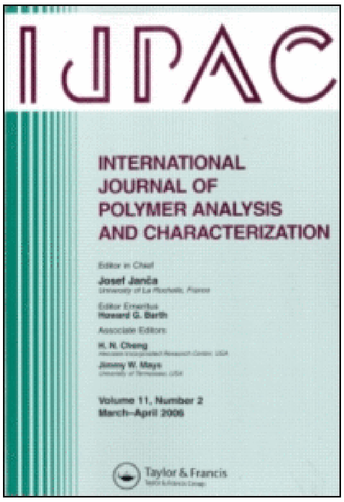

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

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To cite this Article Nacher, L. Sanchez , Amoros, J. E. Crespo , Moya, M. D. Salvador and Martinez, J. Lopez(2007) 'Mechanical Properties of Polyester Resins in Saline Water Environments', International Journal of Polymer Analysis and Characterization, 12: 5, 373 — 390

To link to this Article: DOI: 10.1080/10236660701516557

URL: http://dx.doi.org/10.1080/10236660701516557

International Journal of Polymer Anal. Charact., 12: 373–390, 2007
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ISSN: 1023-666X print
DOI: 10.1080/10236660701516557

Mechanical Properties of Polyester Resins in Saline Water Environments

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Abstract: By evaluating the behavior of unsaturated polyester used in marine environments at room temperature, it is possible to determine its degradation using mechanical characterization parameters. There is a considerable decrease in its mechanical resistance due to the degradation effects. It must also be taken into account that the curing rate of a thermoset resin is one of the most important parameters in its behavior. This study will examine the correlation between the amount of water absorbed at room temperature, the curing rate, and the loss of mechanical properties.

Keywords: Cure behavior; Mechanical properties; Mechanical testing; Resins

INTRODUCTION

Being easy and low cost to process, polyester resins are becoming widely used as composite matrices in civil infrastructure applications, marine and oceanographic research platforms, vessels, water sports, and other uses. A lack of exact knowledge about the degradation mechanisms of these composite materials, durability, and aging, particularly when cured at room temperature, creates a great challenge due to the widespread use

Received 2 March 2007; accepted 17 June 2007.

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of these materials in basic structural components. The main effect of the matrix in composites is to transfer the load to the fiber reinforcement, but the resin or matrix must protect the fibers, prevent the absorption of liquids, provide the material with electrical insulation characteristics, and maintain the geometrical or design properties of the composite. The properties of the matrix that most influence the properties of the composite are its rigidity, resistance, tensile strength, behavior at different temperatures, and corrosion resistance.[1–3]

One of the obstacles to a more general acceptance of polymer matrix composites in civil engineering applications is the polymer matrix's tendency to degrade due to moisture, extreme temperatures, and corrosive chemical environments in general. The problems suffered by infrastructures due to wear over the time during which they are in service is currently one of the main reasons for developing and using advanced materials such as reinforced polymers in naval engineering applications. Thanks to their high specific resistance, lightness, fatigue resistance, and corrosion resistance, these materials are ideal for structural uses in this field.

Unsaturated polyester is the most widely used thermoset resin in industrial applications. One of the industrial fields where it is most commonly used is in marine applications, shipbuilding, oceanographic equipment, and generally in other naval products. For many of these applications, industrial forming processes using manual lamination techniques and post-cure conditions are not suitable because they produce materials with structures that are not fully cross-linked, which can be more easily attacked when in contact with a liquid environment.

Most of the processes involved in the production of unsaturated polyester resin pieces are carried out at room temperature, which means that the curing process is inhibited and the resin is therefore not fully cured. The polyester resins used as matrices form a thermoset network cross-linked structure, which could be described as a combination of three continuous processes, homopolymerization of the polyester and styrene separately and copolymerization of both, which take place with differing reaction rates in the structure at the same time. However, since the rate of styrene double bond conversion is initially less than that of polyester, the styrene monomers may continue reacting after double bond conversion in the polyester chain has finished. The result of this difference in reaction rates is the formation ofmicrogel structures with domains of high cross-linked density in areas where monomers have not reacted, causing clear heterogeneities. This incomplete polymerization can lead to changes in the material's properties with time due to slow residual cure progression, which can lead to low heat stability, low resistance to hydrolysis, and increased susceptibility to degradation due to the absorption of moisture and other chemicals. Consequently, the material has lower heat stability, lower resistance to hydrolysis, and more problems of swelling when in contact with solvents than if it had undergone a full curing process. It is therefore necessary to analyze the mechanisms of polymer degradation in order to optimize the use of suitable materials, production and processing methods, fields of application, and other factors.[4–15]

A lifetime between 50 and 75 years can be considered normal in applications of this kind, for example, in civil applications (civil engineering) such as buildings, bridges, or outdoor applications. Moreover, as the use of polymer matrix composites in marine environments is very well established, the most important characteristic of applications in leisure boats, catamarans, surfboards, windsurfing boards, water sport-related accessories, naval military applications, platforms, oceanographic equipment, underwater structures, and so on must be good resistance to degradation in extreme environments. Very few studies have so far been carried out regarding the long-term effects of moisture, salinity, and alkaline environments on the typical polymers used in these applications. It is therefore necessary to analyze the mechanisms of polymer degradation in order to optimize the use of suitable materials, production and processing methods, and application fields.[6,8,13,16–22]

The mechanisms that cause unsaturated polyester resins to break due to moisture absorption are quite complex. Some authors have shown that the action of water on these resins is a combination of the lixiviation of low molecular mass components initially present in the resin, chemical attack on the ester bonds, and plasticization by the water absorbed. Other authors base their research on the effect of hydrolysis as an irreversible process that is accelerated by the appearance of microcracks in the material.[4,13]

The cure rate or cross-linking of the material's structure is the parameter that most affects the internal structure adopted by the resin during polymerization. The resin's structure has been identified as a determining factor in the behavioral changes observed when it is exposed to solvents. An experiment is therefore carried out to determine the influence of the cure rate, or cross-linking, of the structure on the kinetics of water absorption as a cause of material degradation. Subsequently, the effect of this degradation on the material's mechanical response is examined, as this is a fundamental factor in designing and selecting the best material for a specific industrial application.[1,7,11,12,15,21]

Polymer materials generally absorb moisture in measurable rates when submerged directly in water or when exposed to moist atmospheres. The amount of moisture absorbed depends on the chemical nature of the material. This absorption is characterized by the fact that it has reversible and irreversible effects on the properties and processing of the material. It has been observed that the moisture absorbed acts as a polymer plasticizer, reducing the T_g and its resistant properties, although these effects can be reversible. The water absorbed also leads to physical corrosion, or irreversible mechanical damage, as it brings about the formation of microcracks or cracks and a marked chemical degradation of the polymer structure.[6,23,24]

The cure cycle's influence on the properties of the resin has been studied for a general purpose orthophthalic polyester resin. The cure and post-cure times and temperatures that have been chosen for this experiment are as close as possible to the conditions used in industry.

EXPERIMENTAL SECTION

Materials

The unsaturated polyester resin used in this study was supplied by the company Brenntag Quimica S.A. (Massalfassar, Valencia, Spain), under the trade name PALATAL P4-TV-128. It is an unsaturated polyester resin based on orthophthalic acid and standard glycols, dissolved in styrene, containing an accelerant and a thixotropic agent. It is a product of low viscosity and medium reactivity, with a good ability to impregnate the fiber reinforcement. It is recommended for the production of all kinds of fiberglass-reinforced products such as profiles, motorboats, bodywork, pressed and molded parts, and casings.

Dibenzoyl peroxide was used to cure this resin, in the amount of 2% by weight, supplied by Glasurit GmbH (Münster, Germany).

Sample Preparation

Prior to experimental sample preparation, the kinetics of the cured process was studied by differential scanning calorimetry (DSC) (Mettler Toledo 821^e/400, series STARe-200). During the sample curing reaction, the heat generated is a function of reaction rate in time. In this way, the relation between cured rate, $d\alpha/dt$, and the rate of heat flow measured in DSC, dH/dt, is described by the expression:

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_T}\left(\frac{dH}{dt}\right); \quad \alpha = \frac{\Delta H_x}{\Delta H_T} \tag{1}$$

where ΔH is the total heat generated by the curing reaction under each experimental condition: 23°C, 40°C, and 60°C. All DSC tests were performed at these curing temperatures, and the areas below the curves were integrated to calculate ΔH_T by considering 100% conversion, as reported

Table I. Kinetics parameters on experimental sample preparation

α (%)	Temperature 23°C Time cure (min)	Temperature 40°C Time cure (min)	Temperature 60°C Time cure (min)
40	188	38	15
60	265	81	38
80	395	138	75
90	1100	250	113

Experimental data: $\Delta H_T = 115{,}79\,\mathrm{J/s}$.

in the literature. The graphic representation α versus time for each curing temperature permits the determination of the necessary time for the more representative estimation of the cross-linking degree: 40, 60, 80, and 90%[25–29] (Table I).

All the samples were molded in a casting process with a silicon mold with the tensile test shape; the unsaturated polyester resin was mixed with the dibenzoyl peroxide at room temperature and was poured over the mold for the time and temperature contemplated by the experiment. The purpose was to study the kinetics of the degradation of unsaturated polyester resin in saline water environments for different cure rates: 40, 60, 80, and 90% of cross-linking, obtained for different cure temperatures: room temperature, 40°C, and 60°C, in both cured and post-cured states. The curing process was carried out in a Carbolite oven, model 2416CG (Keison Products, Oregon, USA), on a silicon mold with the specimen shapes standardized in accordance with ISO 527, and the geometry of the samples obtained for casting were in accordance with ISO 527 standard: total length 150 ± 2 mm, narrow area length 80 ± 2 mm, total width 20 ± 0.2 mm, narrow area width 10 ± 0.2 mm, and thickness 4 ± 0.2 mm.

Degradation Process

The procedure followed in the experiment for unsaturated polyester resin degradation in a saline environment follows the guidelines established in UNE-EN ISO 62 standard for determining moisture absorption properties and under controlled conditions. This standard process establishes that the amount of absorbed water is determined by weight gain, obtained for time periods of 24 h, represented in terms of percent of weight change as:

$$M = \frac{Weight_{sample} - Weight_{sampledry}}{Weight_{sampledry}} \times 100 \qquad (2)$$

Before carrying out the experiment, all the samples were dried in an oven at 50° ± 2°C for 24 h and left to cool in a dryer until they reached room temperature. Each test sample was weighed to an accuracy of 0.1 mg on an analytical balance manufactured by Scaltec, model SDK01, and the samples were then placed in the immersion recipient, with distilled water and 35% sodium chloride to simulate the marine environment, at a temperature of 23°C. After being immersed for 24 h, the samples were removed from the water and any water remaining on the surface was wiped off with a clean cotton cloth. The test samples were then weighed again within a minute of being removed from the water. This process was planned for a 500 h test period, which is equivalent to 21 days, weighing the samples each 24 h for quantifying the weight gain for water absorption, as called for in the ISO 62 standard.[30,31]

Having reached the anticipated time for degradation of the material, the following step was to carry out the mechanical characterization of the aged samples and of the samples exposed to the air as a reference series, in order to quantify the material degradation rate.

Mechanical Testing

The tensile properties of the samples under analysis were assessed using the ELIB 30 universal testing machine (S.A.E. Ibertest, Madrid, Spain) in accordance with ISO 527 standard, using a 5 kN load cell with a crosshead speed range of 20 mm/min to test five samples of each kind of material. Shore D hardness measurements were carried out using a Baxlo durometer (Baxlo, Barcelona, Spain) on 4 mm thick samples in accordance with ISO 868 standard, carrying out five tests for each kind of material.

Morphological Study

The tensile fracture surfaces of the different samples were observed by scanning electron microscopy (SEM) using a JSM 6300 model (JEOL USA Inc., Peabody, Mass., USA). The samples were first coated with a thin layer of gold using a coating process in vacuum conditions and a sputtering time of 60 s.[32–35]

RESULTS AND DISCUSSION

As the objective of this work was to assess the behavior of unsaturated polyester resin in saline water at room temperature by observing the water absorption kinetics, it was necessary to quantify two main parameters that are characteristic of the kinetics: the amount of water absorbed and the diffusivity. The best way to determine the behavior of a resin immersed in a liquid is to analyze the absorption kinetics by observing the weight gain of the material in relation to the time.[3,6,9,11,19,36]

As concerns the weight gain due to immersion in a saline medium, Table II shows how the resin in a cured state has a marginally greater absorption capacity than that in a post-cured state. Although there is only a small difference, it can been seen that the material cross-linking state, i.e., the internal structure of the polymer, is fundamental to the polymer's behavior with regard to the absorption in a liquid environment, presenting better behavior in a post-cured state. Heterogeneities in the internal structure of resins due to the three steps that take place during polymerization result in a heterogeneous structure with different levels of cross-linking, causing high moisture absorption levels. Therefore, the resin's state of cross-linking is a fundamental parameter in quantifying and monitoring the kinetics of saline water absorption in the resins studied.[11,12]

Figure 1 shows the weight gain in relation to the time of immersion in saline water of different rates of cure samples at 40°C and in a post-cured state. It also shows that the lower the cross-linking rates of the polyester resin's internal structure, the greater the level of moisture absorption.

Incomplete polymerization and the presence of a large number of ester bonds cause the resin to have lower stability with heat, lower resistance to hydrolysis, and a higher degree of swelling in solvents than with resins in a fully cured state. The hydrolysis of ester groups results in the formation of carboxyl groups with a self-catalytic breakdown. The study of degradation mechanisms takes into account physical as well as chemical factors. Unsaturated polyester resins undergo a slow degradation process when subjected to aging due to the absorption of water molecules.[4,5,9]

The transferred weight coefficient on the test sample surfaces is very high, which means that the tangent of the curves shown in Figure 1 at the start of the test time is very steep. Such absorption kinetics follows a "Fickian" diffusion process, i.e., it follows Fick's law of diffusion, with a diffusivity constant. The curves initially present a linear region and subsequently a concave region that is typical of Fickian diffusion. Assuming that the conditions in which the absorption occurs follow Fick's law of diffusion, the weight changes are calculated using the expression:

$$M = \left\{ 1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{\exp\left[-(2j+1)^2 \pi^2 (Dt/h^2) \right]}{(2j+1)^2} \right\} (M_m - M_i) + M_i \qquad (3)$$

Table II. Comparison of diffusivity and percentage weight gain at 504 h of immersion

		Cured temperature								
		23°C			40°C			60°C		
Degree of cure		60%	80%	90%	60%	80%	90%	60%	80%	90%
Percent weight gain	Cured	—	0.57	0.70	0.65	0.64	0.60	0.63	0.71	0.66
	Post-cured	0.66	0.51	0.67	0.64	0.62	0.57	0.62	0.64	0.62
Diffusion coefficient	Cured	—	2.84	4.74	4.15	4.11	3.38	3.89	4.30	3.94
($\times 10^{-9}$cm^2/s)	Post-cured	4.80	2.32	4.99	3.61	3.65	3.14	3.63	3.30	3.58

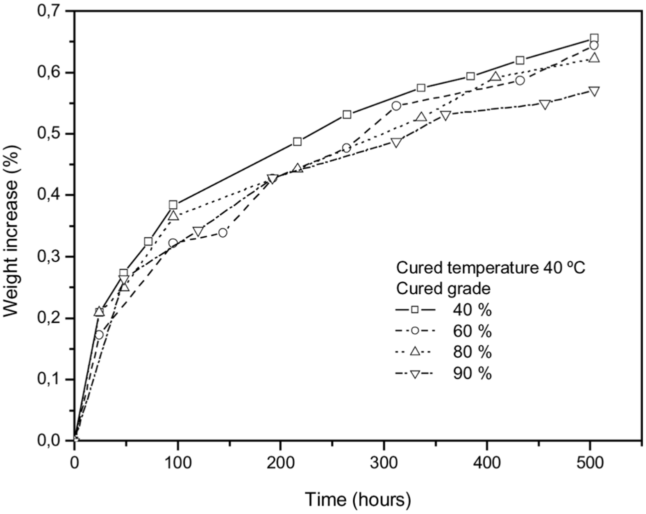


Figure 1. Kinetics of saline water absorption in a post-cured state.

where M_i is the initial moisture content (in this case 0), M_m is the maximum moisture content, h is the thickness of the sample, t is the time, and D is the diffusivity constant obtained for each sample.

As has been noted above, in Fickian diffusion, the absorption kinetics is characterized by two fundamental parameters: the diffusivity and the amount of water absorbed.[3,6,11,12,30,31,36] Some studies have shown that polymer aging by water absorption at high temperatures can cause damage in the form of cracks, microcracks, and other types of morphological changes that enable additional absorption to occur.

Considering the diffusivity coefficient and the weight gain according to the cross-linking rate, a marked parallel can be observed in the two parameters in comparison with the state of the material internal structure determined by the cross-linking rate. Figure 2 shows how for small cross-linking rates the diffusivity coefficient and the weight gain due to immersion in saline water are greater than for high cross-linking rates, i.e., a highly cross-linked internal structure of the resin presents a smaller capacity to absorb water than a structure with a low degree of cross-linking.

An important increase in tensile strength has been observed with the cross-linking grade for each cured temperature. For the cured temperature of 60°C, tensile strength increases from 14.6 MPa for 60% of cross-linking to 34.1 MPa for 90% in reference samples. But in the degradation samples, this increase is from 11.3 to 28.2 MPa. The same effect is

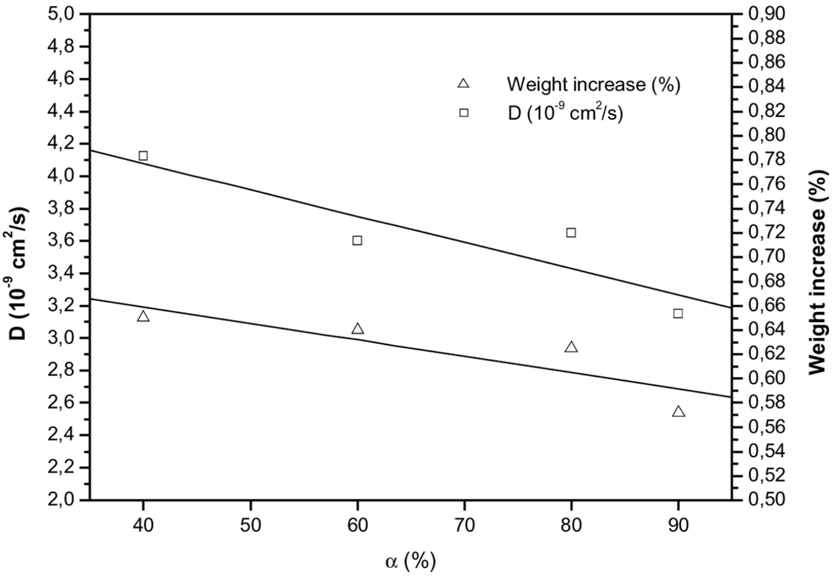


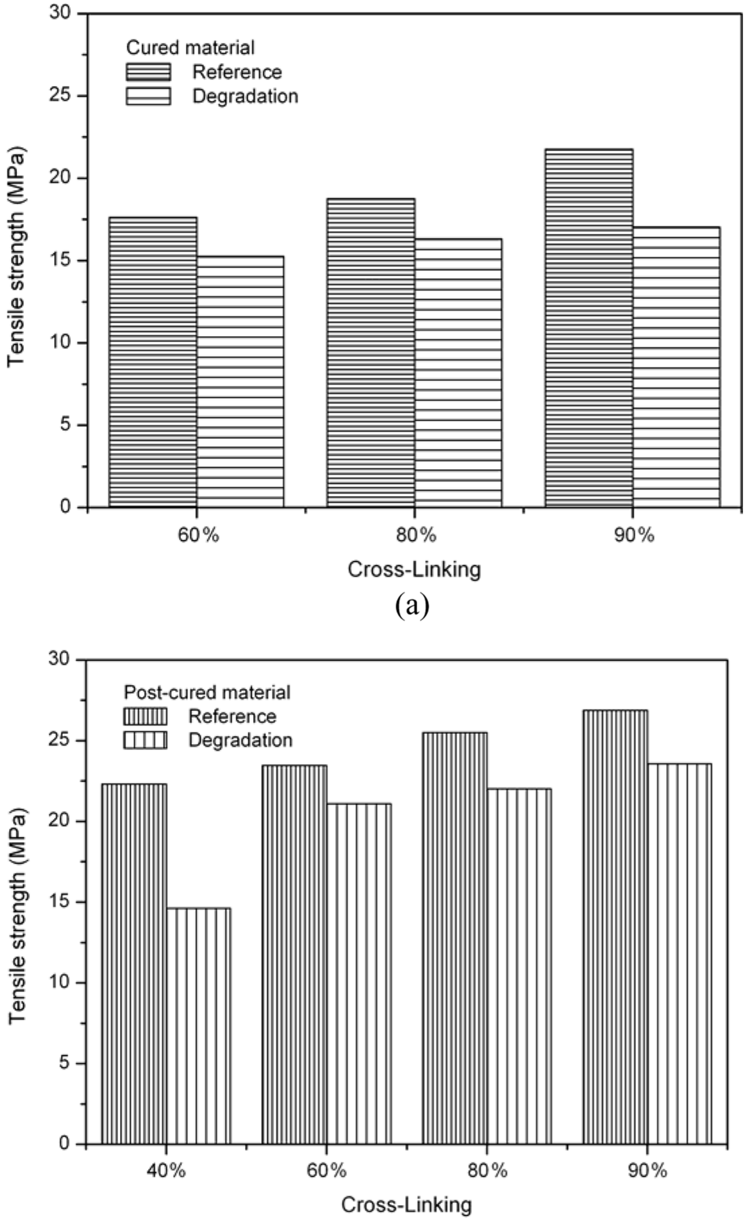
Figure 2. Correlation between the state of cross-linking (α), weight gain, and diffusivity coefficient. Cured at 40°C.

observed under each curing condition. The decrease in tensile strength between reference and degraded samples is around 10–20%.

By quantifying the material's mechanical response to tensile stress it is possible to compare the values obtained for the material's tensile strength as a valid parameter for quantifying the material degradation rate due to immersion in saline water, as can be seen in Figures 3 and 4. As the material's hardness is also a mechanical characteristic of resistance, like the tensile strength, its behavior parallels this.

The exposure of resins to water brings about modifications in the mechanical properties and the test samples' morphology. Moisture absorption acts as a plasticizer and a hydrolysis-promoting agent, reducing the resin's mechanical response, depending on the temperature to which the material has been exposed. The brittleness of the material increases a result of the disaggregation of segments that make unaged resin more flexible.[2,4,5]

There does not seem to be a clear correlation between the considerable decrease in tensile strength in the aged material and the weight change it undergoes, making it difficult to establish a specific relationship between the weight change and the change in mechanical properties of the resin.



(a)

(b)

Figure 3. Variation in tensile strength due to the degradation effects for different cross-linking rates of the resin in state (a) cured and (b) post-cured. Cured at 40°C.

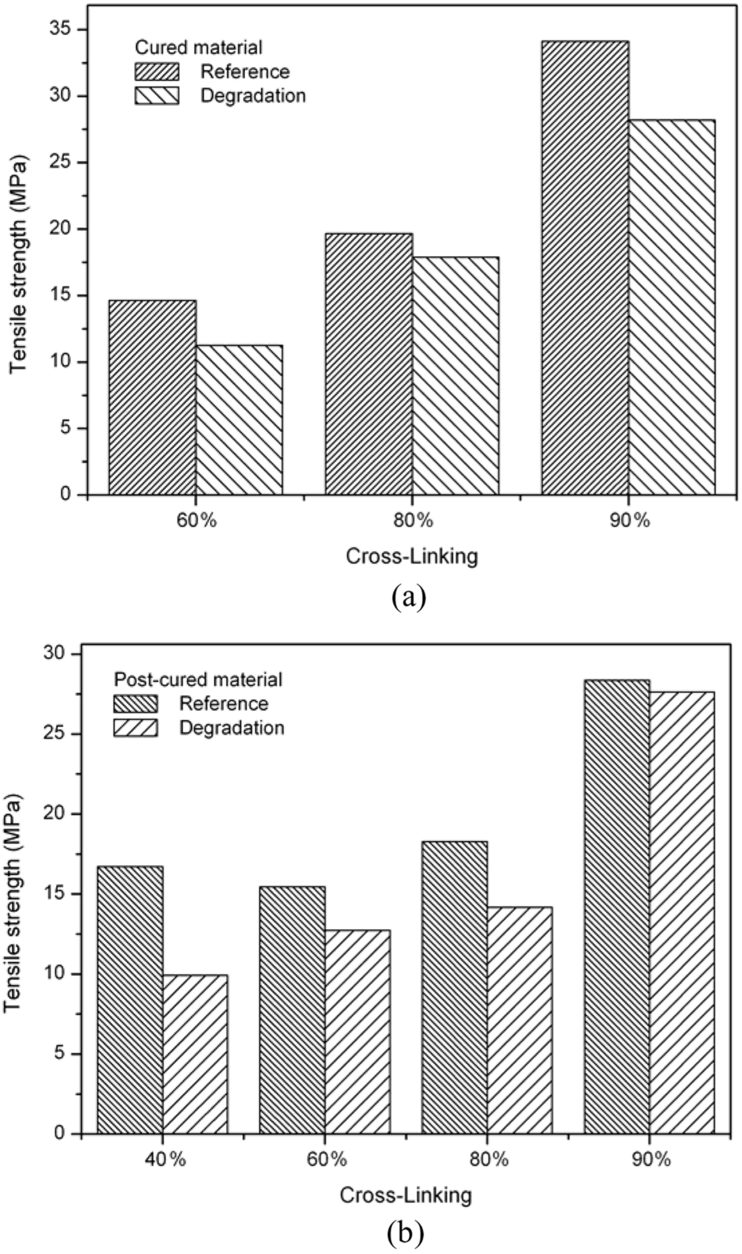
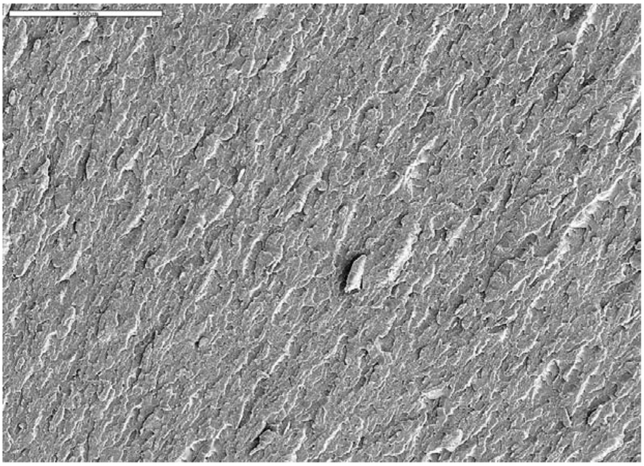
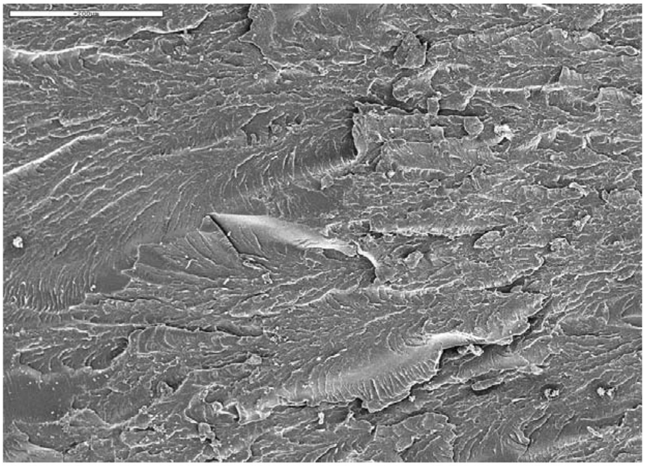


Figure 4. Variation in tensile strength due to the degradation effects for different cross-linking rates of the resin in state (a) cured and (b) post-cured. Cured at 60°C.



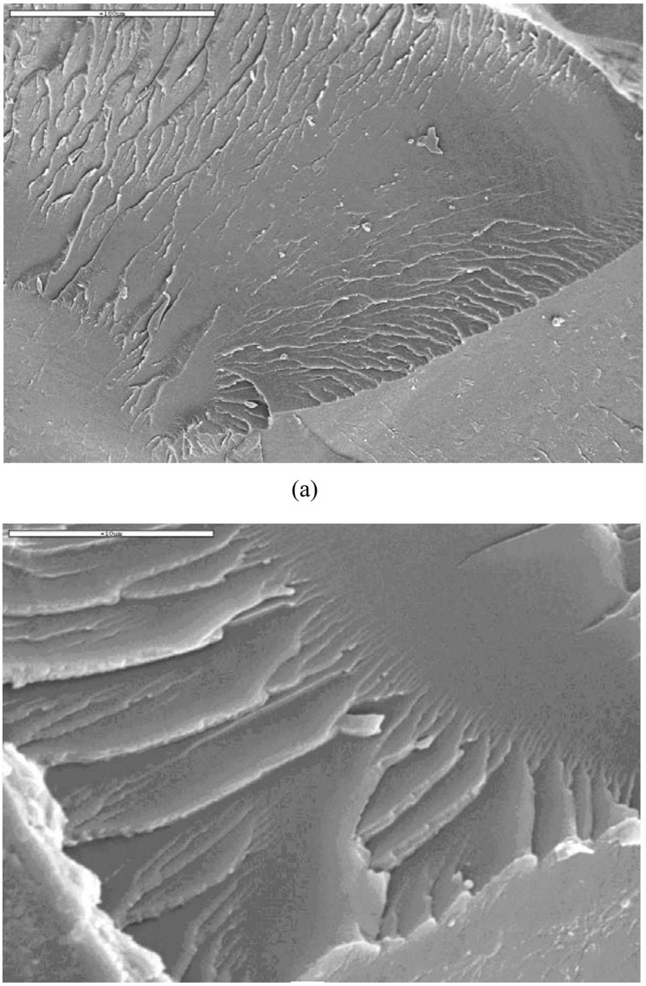
(a)



(b)

Figure 5. Morphology of the fracture surface for 90% cross-linking in a post-cured state (cured at 60°C). Mirror zone (×150). (a) Reference state exposed to the air; (b) state of degradation immersed in water.

If one compares the morphologies of surfaces in a degraded state and in a reference state, no differences can be observed, meaning that the mechanisms causing the material to fracture are the same for both: nucleation of micro-fissures, growth and formation of cracks. The process of saline water absorption carried out in the experiment does not influence the mechanisms that cause the fracture of the material when



(a)

(b)

Figure 6. Detail of the formation of microcracks in a state of degradation immersed in water; (a) (×400), (b) (×4000).

subjected to tensile loads, as can be observed from the fracture morphologies resulting from this test. However, it is interesting to note how the physical appearance of the samples does undergo a considerable change. The samples degraded in a saline environment take on a whitish appearance, losing their transparency and shine. This does not occur with the reference samples, i.e., those that are not degraded.

In terms of the fracture surface morphology, the effect of cross-linking rate of the internal structure resin is not as important as it is from

Table III. Mechanical properties of the polyester unsaturated at different degradation conditions

	Reference				Degradation			
Cross-linking grade	R_m (MPa)	E (MPa)	%A	Hardness	R_m (MPa)	E (MPa)	%A	Hardness
Cured 60°C								
60	14.6	1097	1.7	77.0	11.3	745	1.5	75.1
80	19.7	1146	2.1	78.0	17.9	935	2.4	75.6
90	34.1	1074	1.9	83.8	28.2	1015	4.2	82.6
Post-cured 60°C								
40	16.7	1105	4.3	78.5	10.0	603	2.5	74.6
60	15.5	1054	2.4	79.6	12.7	755	1.3	76.2
80	18.3	967	1.9	79.3	14.2	724	1.9	78.0
90	28.3	1676	1.9	85.4	27.6	997	3.0	84.0
Cured 40°C								
60	17.6	1042	1.7	80.8	15.3	566	2.2	75.1
80	18.8	766	1.8	84.5	16.3	637	2.0	78.3
90	21.7	1344	1.5	86.0	17.0	1082	1.8	79.6
Post-cured 40°C								
40	22.3	1105	4.3	81.3	14.6	473	5.1	76.9
60	23.5	1054	2.4	81.2	21.1	721	3.0	78.5
80	25.5	967	1.9	87.0	22.0	1068	1.9	79.1
90	26.9	1676	1.9	85.0	23.6	1215	2.0	80.8
Cured 23°C								
80	20.8	1255	2.3	82.5	18.3	636	3.6	76.3
90	21.3	1065	2.3	78.6	20.0	893	2.5	79.0
Post-cured 23°C								
60	25.5	976	4.4	85.8	20.1	688	3.3	82.3
80	22.0	1294	2.2	83.4	20.5	694	3.6	80.2
90	25.3	1324	2.3	82.4	23.7	891	3.7	78.2

the point of view of quantifying its mechanical characteristics. However, this analysis leads to the conclusion that the degradation undergone by the material corresponds to the cure rate that it reaches, i.e., the polymer internal structure and the cure conditions that have produced it. At small increases (×150) the smooth appearance area of the fracture surface is rougher in its degraded state. At greater increases it is possible to observe the formation of very marked crack edges in the material in an aged state, indicating a more violent fracture than that of the reference state, which has a more uniform appearance and less voluminous crack ridges. It is interesting to observe the mechanism by which the microcracks or micro-fissures responsible for the material's failure are formed.

CONCLUSIONS

The following conclusions can be drawn from the results obtained in the experiment carried out as part of this study:

- The absorption kinetics resulting from immersion in a saline water environment analyzed during the experimental degradation process of orthophthalic unsaturated polyester resin presents a specific diffusivity constant that is characteristic of the material being analyzed.
- By analyzing the effect of internal cross-linking rate of the resin as a fundamental parameter in its behavior, it can be observed that the diffusivity undergoes a decrease in line with the structure cross-linking rate.
- An analysis of the data obtained shows that the resin internal structure with a high cross-linking rate has a smaller capacity to absorb water than a structure with a low cross-linking rate.
- Concerning the extent to which polyester resin degradation affects its mechanical properties of resistance, there is a considerable decrease in resistance due to the degradation effects, although this does not influence the mechanism that causes the fracture of the material when subjected to tensile stresses.
- The mechanisms that cause the fracture of the material are the same for both the reference samples and the degraded samples. The degradation undergone by the resin due to immersion in saline water does not affect the process by which it fractures.

REFERENCES

[1] Baley, C., Y. Perrot, P. Davies, A. Bourmaud, and Y. Grohens. (2006). Mechanical properties of composites based on low styrene emission polyester resins for marine applications. *Appl. Compos. Mater.* **13**(1), 1–22.

[2] Gautier, L., B. Mortaigne, V. Bellenger, and J. Verdu. (2001). Osmotic cracking in unsaturated polyester matrices under humid environment. *J. Appl. Polym. Sci.* **79**(14), 2517–2526.

[3] Gellert, E. P. and D. M. Turley. (1999). Seawater immersion ageing of glass-fibre reinforced polymer laminates for marine applications. *Composites Part A Appl. Sci. Manuf.* **30**(11), 1259–1265.

[4] Apicella, A., C. Migliaresi, L. Nicodemo, L. Nicolais, L. Iaccarino, and S. Roccotelli. (1982). Water sorption and mechanical-properties of a glass-reinforced polyester resin. *Composites* **13**(4), 406–410.

[5] Apicella, A., C. Migliaresi, L. Nicolais, L. Iaccarino, and S. Roccotelli. (1983). The water ageing of unsaturated polyester-based composites: Influence of resin chemical structure. *Composites* **14**(4), 387–389.

[6] Chin, J. W., K. Aouadi, M. R. Haight, W. L. Hughes, and T. Nguyen. (2001). Effects of water, salt solution and simulated concrete pore solution

on the properties of composite matrix resins used in civil engineering applications. *Polym. Compos.* **22**(2), 282–297.

[7] Chu, W. and V. M. Karbhari. (2005). Effect of water sorption on performance of pultruded E-glass/vinylester composites. *J. Mater. Civ. Eng.* **17**(1), 63–71.

[8] Davies, P., D. Choqueuse, and F. Mazèas. (1998). Composites underwater. In *Progress in Durability of Composite Systems 1998: Proceedings of the Third International Conference on Progress in Durability Analysis of Composite Systems*. Rotterdam: Balkema, pp. 19–24.

[9] Davies, P., F. Mazeas, and P. Casari. (2001). Sea water aging of glass reinforced composites: Shear behaviour and damage modelling. *J. Compos. Mater.* **35**(15), 1343–1372.

[10] Garmendia, J., M. Olaizola, I. Etxeberria, J. C. Franco, and I. Mondragon. (1995). Influence of processing and testing conditions on the mechanical-behavior of sheet-molding compound laminates. *J. Mater. Sci.* **30**(20), 5287–5294.

[11] Karbhari, V. M. (2004). E-glass/vinylester composites in aqueous environments: Effects on short-beam shear strength. *J. Compos. Constr.* **8**(2), 148–156.

[12] Karbhari, V. M. and S. Zhang. (2003). E-glass/vinylester composites in aqueous environments. I: Experimental results. *Appl. Compos. Mater.* **10**(1), 19–48.

[13] Kootsookos, A. and A. P. Mouritz. (2004). Seawater durability of glass- and carbon-polymer composites. *Compos. Sci. Technol.* **64**(10–11), 1503–1511.

[14] Marais, S., M. Metayer, M. Labbe, M. T. Legras, and J. M. Saiter. (1999). Water diffusion in unsaturated polyester films: Effect of plasticization on the glass transition. *Polym. Eng. Sci.* **39**(8), 1508–1516.

[15] Valea, A., M. L. Gonzalez, and I. Mondragon. (1999). Vinyl ester and unsaturated polyester resins in contact with different chemicals: Dynamic mechanical behavior. *J. Appl. Polym. Sci.* **71**(1), 21–28.

[16] Arii, T. and Y. Masuda. (2004). The effect of humidity on thermal decomposition of terephthalate polyester. *J. Anal. Appl. Pyrolysis* **71**(2), 525–536.

[17] Choqueuse, D., P. Davies, F. Mazèas, and R. Baizeau. (1997). Aging of composites in water: Comparison of five materials in terms of absorption kinetics and evolution of mechanical properties. In *High Temperature and Environmental Effects on Polymeric Composites*. Philadelphia, Pa.: ASTM, pp. 73–96.

[18] Davies, P. and D. Petton. (1999). An experimental study of scale effects in marine composites. *Composites Part A Appl. Sci. Manuf.* **30**(3), 267–275.

[19] Hodzic, A., J. K. Kim, A. E. Lowe, and Z. H. Stachurski. (2004). The effects of water aging on the interphase region and interlaminar fracture toughness in polymer-glass composites. *Compos. Sci. Technol.* **64**(13–14), 2185–2195.

[20] Kawaguchi, T., H. Nishimura, K. Ito, T. Kuriyama, and I. Narisawa. (2003). Resistance of glass fiber-reinforced thermoplastics to water hammer. *Polym. Test.* **22**(3), 327–333.

[21] Marais, S., M. Metayer, T. Q. Nguyen, M. Labbe, and J. M. Saiter. (2000). Diffusion and permeation of water through unsaturated polyester resins—Influence of resin curing. *Eur. Polym. J.* **36**(3), 453–462.

[22] Padmanabhan, S. K. and R. Pitchumani. (1999). Stochastic analysis of isothermal cure of resin systems. *Polym. Compos.* **20**(1), 72–85.

[23] Camino, G., A. Y. Polishchuk, and M. P. Luda. (2000). Comparison of the roles of two shrinkage-control led low-profile additives in water aging of polyester resin-glass fiber composites. *Polym. Compos.* **21**(5), 821–831.

[24] Camino, G., A. Y. Polishchuk, M. P. Luda, M. Revellino, R. Blancon, and J. J. Martinez-Vega. (1998). Water ageing of SMC composite materials: A tool for material characterisation. *Polym. Degradation Stab.* **61**(1), 53–63.

[25] Han, C. D. and K. W. Lem. (1983). Rheology of unsaturated polyester resins. I: Effects of filler and low-profile additive on the rheological behavior of unsaturated polyester resin. *J. Appl. Polym. Sci.* **28**(2), 743–762.

[26] Kenny, J. M. and M. Opalicki. (1996). Processing of short fibre/thermosetting matrix composites. *Compos. Part A Appl. Sci. Manuf.* **27**(3), 229–240.

[27] Kubota, H. (1975). Curing of highly reactive polyester resin under pressure—Kinetic studies by differential scanning calorimetry. *J. Appl. Polym. Sci.* **19**(8), 2279–2297.

[28] Sahli, A., R. Granger, and J. M. Vergnaud. (1996). Testing the kinetic and thermal parameters for the cure of an unsaturated polyester. *Thermochim. Acta* **285**(2), 277–288.

[29] Salla, J. M. and X. Ramis. (1996). Comparative study of the cure kinetics of an unsaturated polyester resin using different procedures. *Polym. Eng. Sci.* **36**(6), 835–851.

[30] Riccieri, J. E., L. H. De Carvalho, and A.Vazquez. (1999). Interfacial properties and initial step of the water sorption in unidirectional unsaturated polyester/vegetable fiber composites. *Polym. Compos.* **20**(1), 29–37.

[31] Springer, G. S. (1980). Environmental effects on glass fiber reinforced polyester and vinylester composites. *J. Comp. Mater.* **14**, 213–232.

[32] Cao, X. and L. J. Lee. (2003). Control of shrinkage and residual styrene of unsaturated polyester resins cured at low temperatures: I. Effect of curing agents. *Polymer* **44**(6), 1893–1902.

[33] Dash, B. N., A. K. Rana, H. K. Mishra, S. K. Nayak, S. C. Mishra, and S. S. Tripathy. (1999). Novel, low-cost jute-polyester composites. Part 1: Processing, mechanical properties, and SEM analysis. *Polym. Compos.* **20**(1), 62–71.

[34] De La Caba, K., P. Guerrero, J. Gavalda, and I. Mondragon. (1999). Fracture behavior-morphology relationships in an unsaturated polyester resin modified with a liquid oligomer. *J. Polym. Sci. Part B Polym. Phys.* **37**(14), 1677–1685.

[35] Liu, C. H., T. L. Yu, and C. C. Chen. (2002). Effect of curing temperature on the morphology of unsaturated polyester resin blended with poly(vinyl acetate). *Polym. Eng. Sci.* **42**(3), 567–581.

[36] Benameur, T., R. Granger, and J. M. Vergnaud. (1994). Correlations between the state of cure of unsaturated polyester coatings and their behaviour to water at 60°C. *Polym. Test.* **14**, 35–44.