss of mass starting at 168 h of exposure has been observed. This reduction stabilizes at the end of 235 h to reach 2.5 %.

The thermoset sample includes carbonyl rings (C=O) and peroxide (-O-O-) and have bonds dissociation energies corresponding respectively to 290 nm and 400 nm of wavelength in ultraviolet spectrum, so bonds dissociation that is begun by the absorption of the UV radiance causes cleavage and/or chains reticulation[14].

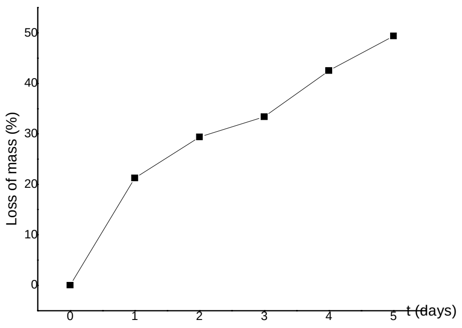


Fig. 8. Sample mass variation *versus* the immersion time

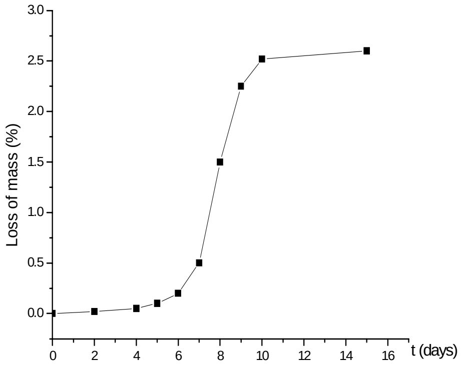
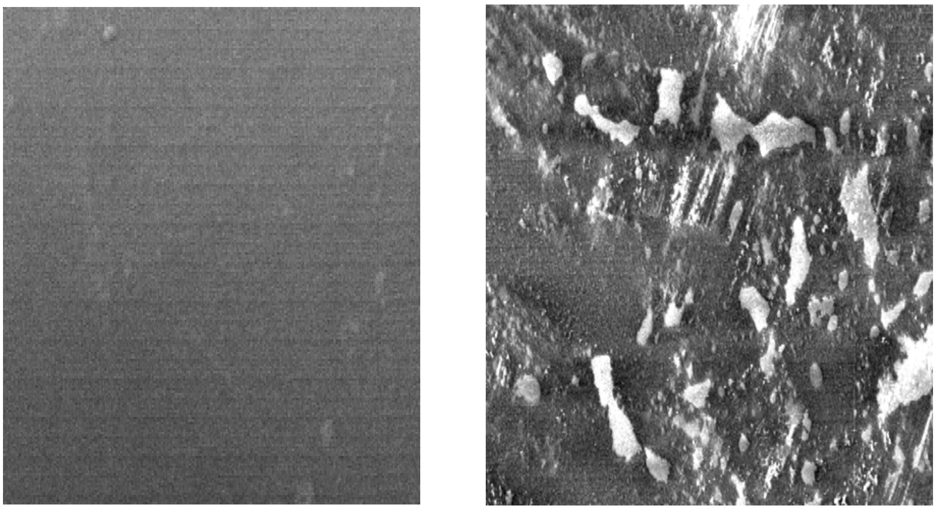


Fig. 9. Sample mass variation *versus* exposure time in the solarbox

Reactions of chains cleavage (separation) will induce molecular weight reduction in surface (outer surface) of the exposed sample, causing the erosion of low molecular weight fragments. The consequence to this process a substantial loss of polymer resin surface is expected (Fig. 9), this has been emphasized in the case of the continual exposition of an unsaturated polyester matrix composite where the authors observed the uncovering of some fibers[1]. It is noted that in particular a change of initial state of sample surface in terms of colour and brightness. This result has already been reported by many authors who specify that UV exposure effects or photodegradation are usually confined to superior part, some microns of the surface. The chemical changes induced by UV exposure are the result of a complex whole of processes involving the combined effect of UV and oxygen:direct photodegradation (photo-decomposition, photo-oxidization starting) and chromophores photosensitized[15,16].

Apropos the irradiation test, the incidental flux energetic profile is constituted of fast, thermal and epithermal neutrons. In comparison with the standard sample (non-exposed) it is shown that the damage degree is an increasing process with the exposure. From literature data and bibliographic material concerning the description of irradiation effects on polymers, one can advance several reactions, which are in competition such as reticulation, chain break and oxidation by radical mechanism[17,18]. It is now established that the chains tendency to reticulate or to break depends strongly of the bond energy between monomers units. In present case the incidental particle of high energy fast neutrons whose energy is greater or equal to 2 mev, is braked by the target with a nuclear shock during which the incidental particle transmits a part of its energy to an atom. If the energy transfer is sufficient, the nuclear shock permits to drive out an atom of its site the latter will return positioning interstitially, the energy used oversteps probably the energy threshold (displacement energy). This fast neutrons collision with target cores proceeds to an indirect ionization by the preliminary creation of excited secondary species that will generate ionization. Scanning electron microscopy (SEM) performed with an acceleration tension of

0.7 kV (Fig. 10) shows clearly the caused damage. This observation seems to indicate the presence of major chain breaks for the sample bombarded during 1.5 h. Let us note that the presence of benzenic cores improves behaviour toward radiations[19] indeed the chemical function recognized as the most stable to radiations is the aromatic ring. This ring after excitation returns to the fundamental state with a very weak rate of bond break. This property is assigned to the relocation of π electrons that distribute absorbed energy on a significant number of bonds[20].



0.7 KV X30 500 µm
(a)

0.7 KV X30 500 µm
(b)

Fig. 10. Micrographies (SEM) (a) standard sample, (b) damaged sample

In order to value the rigidity of these material, the Young's modulus (ultrasonic scanning principle) was determined. The values are 7.17, 7.60, 8.39 and 8.96 Gpa, respectively for blank samples (non-exposed), 0.5, 1.0 and 1.5 h exposure ones. Thus, an increase of Young's modulus can be interpreted in terms of reticulation, provided to use the level of irradiation dose[21]. Polymer properties evolution depends on operative conditions of the atmosphere in which irradiations are applied. This reticulation that provokes resin hardening strengthens the sample. It is noted as well that the released γ-photons have insufficient energy to provoke nuclear reactions in radiated material but they rather break bonds between atoms and generate free radicals in the material. The modulus value varies from 6 to 25 %, this suggests an approach for quite important point related to mechanical behaviour *i.e.*, it is ruled by structural state in macromolecular scale that is to say chain length, reticulation density or rather by the structural state on molecular scale *i.e.*, carbonyl, acids, hydroperoxides, *etc*.

Conclusion

We were interested in a matrix constituted by an unsaturated polyester resin. In order to evaluate the deterioration and the damage of unsaturated polyester resin material, a comparative characteristics between the standard and deteriored samples are carried out. Under the action of hot water and acetone solvent, we observed cracks, fissure, craze, flaky surface as well as a regular damage. These aspects are estimated by SEM, GPC, FTIR analysis. In photodegradation, a loss of weight of the resin has been observed. This is the result of a complex reactions implying the combined effect of UV radiation and oxygen. The exposures to a neutron flux led to an increase in the Young modulus which can be interpreted in term of reticulation considering the amount of irradiation. The relations between structure and mechanical properties has been developed.

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