

Aging study of linseed oil resin/styrene thermosets and their composites with wood flour

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Abstract: The changes in the properties of new crosslinked polymers based on renewable resources and their derived composites have been monitored as a function of time; this knowledge being necessary to estimate their behavior in final applications. Rigid thermoset polymers prepared by free radical polymerization of resins obtained from linseed oil and styrene and composites reinforced with wood flour were evaluated in different environmental conditions and at different times after their preparation. The action of atmospheric oxygen on the unsaturated groups in fatty acids produces chemical changes in these polymers, which affect the properties of the cured materials. These changes were analyzed using Fourier transform infrared spectroscopy, dynamic mechanical analysis and mechanical testing. An increase in the modulus with time was observed during exposure of the samples to dry conditions, or humid environments (60% relative humidity), with or without UV irradiation. The reaction with oxygen appears to be accelerated when the materials are subjected to UV irradiation, showing a large effect on the glass transition temperature.

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Keywords: linseed oil resins; aging; mechanical properties; oxidative polymerization

INTRODUCTION

Research work on the synthesis of polymeric precursors and the production of composite materials from natural sources has been growing in recent years as an answer to the search for new eco-friendly materials that could be used as alternatives to petroleum-based synthetic products.¹ In this context, vegetable oils and wood flour are particularly interesting, since they are raw products widely available from renewable resources throughout the world and at a relatively low cost. Vegetable oils also present numerous reactive sites where it is possible to introduce polymerizable groups by chemical modification.²

Natural oils are triglycerides of fatty acids, which have between zero and three carbon–carbon double bonds. In particular, linseed oil contains a high percentage of linolenic acid, having three unsaturations (unsaturated groups) per fatty acid chain, which are capable of reacting with atmospheric oxygen to form a three-dimensional network. For this last reason, linseed oil has been widely used in the paints industry as a ‘drying oil’.^{3,4} However, these unsaturations are not very reactive in free radical copolymerization reactions with other comonomers such as styrene. Thus, in order to introduce highly reactive unsaturations, the oils can be converted mainly to monoglycerides

in a first reaction step. Then, they can be reacted with maleic anhydride through their alcohol groups, to incorporate maleate groups, which provide more reactive unsaturations.^{5,6}

The modified oil can be mixed with a reactive diluent such as styrene and cured in the presence of an initiator by free radical polymerization. As a first approach, the thermally initiated reaction of the fatty acid unsaturations with styrene might be proposed. However, it was reported that reaction between styrene and drying oils under those conditions was unsuccessful and the resulting products consisted primarily of a dispersion of polystyrene in oils.⁷ In contrast, when the copolymerization was initiated by peroxides, the reaction between drying oils and styrene was possible.⁷ However, in the free radical polymerization of a linseed oil-based resin and styrene, the more reactive unsaturations are preferentially consumed and these correspond to the C=C bonds of styrene and those of the maleates in the synthesized resin.

Thus, the unsaturations present in the fatty acid chains have a very low participation in the styrene copolymerization. Because of that, the chains that do not react to become elastic chains of the network remain as dangling chains (defects in the network

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structure) and have a plasticizing effect on the thermoset. This type of structure prevails at short times and progressively changes as the material ages in contact with the surrounding air.

Given enough time, oxygen slowly diffuses into the sample, triggering new chemical reactions and producing changes in the properties of these materials. Chemical reactions include oxidative polymerization and degradative processes (among the most important). Oxidative polymerization occurs after an induction period where the natural antioxidants are consumed.^{8,9} Then, the oxygen concentration in the sample becomes important and dehydrogenation of a methylene group located between two double bonds of the fatty acid chain occurs by means of the oxygen. A radical is formed, which starts a chain reaction, leading to the formation of a hydroperoxide.^{4,9,10} Hydroperoxides are unstable and decompose to form new free radicals that lead to crosslinked structures.^{9,10} The fatty acid chains that initially acted as plasticizers become part of the network after this reaction, and the mechanical performance of the materials is notably improved. In contrast, oxidative degradation is also possible under natural and accelerated weathering conditions, which may produce chain scissions and the formation of volatile products. These processes with opposite effects on the material properties can occur simultaneously, complicating the analysis of the results.¹¹

In spite of this, the analysis and understanding of the resulting behavior in new polymeric materials is of great importance to predict their fitness to fulfill the requirements for an envisioned application. Thus, the aim of the work reported in this paper was to investigate the change in properties of a linseed oil-based resin/styrene thermoset exposed to dry, wet and accelerated weathering conditions. A composite material formulated with this polymer as the matrix and wood flour as the filler was also evaluated.

EXPERIMENTAL

Materials

An unsaturated resin was synthesized from linseed oil (acid value: 77.4 mg KOH g⁻¹; saponification value: 199.8 mg KOH g⁻¹) supplied by Grainer SA (Entre Rios, Argentina) and was used without further purification. Glycerol used in the glycerolysis reaction was 99.5% pure (Cientifica Central, Buenos Aires, Argentina). A neutral commercial soap without additives was used as emulsifier catalyst for this reaction. In the maleinization reaction, maleic anhydride and 2-methylimidazole (as a catalyst), both from Fluka, were used. The resin from linseed oil was further copolymerized with styrene using benzoyl peroxide (Lucidol 0.75, Akzo Chemical SA) as radical initiator.

Composite materials were manufactured using dried pine wood flour (J Do Santos Freire, Buenos Aires, Argentina) as filler and the linseed oil-based resin crosslinked with styrene as matrix.

All the wood flour particles passed through a mesh 40 sieve (US Standard) and were retained by a mesh 100 sieve, corresponding to average particle sizes of 150 to 250 µm. The wood flour was dried in an oven at 75 °C for 48 h before being used.

Synthesis of the linseed oil-based resin

The linseed oil resin was synthesized in two main steps (Fig. 1, steps (a) and (b)). In the first step, the glycerol was heated at 220–230 °C for 2 h under nitrogen atmosphere to remove trace amounts of water. Then, the glycerolysis reaction was carried out using a weight ratio of 2 g of linseed oil to 1 g of glycerol, and adding the linseed oil in five steps at 1 h intervals. Subsequently, a commercial soap (1 wt%) was also incorporated and the solution was heated for 5.5 h at 220–230 °C. The reaction flask was then cooled by immersion in an ice and salt mixture down to room temperature. Approximately 50% of the initial excess of glycerol was removed. The product of this step was mainly the monoglyceride and minor amounts of diglyceride and glycerol.

In the following step, the glyceride/glycerol mixture and the maleic anhydride were loaded at a 1.5:1 weight ratio in a reactor equipped with a mechanical stirrer and heated at 80 °C for 5.5 h. Then, 0.6 wt% of 2-methylimidazole (catalyst) and 500 ppm of hydroquinone (free radical inhibitor used to protect maleate unsaturations) were added to the mixture. The linseed oil-based resin, obtained as a viscous liquid, was stored in a refrigerator (8 °C) for further use.

Linseed oil resin/styrene crosslinking

The synthesized resin was mixed with 40% (by weight) of styrene and 2.5% (by weight) of benzoyl peroxide (Fig. 1, step (c)). The mixture was filled in a closed mold and placed in an oven at 50 °C for 1.5 h; the temperature was then increased at a rate of 1 °C min⁻¹ up to 90 °C. Curing took place at this temperature for 1.5 h and then the samples were post-cured at 150 °C for another 1.5 h.

Two types of molds were used. To obtain plaques, the reactive mixtures were poured between two plane glasses separated by a rubber cord and kept together with metal clamps. To obtain cylinders, glass tubes of 5 mm interior diameter were used. In both cases, the molds were previously treated with a silicone release agent.

Composite materials

Plaques of the composite containing 40% by weight of wood flour with respect to total weight were manufactured by compression molding. The dried filler and the reactive mixture (linseed oil resin, styrene and benzoyl peroxide) were mixed in an intensive mixer at room temperature and 50 rpm. The resulting paste was filled in a cylindrical metal mold (145 mm diameter and about 3 mm thick). The heating program was the same as that used to obtain the unfilled thermoset, but the curing step (90 °C) was carried

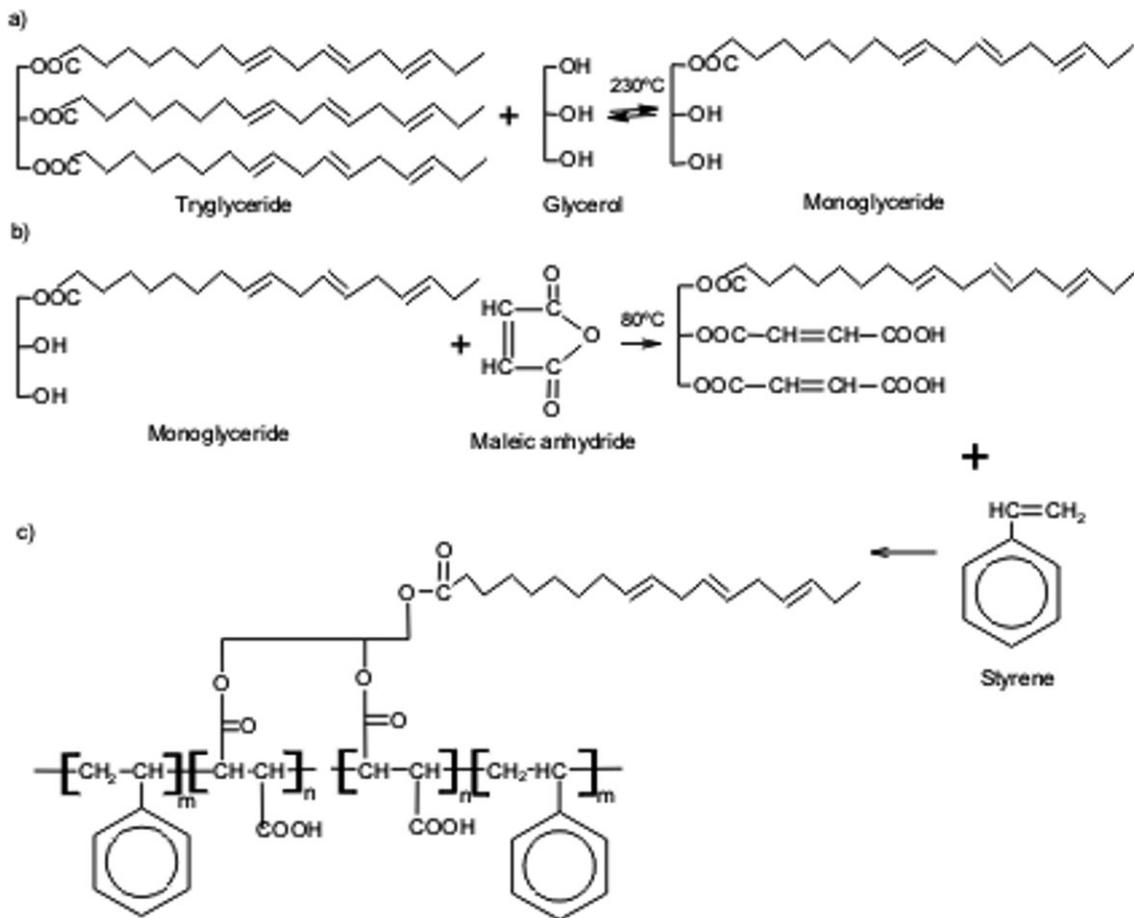


Figure 1. Scheme of synthesis of the linseed oil-based resin and subsequent copolymerization with styrene.

out under a pressure of 4 MPa to ensure material cohesion.

Weathering conditions

The samples were conditioned in three different ways:

- (i) Dry samples were stored in a nonevacuated desiccator containing silica gel to maintain low humidity and in a normally illuminated area at room temperature.
- (ii) Specimens were dried until constant weight and then were exposed to controlled humid environments of 60% relative humidity (RH), prepared in hermetic containers at room temperature and containing aqueous glycerol solutions with concentrations of 72% by weight to ensure 60% RH, respectively.¹² The weight changes due to moisture absorption were recorded as a function of time until no further change was detected: that is, when the sample reached its equilibrium moisture content (EMC). The measurements were performed on at least four specimens.
- (iii) Accelerated artificial weathering was carried out in light exposure and weathering equipment, model Suntest CPS/CPS+, from Atlas Material Testing Solution, operating with an NXE 1500B xenon lamp with irradiance of 500 W m^{-2} and wavelengths between 300 and 800 nm. The

chamber was maintained at 50°C and 60% RH. The test was performed with cycles that alternated periods of 4 h of exposure and non-exposure to irradiation. Samples were subjected to the aging process for different times.

Characterization

Fourier transform infrared (FTIR) spectroscopy

A thin film was obtained on windows of NaCl by curing a thin coating of the linseed oil resin/styrene mixture. This film was then characterized using transmission FTIR spectroscopy. The copolymers obtained in plaques of 3 mm of thickness were reduced to powder to be characterized using DRIFT spectroscopy. All spectra were recorded at 2 cm^{-1} resolution with the use of a Genesis II FTIR spectrometer. Reported results are the average of 32 scans.

Mechanical testing

The properties of the linseed oil resin/styrene thermosets were determined using compression, flexural and dynamic mechanical tests. The composite materials were tested in static three-point bending tests.

Compression specimens were cylinders cut with a height/diameter ratio of 1.5 to 2.0 (ASTM D695M). The top and bottom faces were carefully machined to be parallel.

Three-point bending tests were performed in accordance with ASTM D790-93 standard. Specimens of approximately $60 \times 10 \times 3 \text{ mm}^3$ were cut from the molded plates for testing.

All the static tests were carried out at a crosshead speed of 2 mm min^{-1} and at room temperature using an Instron 8501 universal testing machine. The specimen dimensions were measured with calipers up to $\pm 0.01 \text{ mm}$. At least four replicate determinations were made for each sample to ensure the reproducibility of the results.

Dynamic mechanical tests were performed using a Perkin Elmer dynamic mechanical analyzer, DMA 7e, using the three-point bending fixture (specimen platform of 15 mm length) to determine the loss tangent ($\tan \delta$) of the samples under nitrogen atmosphere. The specimens were cut to $20 \times 3 \times 2 \text{ mm}^3$. The dynamic and static stresses were kept at 100 and 200 kPa, respectively. The frequency of the forced oscillations was fixed at 1 Hz and the heating rate was $10^\circ \text{C min}^{-1}$.

RESULTS AND DISCUSSION

Characterization of the linseed oil-based resin

The results of each of the steps in the synthesis of the linseed oil-based resin were followed using different analytical techniques and they were described and discussed in detail in a previous publication.⁶

As a brief summary, the ^1H NMR spectra showed that the peak appearing at 5.3 ppm corresponding to the unsaturations in the fatty acid chains of the oil was present with similar intensity after modification of the oil. The degree of isomerization of maleate to fumarate was almost negligible and the maleate protons (6.3 ppm) to fatty acid protons (5.3 ppm) ratio was 0.65, which is in the range found by other authors.⁵

The gel permeation chromatograms of the final resin showed a wide distribution of products, corresponding to diglyceride monomaleates and monoglyceride mono- and bismaleates and glycerol tris- and bismaleates.⁶

For the reaction conditions used, the final resin obtained was completely soluble in styrene.

Spectroscopic analysis

Among the different parameters that can influence the drying or curing of this type of material, the thickness is one of the most important. A thin sample allows uniform diffusion of oxygen, so that the process of oxidative polymerization can take place rapidly, simultaneously with the free radical copolymerization mentioned before. A large sample thickness and a surrounding closed mold make the penetration of oxygen into the sample difficult.⁴ Thus, the C=C double bonds of the fatty acid chains, which are less reactive than the unsaturations of maleates and of styrene, remain unreacted. In contrast, if the reactive mixture is cured as an open film, some

styrene may be evaporated before complete curing and small traces of maleic anhydride (residue of the maleinization reaction) can sublime before the sample is completely cured. Simultaneously, oxygen can diffuse in the film more rapidly and produce an oxidative polymerization of the fatty acid chains in the resin.

Figure 2 shows a comparison of the FTIR spectra of a thin film (Fig. 2(A)) and that of a plaque of 3 mm of thickness (Fig. 2(B)), both obtained one day after sample preparation. Although the batch of the reactive mixture and the curing cycle were the same for both preparations, it is clear that the materials obtained are different. The fatty acid C=C bonds in the film have the possibility of undergoing oxidative polymerization during curing, while in the plaque the diffusion of oxygen is not as easy and these C=C bonds are preserved after the radical copolymerization in the plaque. An important difference between the spectra is the presence of a wide band at 3450 cm^{-1} attributed to hydroxyls corresponding to the formation of some oxidation products present in the sample cured as a film.^{4,11} Moreover, the spectrum of the film shows the disappearance of almost all =C-H deformations, while the plaque presents a *cis* =C-H stretching band at 3010 cm^{-1} and the corresponding deformation band at 762 cm^{-1} . Also, there is a significant difference in the width of the carbonyl band at 1740 cm^{-1} . The spectrum of the thick sample presents bands at 1780 and 1858 cm^{-1} corresponding to traces of maleic anhydride from the maleinization reaction in the synthesis of the linseed oil resin. These bands do not appear in the thin sample since maleic anhydride can sublime. The possible reactions during the oxidation of the dangling unsaturated fatty acid chains are shown in Fig. 3.

Mechanical characterization

Figure 4 shows the flexural modulus of dry and wet (60% RH) samples as a function of the time

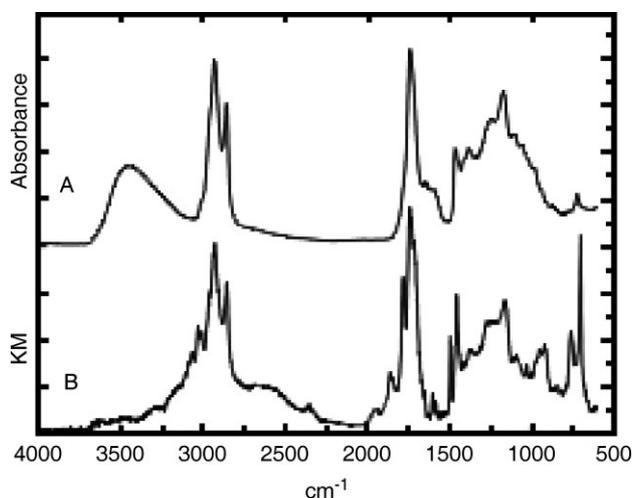


Figure 2. FTIR spectra one day after sample preparation: (A) sample prepared as a thin film; (B) sample prepared as a plaque of 3 mm in thickness.

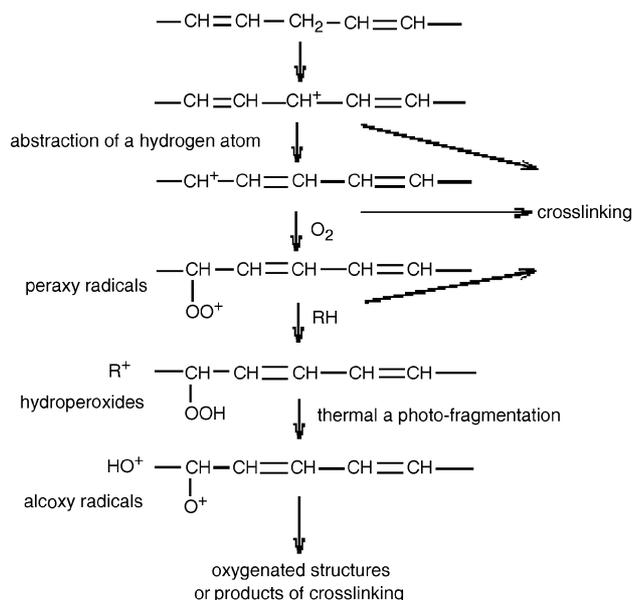


Figure 3. Oxidative polymerization mechanism of drying oils.

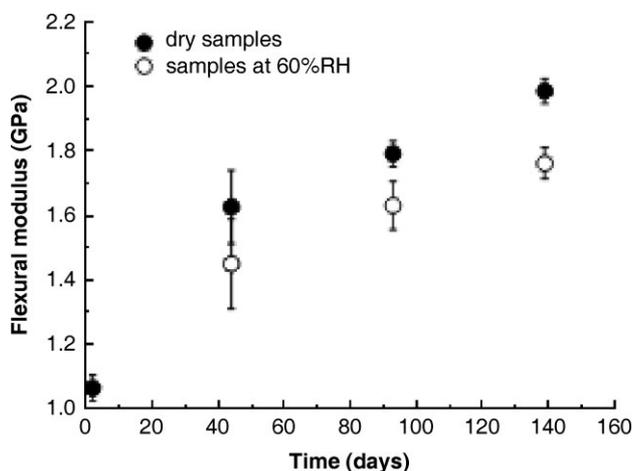


Figure 4. Flexural modulus of dry and wet (60% RH) samples as a function of the time after curing.

after their preparation. This property increases during the whole period of time analyzed as a result of the chemical changes in the polymer. Although crosslinking and degradative processes have the possibility of occurring simultaneously when these materials are in contact with oxygen, the results indicate that the crosslinking are the more important reactions for the conditions and period of time analyzed. The increasing crosslinking density leads to the increase of the modulus, since the initially dangling chains form chemical bonds to the network, becoming elastically active chains. The molecular mobility is consequently reduced and the rigidity of the material increased. It can be noticed that the largest change in the modulus takes place between 0 and 40 days and then the change is more gradual. This behavior can be explained by the increased crosslinking density, which reduces the permeability of oxygen in the outer layers of the sample, and thus reduces the reaction rate through the sample.⁴ As time goes on, the diffusion

of oxygen in the sample is reduced, as well as the crosslinking reaction rate. Obviously, the reduction of this rate is also the result of the decreasing number of unsaturations as the conversion approaches unity.

The material exposed to controlled humidity suffers the plasticizing effect of water molecules, so the modulus becomes lower than that of the dry samples. As the time of exposure increases, the material absorbs more humidity until reaching the equilibrium content. Also, the material is undergoing other changes (chemical changes) because of the presence of oxygen in it. Thus, under the action of combined factors, the diffusion of oxygen can also be modified.

Figure 5 shows the ultimate stress and deformation in bending tests as a function of time after sample curing, for samples exposed to 60% RH. The data at $t = 0$ are not included in the figure because the samples suffered large deformations without breakage. The trend is similar for both properties, showing a rapid decrease at short times that becomes moderate at longer times, apparently approaching an equilibrium value. The decrease in ultimate stress occurs because the material becomes more fragile as the crosslinking density increases and its failure occurs at lower stress values. Moreover, the increase in water content in the sample with the time (before reaching equilibrium) also contributes to the decrease in the strength.

Regarding the ultimate deformation of the material, the effect of increasing rigidity due to crosslinking seems to be stronger than the plasticizing effect of absorbed water.

Table 1 presents all the results obtained in the compression tests of the dry samples. It can be observed that the compressive modulus increases with time after curing, as mentioned before. Comparing the modulus of dry and irradiated samples, 44 days after curing, it is clear that the material that was in the UV chamber reached higher modulus due to accelerated crosslinking. Under UV irradiation, the formation of radicals leads to oxidation products, chain scissions as well as crosslinking reactions due to radical recombinations.¹³ In this case, exposure to the xenon lamp radiation accelerates the chemical processes

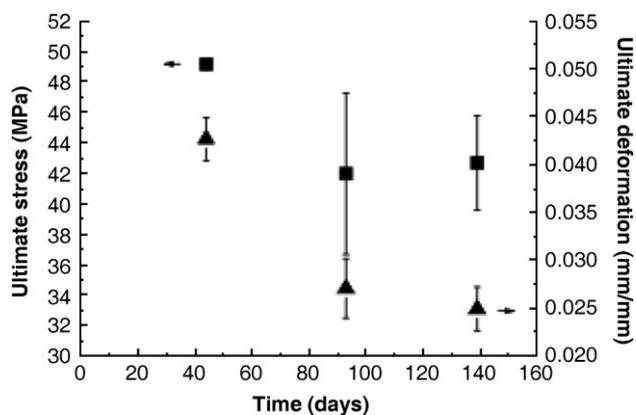


Figure 5. Ultimate stress and deformation of wet samples (60% RH) as a function of the time after preparation.

Table 1. Compression properties of dry samples

Days	Modulus (MPa)	Yield stress (MPa)	Yield deformation (mm mm ⁻¹)	Ultimate stress (MPa)	Ultimate deformation (mm mm ⁻¹)
2	723.4 ± 66.3	21.67 ± 1.87	0.0637 ± 0.0109	–	–
44	868.9 ± 33.2	25.83 ± 0.81	0.0465 ± 0.0046	25.75 ± 1.93	0.3143 ± 0.0577
93	960.9 ± 56.4	31.17 ± 2.08	0.0530 ± 0.0059	29.22 ± 1.98	0.3456 ± 0.0232
139	963.9 ± 65.8	28.21 ± 0.70	0.0946 ± 0.0050	26.41 ± 0.42	0.3074 ± 0.0543
44 ^a	994.6 ± 35.4	32.25 ± 0.53	0.0535 ± 0.0033	33.48 ± 1.67	0.3329 ± 0.0293

^a Samples subjected to UV irradiation in a controlled humidity chamber for 18 days (60% RH).

involving polymerization as the most important mechanism.

The yield and ultimate stress increase with time, with a maximum at 93 days, and then they decrease. The atmospheric exposure produces several changes in this type of material, such as polymerization, oxidation and chain scission, among others. These changes have in many cases opposite effects on the mechanical properties. The increase at short times can be explained by the prevailing effect of polymerization reactions leading to the formation of a more crosslinked network. At longer exposure times the number of chain scissions seems to overcome the crosslinking reactions and, as a result of these degradative processes, a reduction in the properties is observed.

Despite the error of the initial measurement, Table 1 shows that yield deformation seems to grow with time during the period considered of 139 days.

The ultimate stress and ultimate deformation do not change much with time. Clearly, the material undergoes an important plastic deformation after yielding, and it breaks at a deformation 3 to 6 times larger than that at yield.

The irradiated sample shows higher stress and deformation at rupture which can be related to a more complete crosslinking reaction.

The values obtained for the bending modulus are much higher than those for the compression modulus, particularly at long times, for dry aged samples. This difference may be due to the effect of the geometry of the specimens, which are relatively very thin in flexural tests and offer two wide faces to the surrounding air that facilitates oxygen diffusion into the sample. Other explanations may be related to compression test difficulties as stated by other authors.^{14,15}

Table 2 presents the flexural modulus 44 days after sample preparation for dry, wet and irradiated samples. As was mentioned in the discussion of Fig. 2, the wet sample has a lower modulus than the dry sample. However, the sample placed in the

UV chamber has a higher modulus, even when it was also subjected to a humid environment. Again, this indicates that crosslinking is higher in the latter case (UV and humidity chamber) and this agrees with the results found in compression tests.

Table 3 presents the results obtained for a composite material containing 40% of wood flour in its formulation. It is evident that the material undergoes an important change of its properties from the moment of its preparation. During the oxygen-activated crosslinking, previously unbounded segments of polymer are connected through new covalent bonds. As the reaction proceeds to low and medium crosslinking levels, strength, elasticity and toughness also increase. At higher crosslinking levels further increases in strength and elasticity are obtained but at the cost of the embrittlement of the sample, and the elongation at break decreases greatly. The dry composite tested at 654 days after curing shows an increase in moduli, ultimate stress and deformation that can be related to increasing crosslinking. Furthermore, the composite material further exposed 18 days in the UV chamber shows values of modulus and ultimate stress that are more than double the values measured for a dry composite shortly after preparation. Also, the deformation at break is reduced because the sample becomes more brittle.

Accelerated conditions

Figures 6 and 7 present the flexural modulus (E_b) and the glass transition temperature (T_g , temperature of the maximum in the $\tan \delta$ curve obtained in dynamic mechanical analysis tests) as a function of the time of storage in the UV chamber. All the samples used

Table 2. Flexural modulus (MPa) of dry, wet (60% RH) and irradiated (18 days) samples at 44 days after preparation

Dry samples	Samples at 60% RH	Samples in UV chamber
1625.0 ± 113.9	1447.9 ± 139.3	1766.9 ± 118.9

Table 3. Flexural properties of the composite material with 40% by weight of wood flour

	Modulus (MPa)	Ultimate stress (MPa)	Ultimate deformation (mm mm ⁻¹)
Dry composite at 7 days after preparation	1471.6 ± 317.7	19.87 ± 6.61	0.0166 ± 0.0023
Dry composite (654 days after preparation)	2115.7 ± 302.9	32.15 ± 6.60	0.01817 ± 0.020
Composite (654 days after preparation and 18 days in the UV chamber)	3188.0 ± 129.7	42.63 ± 2.41	0.0143 ± 0.0011

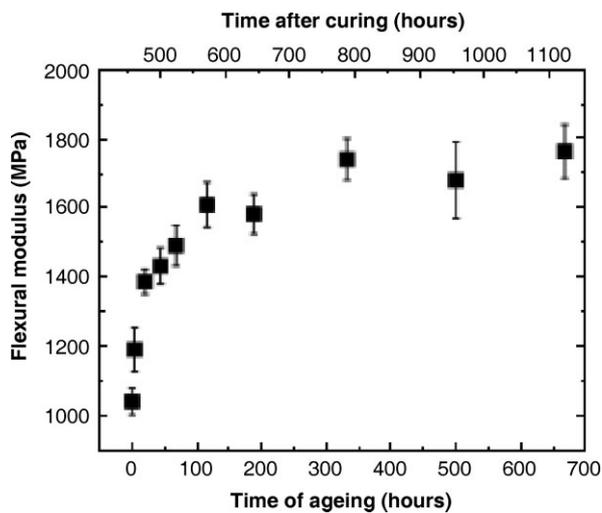


Figure 6. Flexural modulus of irradiated samples at different times of exposure in the UV chamber.

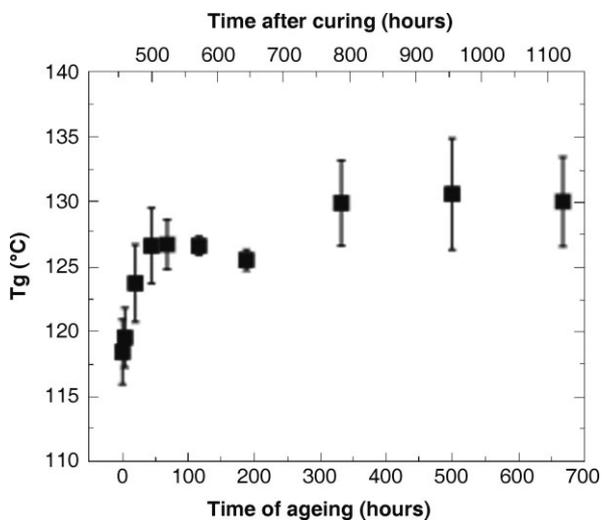


Figure 7. Glass transition temperature (T_g) obtained using dynamic mechanical analysis at different times of exposure in the UV chamber.

in the UV irradiation study had been crosslinked with styrene before the test, and the beginning of the UV study is coincident with a period of 19 days after sample preparation. The most significant changes were detected in the initial part of aging with important increases in both, E_b and T_g . After approximately 100 h of aging, the changes are more gradual until reaching a plateau at long exposition times in the UV chamber, with E_b and T_g values of the order of those usually reported for synthetic polyester resins.¹⁶

CONCLUSIONS

The aging of a linseed oil resin/styrene thermoset and a derived woodflour composite was studied under three

different test conditions: dry, humid and subjected to UV irradiation. Monitoring of compression and flexural properties clearly indicated the effect of a crosslinking reaction taking place during relatively long periods of time. This reaction is identified as corresponding to oxidative mechanisms that involve the unreacted unsaturations of the linseed oil chains.

The samples show an improvement in their mechanical properties, modulus and yield stress over time, the most important changes occurring during the first weeks after preparation. UV irradiation of the samples accelerated these chemical changes, so that the material reached properties similar to those obtained using synthetic unsaturated polyester resins. Humid environments reduce the mechanical performance of the materials, but do not inhibit the ongoing oxidative aging process.

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