DEVELOPMENT OF NA ESTER VINYL POLYMERIC MATRIX FOR COMPOSITES DESIGNED FOR THE FILAMENT WINDING PROCESS AND EFFECT OF WATER ABSORPTION ON MECHANICAL PROPERTIES

Ledjane Lima Sobrinho
UFRJ/COPPE Bloco I sala 222 Centro de Tecnologia UFRJ
Ledjane@metalmat.ufrj.bre-mail

Marysilvia Ferreira
UFRJ/COPPE Bloco F sala 210 Centro de Tecnologia UFRJ
mari@metalmat.ufrj.br
Fernando Luiz Bastian
UFRJ/COPPE Bloco I sala 222 Centro de Tecnologia UFRJ
fbastian@metalmat.ufrj.br

Abstract. *The study of the resin used as the polymer matrix for composite materials is important because the matrix exerts great influence in the final properties of the composite. The aim of this study is to develop a polymer matrix using a vinyl ester resin produced by the filament winding technique. Therefore, vinyl ester resin systems have been developed from Derakane 411-350 resin. These systems were produced by varying the percentage of cure agent and accelerator. The system which presented the best behavior in tension (Yong's modulus = 2,42 GPa,tensile strength = 47,67 MPa, elongation = 7,31 % and fracture toughness 2,67 J), adequate gel time and exothermic peak for the manufacture process was submitted to hygrothermal aging by immersion in water at 60°C for a maximum period of 64 days. Additionally, different polymeric system with the Derakane 8084 vinyl ester resin was developed, which was submitted to immersion in water at 60°C and room temperature, for 36 days. The mechanical properties were evaluated before (Yong's modulus = 2,55 GPa, tensile strength = 56,06 MPa, elongation = 5,37 % and fracture toughness 2,32 J) and after aging (at room temperature, Yong's modulus = 2,50 GPa, tensile strength = 56,79 MPa, elongation = 5,08 % and fracture toughness 2,51 J and at 60ºC, Yong's modulus = 2,15 GPa, tensile strength = 40,58 MPa, elongation = 2,00 % and fracture toughness 0,47 J). Calorimetric and micro structural analyses were done in order to characterize the samples.*

Keywords: *composite material, polymer and filament winding*

1. Introduction

Vinyl ester resins (VERs) consist of a multi-methacrylate oligomer (typically bisphenol-A based) and styrene as a reactive diluent. These materials were developed in an attempt to combine the mechanical and thermal properties of epoxy resins with the rapid cure of unsaturated polyester resins and this property optimization makes them particularly suitable as the matrix for large, high performance glass reinforced composites (Timothy *et al.,* 2002).

The crosslinking reaction of VERs proceeds by free-radical polymerization with organic peroxides and hydroperoxides as initiators. Rapid decomposition of initiators may occur under heat or by the use of promoters, such as salts of metals like cobalt octoate or naphthenate, at low temperature (Li *et al*., 1999 and Martin *et al.,* 2000).

Fiber-reinforced vinyl ester is increasingly used in various industrial applications. In order to assess the overall performance of the composite materials, it is essential to understand also the individual the role of the matrix materials. Mechanical properties of neat resins are fundamentally important to study because initial damage in composite is controlled by matrix cracking. The environmental effect of moisture on the resins is of significant interest, since wet environments compromise the mechanical stability of composites due to water sorption of the matrix. The main effects to water absorption in polymeric matrix are plasticization, changes of physical properties and hygrothermal degradation (Han and Drazal, 2003).

2. Experimental

2.1. Materials

The vinyl ester resins used in this study were: epoxy vinyl ester resin Derakane® 411-350 and epoxy vinyl ester resin Derakane® 8084 both provided by Dow Chemical Co. and diluted with 45 wt% of styrene monomers. Methyl ethyl ketone peroxide supplied as Butanox LPT (provided by Akzo Nobel) was used as the initiator, and a solution of 6,0% of cobalt octoate (provided by Akzo Nobel) was used as the activator.

2.2. Preparation of samples

The polymers systems in the resin 411-350 were prepared by first mixing the resin with the accelerator (activator), followed by the addition of the initiator (Butanox). Nine formulations were preparated. The experimental conditions are: Butanox (wt%): 1,5, 2,0 and 2,5; Co (wt%): 0,3, 0,5 and 1,0. No post cure was applied and ambient curing exceeding 15 days preceded mechanical testing.

The system which presented the best behavior was submitted to hygrothermal aging and additionally. A different polymeric system with the Derakane 8084 resin was developed with a post-curing of 2h at 99ºC. The materials were mixed for least 1 min and were cast in silicone rubber moulds. After 24 h the specimens were pulled out from the moulds and their surface and edges were ground to remove any surface defect and to guarantee specimens with flat and parallel sides. The nominal dimensions of the test specimens used are shown in Figure 1.

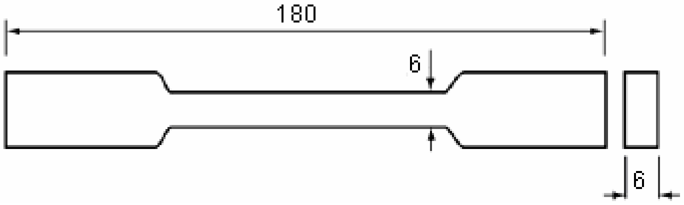


Figure 1. Tensile specimens. All dimensions are in millimeters.

2.3. Mechanical analysis

The tensile tests of the resins were conducted at room temperature on an Instron mechanical testing machine (model TTDML), according to ASTMD638-91.

2.4. Water sorption

The 411-350 resin which presented best mechanical properties was then aged in distilled water at 60ºC for different time periods (16, 36 and 64 days).

The 8084 resin was aged in distilled water at room temperature and at 60ºC for 36 days.

These thermally aged samples were subjected to tensile tests to evaluate the influence of the hygrothermal conditions on the tensile properties

2.4. Differential thermal analysis

Differential Scaning Calorimeter (DSC) thermograms were obtained using a Perkin-Elmer DSC-7 apparatus in the temperature range of 40ºC to 200ºC.

3. Results and Discussion

The effect of the addition of different contents of cure agent (Butanox) and the activator (Co) on the mechanical properties of vinyl ester resin was studied by using an experimental design scheme. Table 1 shows the design matrix with the codified, uncodified and the dependent variables analysed in this work.

The results showed that there is an interaction between the process variables analysed, Butanox and Co contents, on the mechanical properties (maximum stress, Young’s modulus, toughness and elongation at rupture). It was also observed that the ratio between cure agent contents and activator is very important. Depending on the Butanox /Co ratio, samples with high rigidity or high toughness may be obtained, because this ratio produces macromolecular networks with every different mechanical property.

Table 1. Variables analysed and tensile properties of the polymeric systems development.

Polymeric Systems	Butanox (wt. %)	Cobalt (wt%)	Exotherm Peak (ºC)	Gel Time (estimate) (min)	Properties Mechanical			
					$\overline{\sigma}_{\max}[MPa]$	$\overline{\varepsilon}[\%]$	$\overline{E}[GPa]$	$\overline{Toughness}[J]$
1	1,5	0,3	99,90	60,54	47,67± 3,81	7,31± 1,34	2,42± 0,20	2,67± 0,60
2	2,0	0,3	114,21	42,42	48,54± 4,10	2,45± 0,87	2,79± 0,15	0,64± 0,37
3	2,5	0,3	128,6	34,41	56,61± 1,93	0,56± 0,02	2,09± 0,08	0,12± 0,04
4	1,5	0,5	59,8	79,04	52,88± 2,59	3,39± 1,13	2,64± 0,22	1,39± 0,72
5	2,0	0,5	96,33	43,50	50,54± 4,16	2,63± 0,69	2,77± 0,25	0,77± 0,37
6	2,5	0,5	117,52	31,08	55,19± 5,62	3,31± 1,34	3,02± 0,43	1,16± 0,66
7	1,5	1,0	42,81	75,0	37,43± 2,91	1,38± 0,20	2,71± 0,18	0,26± 0,10
8	2,0	1,0	90,62	63,23	43,72± 2,54	0,52± 0,04	2,05± 0,10	0,16± 0,03
9	2,5	1,0	118,0	35,00	54,12± 1,45	2,63± 0,18	2,43± 0,16	1,58± 0,08

The Figure 2 illustrates the typical stress-strain behaviour of the polymeric systems.

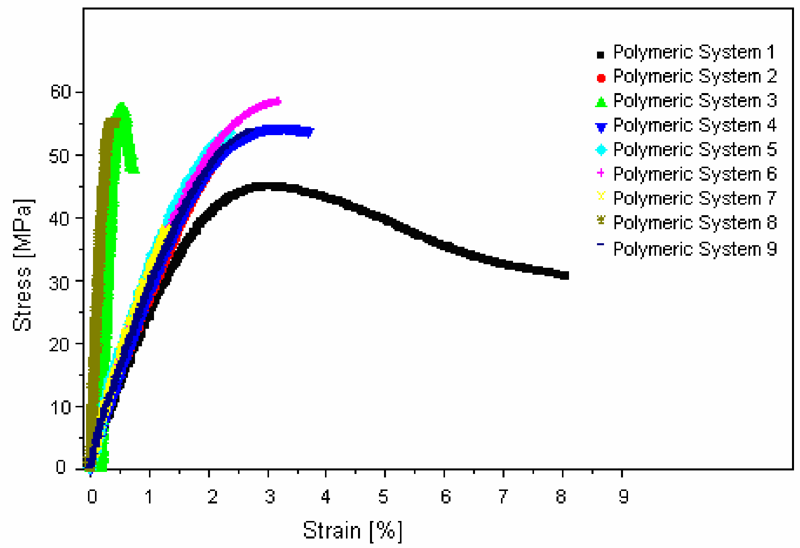
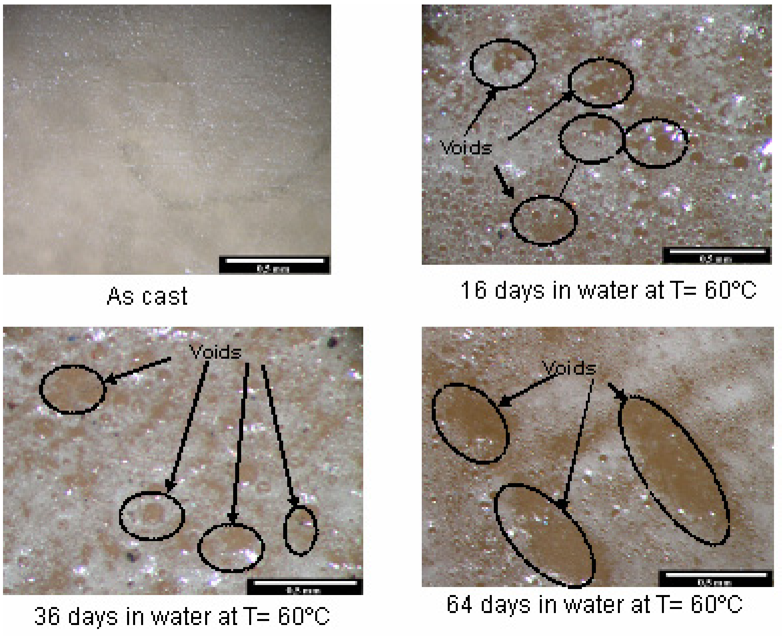


Figure 2. Typical stress-strain curves in the nine polymeric systems development.

The polymeric system 1 which presented the best behavior in tension, exotherm peak and estimated gel time adjusted to the objective of the work was submitted to hygrothermal aging by immersion in water at 60°C for a maximum period of 64 days.

Voids on the surface of the samples were quite evident after long immersion time in water, as shown in Figure 3. The surfaces of the not aged samples appeared smooth when examined by stereoscopic microscopy. After an ageing time, all the samples show the formation of a large number of voids randomly distributed on the surface.



As cast

16 days in water at T= 60°C

36 days in water at T= 60°C

64 days in water at T= 60°C

Figure 3. Micrographs of the surface in the samples before and after hygrothermal ageing.

Tensile tests were made with samples of the resin after thermal ageing in water for 16, 36 and 64 days. Figure 4 shows typical stress-strain behaviour of the samples and the results of the tests are reported in Table 2.

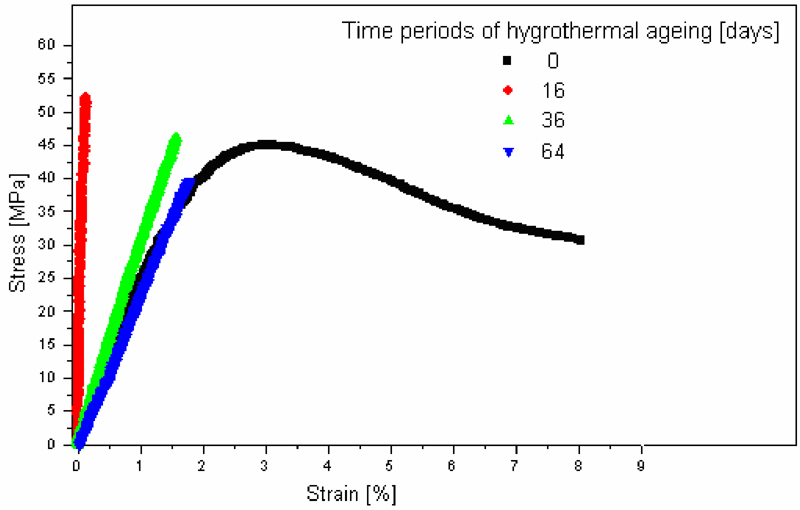


Figure 4. Typical stress-strain curves of the samples before and after hygrothermal ageing.

An increase of elastic moduli and a reduction of elongation at fracture was observed after ageing for 16 days and can be attributed to post-curing in water due reaction of the residual styrene monomer. The DSC thermogram analysis gave similar information. Increase in glass transition temperature (T_g) was observed in the resin as post-cured in water when the residual monomer was completely exhausted, as shown by the Figure 5. On the other hand, the increase observed in the values of the strain and decrease in values of the T_g (Figure 5) could be related to plasticization of the resin after 36 and 64 days of ageing.

Table 2. Average tensile properties of the samples

Samples	$\overline{\sigma}_{\max}[MPa]$	$\overline{\varepsilon}[\%]$	$\overline{E}[GPa]$	$\overline{Toughness}[J]$
0 days in water	47,67	7,31	2,42	2,67
DESVPADP	3,81	1,34	0,20	0,60
16 days in water	53,93	0,19	32,59	0,035
DESVPADP	1,65	0,02	1,56	0,009
36 days in water	46,18	1,38	2,81	0,34
DESVPADP	1,88	0,02	0,19	0,04
64 days in water	38,74	1,65	2,37	1,07
DESVPADP	3,23	0,12	0,14	0,01

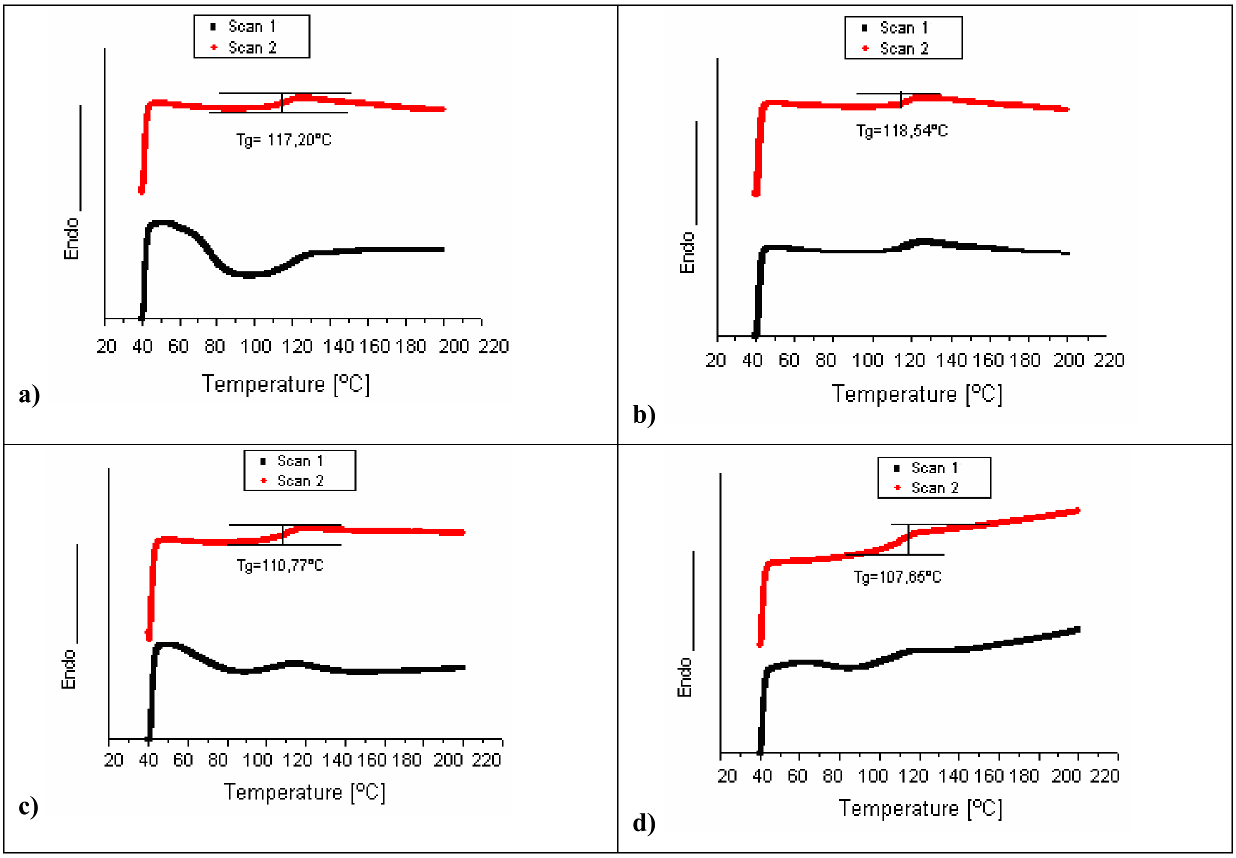


Figure 5. DSC thermograms of specimens: a) not aged, b) 16 days ageing, c) 36 days ageing and d) 64 days ageing.

Figure 6 illustrates the typical stress-strain behavior of the system polymeric Derakane 8084 resin and the results of the test are reported in Table 3.

The result showed that in the polymeric 8084 system is a commercial elastomer-toughened. The mechanical properties were higher than those of the polymeric system 1 in the 411-350 resin.

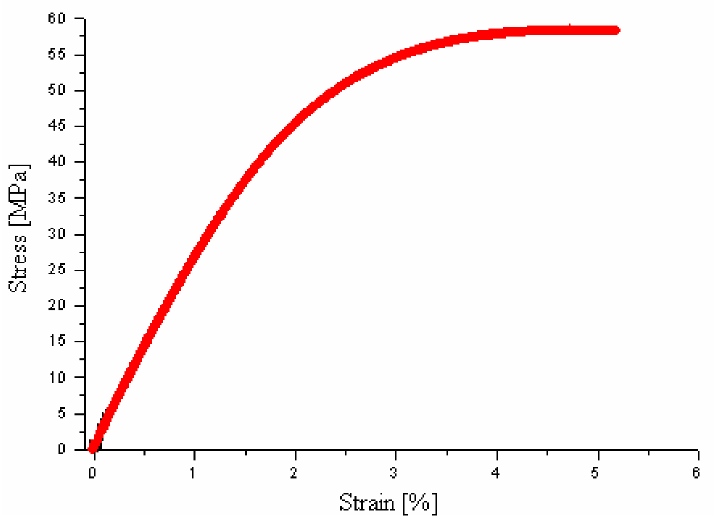


Figure 6. Typical stress-strain curve in the polymeric systems 8084 development

Table 3. Average tensile properties of the samples

Sample	$\overline{\sigma}_{\max}[MPa]$	$\overline{\varepsilon}[\%]$	$\overline{E}[GPa]$	$\overline{Toughness}[J]$
Resin 8084	56,79	5,08	2,50	2,51
DESVPADP	1,72	0,79	0,13	0,27

The polymeric system was submitted to hygrothermal ageing by immersion in distilled water at room temperature and at 60ºC for 36 days. Considerable increase in stability was observed due to post-cure of the resin. As shown in Figure 7, no change was observed on the surface of the samples.

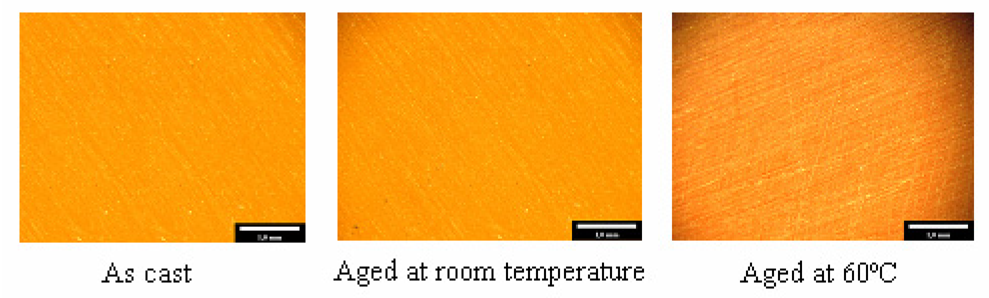


Figure 7. Micrographs of the surface in the samples before and after hygrothermal ageing.

Tensile tests were made with samples of the resin after ageing in water. Figure 8 shows characteristic tensile curves of the samples and the results of the tests are reported in Table 4. A decrease of maximum stress and an increase of toughness and elongation at rupture were observed only after the ageing at 60ºC.

As well as in the 411-350 resin in the 8084 resin as small post-cure in water at 60ºC was observed when the residual monomer was completely exhausted. The DSC thermogram (Figure 9) shows increase in glass transition temperature (T_g) of this sample.

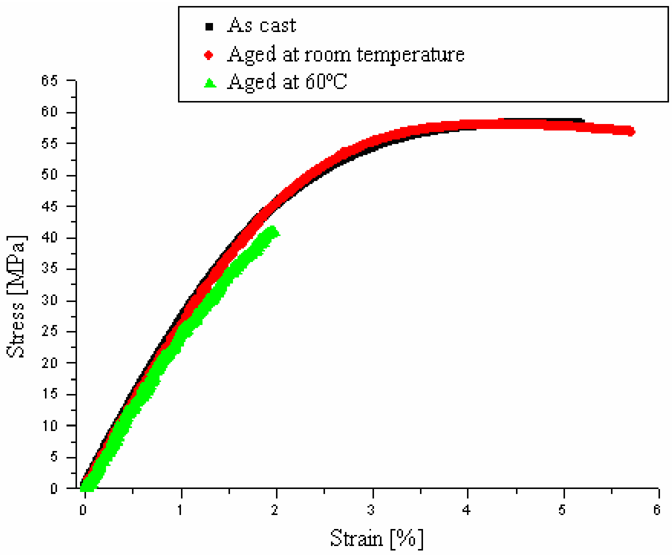


Figure 8. Stress-strain curves of samples before and after hygrothermal ageing

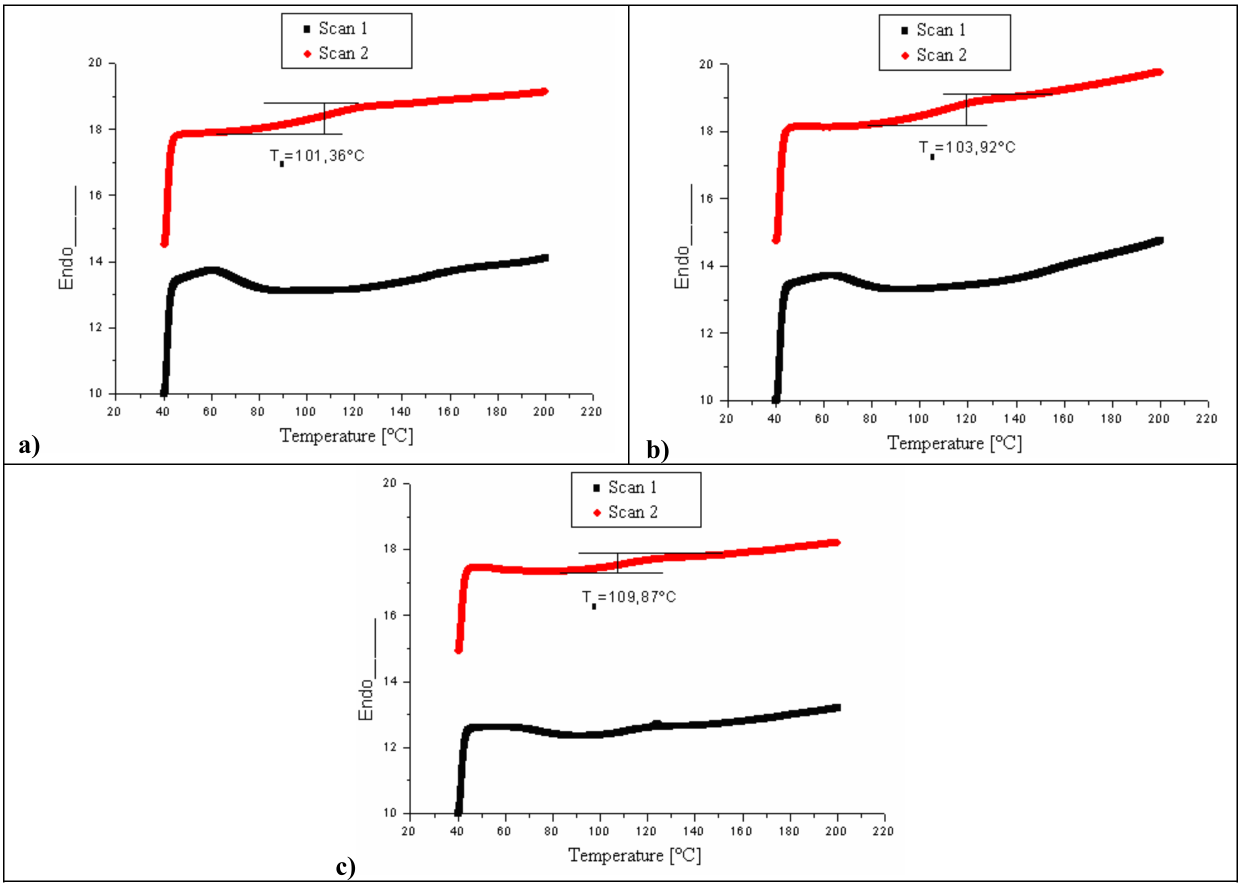


Figure 9. DSC thermograms of specimens: a) not aged, b) aged at room temperature, c) aged at 60ºC.

Table 4. Average mechanical properties of resin before the aging process.

Samples	$\overline{\sigma}_{\max}[MPa]$	$\overline{\varepsilon}[\%]$	$\overline{E}[GPa]$	$\overline{Toughness}[J]$
As cast	56,79	5,08	2,50	2,51
DESVPADP	1,72	0,79	0,13	0,27
Aged at room temperature	56,06	5,37	2,55	2,32
DESVPADP	2,15	0,75	0,25	1,05
Aged at 60ºC	40,58	2,00	2,15	0,47
DESVPADP	1,28	0,12	0,10	0,06

4. Conclusions

The results show that there cure agent and activator contents ratios and their concentrations in the resin influence the mechanical properties (Young's modulus, elongation at rupture, maximum stress and toughness) of the resulting material. The exposure of the 411-350 resin to distilled water at 60ºC produced modifications on the mechanical properties and the morphology of the samples. The degradation mechanisms may be associated to both the low chemical resistance of the materials and possible migration of some of the components initially present in the thermoset. This is evident from the increase of the glass transition temperature and the related weight losses observed for the samples aged.

The results show that the resin system 8084 presents greater potential to be used as the polymer matrix for a composite filament wound due to presenting greater mechanical stability.

5. Acknowledgments

The authors acknowledgments the financial assistance of CAPES and CNPq.

6. References

Han, S. O., Drazal, L. T., 2003, "Water Absorption Effects on Hydrophilic Polymer Matrix of Carboxyl Functionalized Glucose Resin and Epoxy Resin", European Polymer Journal, Vol.39, pp. 1791-1799.

Li, L., Sun, X., Lee, J., 1999, "Low temperature cure of vinyl ester resins", Polymer Engineering and Science, Vol.39, pp.646-656.

Martin, J. S., Laza, J. M., Morrás, M. L., Rodrígues, M., León, L. M., 2000, "Study of the curing process of a vinyl ester resin by means of TRS and DMTA", Polymer, Vol. 41, pp. 4203-4211.

Timothy, F. S., Cook, W. D., Forsythe, J. S., 2002, "Kinetics and network structure of thermally cured vinyl ester resins", European Polymer Journal, Vol. 38, pp. 705-716.

7. Responsibility notice

The authors are the only responsible for the printed material included in this paper.