

# Natural and Artificial Weathering Effects on Cold-Cured Epoxy Resins

Mariateresa Lettieri,<sup>1</sup> Mariaenrica Frigione<sup>2</sup>

<sup>1</sup>*Institute of Archaeological Heritage, Monuments and Sites, Italian National Research Council (CNR-IBAM), Prov.le Lecce-Monteroni, 73100 Lecce, Italy*

<sup>2</sup>*Department of Innovation Engineering, University of Salento, Via per Monteroni, 73100 Lecce, Italy*

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**ABSTRACT:** Three cold-cured epoxy resins, specifically designed as structural adhesives for rehabilitation or renewal applications of civil infrastructures and cultural heritage, were submitted to natural and artificial weathering. We evaluated the variations in the thermal and mechanical properties and color changes after an artificial treatment carried out at 70°C and 75% relative humidity and after natural weathering, performed in two areas of South Italy, both located adjacent to the Mediterranean

Sea. The variations in properties due to both natural exposure and artificial weathering were qualitatively similar. However, the selected artificial weathering procedure appeared excessively severe compared to the weathering that occurred after outdoor exposure. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1635–1645, 2011

**Key words:** ageing; calorimetry; mechanical properties; thermosets

## INTRODUCTION

The use of epoxy resins in the restoration field is frequently aimed at structural consolidation. Because these resins exhibit high adhesion properties, they are usually used for glue-detached parts and for the readherence of large stone fragments to mass stone.<sup>1,2</sup> The addition of suitable fillers (e.g., powdered stone) to the original formulation allows one to obtain excellent products for both repairs and gap fillings.<sup>3,4</sup>

The epoxy resins used in civil engineering repair operations and in cultural heritage restoration are cold-cured resins; that is, they are based on bisphenolic epoxies that, for practical and economical reasons, are cured at ambient temperatures. Consequently, long curing times (on the order of weeks) are necessary to achieve sufficient mechanical properties, and a moderate glass-transition temperature ( $T_g$ ), that is, never greater than 65–70°C, is attainable by these systems.<sup>5</sup>

The crosslinking reactions taking place in epoxy resins at ambient temperatures are often not completed because of kinetic restraints, even when long curing times are used. As a result, the exposure to a temperature slightly higher than ambient temperature

causes an increase in  $T_g$  and, in turn, the strengthening and stiffening of the system. On the other hand, the absorption of external water, both in liquid or vapor form, produces a decrease in the initial  $T_g$  of the resin, which affects the mechanical properties and may enable the postcuring process that takes place at lower environmental temperatures.

Epoxy resins exposed to sunlight can undergo oxidative processes promoted by UV radiation that yield chain scissions;<sup>6</sup> this produces weight loss and a reduction of the performance of the materials.

Physical aging can also take place in cold-cured epoxy resins; this leads to a reduction in the polymer's free volume over time, that is, in a densification, with a consequent modification of all of the mechanical, temperature-dependent properties. Physical aging in the glassy state is very slow, whereas it proceeds rapidly at temperatures close to  $T_g$ . This latter is the case of cold-cured resins, in which  $T_g$  can be easily approached and even exceeded by the external temperature. Physical aging is a thermoreversible phenomenon, which can be erased when the polymer is heated above its  $T_g$ . When the service temperature exceeds  $T_g$  of aged adhesive resins, a rejuvenation of the resin takes place, and the initial properties are recovered. Cold-cured epoxy resins exposed to natural weather, therefore, are constantly subjected to aging and rejuvenation processes that take place in nonisothermal conditions, depending on the actual meteorological weather.<sup>7</sup>

From the previously discussed considerations, it is clear that there is a pressing need to find reasonable

Correspondence to: M. Frigione (mariaenrica.frigione@unisalento.it).

tools to ascertain the behavior of these systems when they are exposed to environmental agents, that is, to establish their durability. Existing data on the durability performances of cold-cured epoxies in this specific field are scarce, not well documented, and often contradictory. On the other hand, the lack of data on their long-term behavior, particularly in aggressive environments, represents a major drawback to the wider use of such qualified materials.<sup>8</sup>

Field monitoring is recognized as the only effective method for assessing the long-term behavior of materials. However, reliable studies of durability require long periods of natural exposure, and where lifetimes greater than many decades are expected, as in the field of building materials, it is not possible to plan real-time outdoor exposure to predict the durability of the materials.

In standardized procedures, proposed to achieve accelerated weathering, one or more weatherlike conditions are intensified to levels greater than those occurring naturally. Some committees work to standardize the methods for accelerated and natural durability testing; as a result, many standard procedures have been published in recent years, first by ASTM and by ISO. None of these standards, however, imposes rigid conditions, particularly on the duration of the tests, which is often left to the experience of the researcher, supported by general guidelines for the choice of the main test parameters that need to be changed to suit any particular application. In fact, the weathering conditions should be selected to reproduce, as close as possible, the natural conditions where the materials are intended to be used. A rationale prediction through accelerated procedures must include, for each material, a correlation between the results obtained under natural and artificial weathering conditions.<sup>9–11</sup> This would require, in turn, a huge number of carefully selected procedures based on both natural and artificial exposures.

The studies reported in the literature dealing with the effects of accelerated weathering on heat-cured epoxy resins, which are used as adhesives and matrices for composites, are fairly limited.<sup>12</sup> The main problem remains to clearly explain how these aging procedures can be correlated to the real times of the natural exposure. Moreover, only a few studies have been published dealing with the weathering of cold-cured epoxy resins, as well.

In this article, the properties of cold-cured epoxy resins subjected to either natural weathering or an artificial weathering procedure, are illustrated. To this aim, outdoor exposure and treatments consisting of simultaneous exposure to a mild temperature and a high relative humidity (RH) level, carried out in a climatic chamber, were performed. The thermal and mechanical properties and changes in the weight, measured after either natural or artificial weathering,

are discussed. Color variations were also evaluated at different stages of the artificial weathering.

## EXPERIMENTAL

### Materials

Three commercial cold-cured epoxy resins—materials widely used in the field of the rehabilitation and restoration of buildings—were studied. All of the systems consisted of bisphenolic resins hardened with mixtures of amines, able to cure the epoxies at ambient temperature. The details of composition and other information for all of the systems analyzed are described in the following paragraphs.

A1 resin (Mapei S. p. A., Milan, Italy) was provided as two components: Part A was based on diglycidyl ether of bisphenol A, and part B was a mixture of polyethylenamine, xylenediamine, and nonylphenol used as a curing agent. Samples of this resin were prepared with the recommended ratio, that is, resin–hardener = 4 : 1 by weight.

A2 resin (Sika Italia S. p. A., Peschiera Borromeo, Milan, Italy) was a bisphenolic resin (part A) hardened with 3-aminomethyl-3,5,5-trimethyl cycloesilamine (part B). The recommended ratio of resin to hardener (2 : 1 by weight) was used to prepare the specimens.

A3 resin (Sika Italia S. p. A., Italy) was based on a bisphenolic resin hardened with 3-aminomethyl-3,5,5-trimethyl cycloesilamine (part B). Part A also contained an inorganic filler (ca. 40 wt % of the total weight of the cured mixture). The recommended ratio of part A to part B (4 : 1 by weight) was used to prepare the specimens.

For commercial reasons, additional details on the chemical composition and structure of the systems were not available.

Samples of each system were prepared and cured at a temperature of  $23 \pm 2^\circ\text{C}$  and an RH of  $50 \pm 5\%$ . We stored the specimens, produced by pouring the liquid mixture in standard molds (dimensions:  $90 \times 10 \times 4 \text{ mm}^3$ ), in a dark area.

### Treatments

Before the exposure of the specimens to artificial weathering, to prevent misinterpretation of the results, we verified that the curing reactions were slowed down, that is, the curing process was stopped.  $T_g$  was used to monitor the cure, and the resins were judged cured when their  $T_g$  leveled off. This occurred after about 4.5 months of curing at ambient temperature. However, this did not necessarily mean that the curing reactions were completed because a small residual heat of reaction ( $\Delta H_r$ ) was still measured on most of the specimens by calorimetric analysis.

A standard artificial weathering test was, then, carried out in a climatic chamber (Milan, Italy) (Perani-Model UC 1000/20). The samples were left at  $70 \pm 2^\circ\text{C}$  and  $75 \pm 5\%$  RH for different time spans, up to 34 days. The weathering conditions followed procedure C reported in the ASTM D 756-93 standard.<sup>13</sup> A high temperature and high moisture levels were only taken into account. UV aging was overlooked to simulate the environmental conditions of these epoxy resins, which are mainly used in applications where the UV exposure is negligible. A similar practice was reported as leading to thermohygroscopic conditions comparable and close to those obtained after 2 years of natural weathering in the western Mediterranean basin.<sup>14</sup>

With regard to the natural weathering procedure, the samples were exposed outdoors without any protection to environmental agents. The A1 system was exposed after about 4.5 months of curing at ambient temperature, whereas the A2 and A3 specimens were placed outdoors in a previous stage of the research, after a 10-day cure at ambient temperature, according to the recommendations of the suppliers.<sup>7,15</sup> All of the specimens were exposed in south Italy, the A1 system in Lecce (latitude =  $40^\circ 20'$  N and longitude =  $18^\circ 07'$  E) and the A2 and A3 systems in Fisciano (Salerno, latitude =  $40^\circ 46'$  N and longitude =  $14^\circ 47'$  E), both located adjacent to the Mediterranean Sea. The specimens were placed horizontally. The A2 and A3 specimens were subjected to natural weathering for up to 36 months, as reported in a previous article.<sup>7</sup> The A1 system was exposed in a subsequent stage of the research and was subjected to natural weathering for up to 43 months. Table I reports the average values of the temperature, humidity, rain, and UV light dose measured during the exposure period of the A1 system by the Laboratory of Climatology at the University of Salento.

Some of the specimens were removed periodically to perform the experimental tests, as described in the next paragraph.

### Analytical techniques

The thermal and mechanical properties of the epoxy resins were determined through differential scanning calorimetry (DSC) and flexural mechanical tests in three-point bending mode, respectively. Weight variations were also determined. The analyses were carried out at the end of any artificial weathering treatment and periodically repeated during natural exposure. At the end of each artificial weathering treatment, the color changes ( $\Delta E$ 's) were evaluated. In addition, the same investigations were performed before the weathering procedures on untreated sam-

**TABLE I**  
Meteorological Data Relative to the Lecce Site Measured During the Investigated Exposure Period for the A1 System

	Daily average (minimum to maximum)	
	2005	2006
Temperature ( $^\circ\text{C}$ )	17 (−1 to 37)	17 (−2 to 39)
RH (%)	71 (19 to 100)	72 (14 to 100)
Solar light dose ( $\text{MJ}/\text{m}^2$ )	15 (1 to 27)	11 (1 to 20)
Rain ( $\text{mm}/\text{day}$ )	1.2 (0.0 to 42.0)	—

ples stored indoors and, hence, not subjected to any weather factors.

DSC was performed with thermal dynamic scans between 0 and  $300^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  under a nitrogen atmosphere. A DSC 822 Mettler calorimeter (Mettler Toledo, Novate Milanese, Milan, Italy) was used, and the thermal properties [ $T_g$ , relaxation enthalpy ( $\Delta H_{\text{rel}}$ ), and residual crosslinking enthalpy] were calculated as the average of at least three measurements.

Flexural mechanical tests were carried out in three-point bending with a Lloyd LR-MK4 dynamometer, according to the standard listed in ref. 16. The experiments were performed at room temperature with a support span of 60 mm and a crosshead rate of 2 mm/min. The flexural mechanical properties (i.e., flexural modulus and maximum flexural strength) were calculated as the average of five measurements.

Weight measurements were registered with an analytical balance (Sartorius, model BP 2215, Sartorius Stedim Italy S.p.A., Bagno a Ripoli, Florence, Italy) with an accuracy of  $\pm 0.1$  mg.

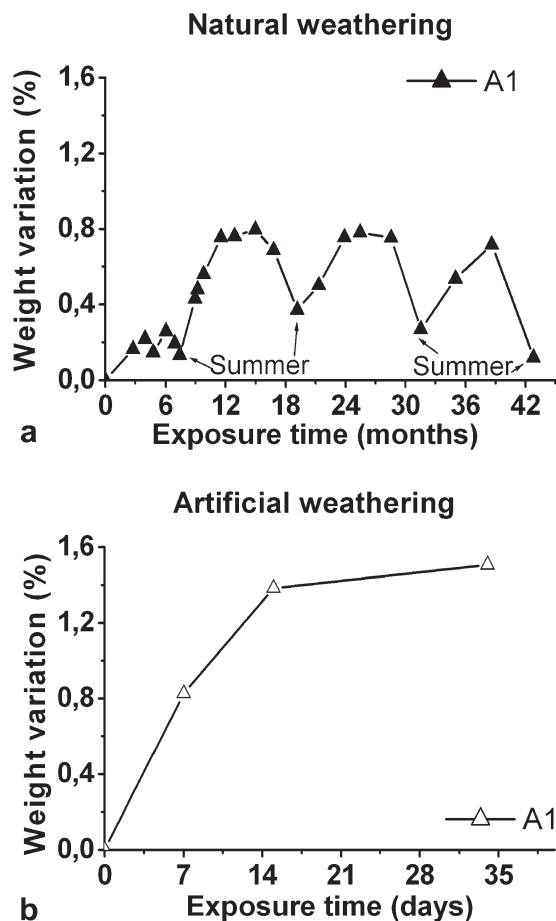
Color measurements were performed with a Minolta Chroma Meter CR300 colorimeter (Konica Minolta Sensing Inc., Osaka, Japan) with CIE standard illuminant C. Ten measurements were performed on each sample, and the colorimeter was recalibrated to a white calibration plate at the start of each measuring session.  $\Delta E$ 's were calculated through the  $L^*a^*b^*$  system,<sup>17</sup> with the mean values determined on five samples. The color measurements were carried out on the artificially weathered samples and, for A1 system only, on the naturally exposed specimens.

## RESULTS AND DISCUSSION

### Weight variations and thermal analysis

The variations of weight of the three systems studied after natural and artificial weathering were first analyzed.

In Figure 1(a,b), the variations in weight of system A1 as function of the exposure time for natural and



**Figure 1** Weight variations measured for system A1 as function of the exposure time for (a) natural weathering and (b) artificial aging.

artificial weathering, respectively, are reported. The natural exposure yielded weight variations strictly dependent on the weathering conditions: during wet periods, greater amounts of water were absorbed, and weight gain was observed; the following warm and dry season enhanced the evaporation of water (or solvents), and then, the weight decreased. In the case of the artificial weathering treatment, on the other hand, a desorption stage was never observed because the specimens were constantly stored at a fixed RH level. A continuous increase in weight, attributed to the absorption of water, was observed with exposure time in the artificially weathered samples.

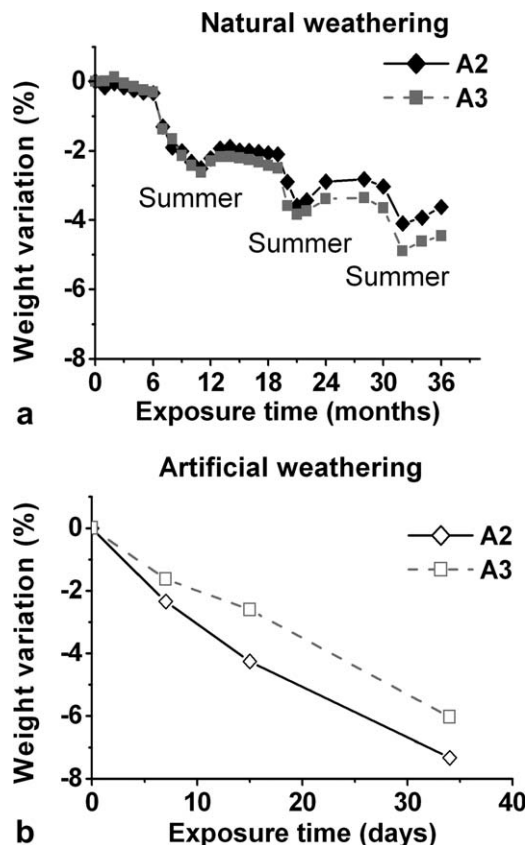
With regard to the A2 and A3 systems, Figure 2(a) shows the percentage weight loss, normalized with respect to the initial weight, of these systems during the 36-month natural exposure. For specimens of system A3, the weight calculated for the effective resin content is reported; that is, the weight of the filler, which did not absorb water, was neglected. The environmental conditions occurring just before the analysis of the samples affected the changes in weight. For instance, the loss of weight correspond-

ing to the summer periods (due to the evaporation of water or solvents) was partially reduced in the months following (due to the regain of water). The overall decrease in weight was also attributed to the degradation processes due to thermal or UV aging, which led to the loss of dangling chains.<sup>18–21</sup>

When the samples were subjected to the artificial procedure, the same qualitative trend was observed [Fig. 2(b)]; that is, the weight of both systems decreased with the exposure time when the effects of the specific weathering conditions mentioned, that is, the fluctuations, were excluded. This result let us suppose that during the natural weathering, the variations in weight due to UV action was negligible. In fact, a significant weight loss was also measured in the samples subjected to the artificial weathering and not exposed to UV radiation.

The different behavior observed for the A2 and A3 systems exposed to artificial weathering with respect to A1 is discussed later in the text.

The analysis of the variations in  $T_g$  of the A1, A2, and A3 systems after natural and artificial weathering demonstrated that the artificial aging procedure that we used led to different effects with respect to those found after natural weathering; these were, in particular, more severe for the A2 and A3 systems



**Figure 2** Weight variations measured for systems A2 and A3 as function of the exposure time for (a) natural weathering and (b) artificial aging.



TABLE II  
Maximum Variations in  $T_g$  ( $\Delta T_g$  max) After Natural and Artificial Weathering

	A1		A2		A3	
	Natural	Artificial	Natural	Artificial	Natural	Artificial
$\Delta T_g$ max ( $^{\circ}\text{C}$ )	-7 to 14	5	-3 to 2	-11	-9 to 4	-10

(Table II). For the latter, the maximum variations in  $T_g$  measured after prolonged external exposure never reached the values measured on the samples subjected to the artificial weathering.

As reported elsewhere,<sup>7</sup> the natural exposure produced in the A2 and A3 systems reductions in  $T_g$ , which were, to some extent, reversible. The decreases in  $T_g$  were attributed to the plasticization effect of water absorbed during natural weathering. Higher  $T_g$  values were measured during the warmest season because the water absorbed partly evaporated. It was possible that a postcure process took place in addition, which concurred with the increase in  $T_g$ . The UV degradation could have contributed to the decrease in  $T_g$ .<sup>22,23</sup>

In Figure 3, the variations in  $T_g$  of the A2 system, measured during artificial weathering and relative to the initial value calculated for the unexposed specimens, are reported. A  $T_g$  of  $46^{\circ}\text{C}$  was measured on specimens of the A2 system kept at ambient temperature for 4.5 months, that is, before artificial aging. Similarly, Figure 4 is relative to the A3 system, whose initial  $T_g$  after a 4.5-month curing time at ambient temperature was  $50^{\circ}\text{C}$ .

The artificial weathering procedure caused in both cases much more severe reductions in  $T_g$  than the natural exposure, especially at higher exposure times. These reductions could again be explained in terms of a strong plasticization effect due to the thermohygroscopic treatment performed during the artificial weathering. We could not exclude, however, other irreversible effects (e.g., hydrolysis or thermal

degradation) concurring in the reduction of the  $T_g$  of the systems subjected to this severe environment. In particular, the decrease in  $T_g$  could be related to microstructural modifications, such as chain scission, which reduced the effective crosslinking density.<sup>18,24,25</sup> In addition, the loss of material, as determined by weight measurements for both the A2 and A3 systems, particularly after artificial weathering, supported the hypothesis of the loss of dangling chains as a consequence of degradation.<sup>18,20</sup>

Figure 5 shows the variations in  $T_g$  of the A1 system measured during natural weathering [Fig. 5(a)] and artificial [Fig. 5(b)] weathering relative to the initial value, that is,  $53^{\circ}\text{C}$ , calculated for unexposed specimens kept in both cases for 4.5 months at ambient temperature. The  $T_g$ 's found for this system after the thermohygroscopic treatment and at longer times of natural weathering were generally higher than those measured for the untreated samples.

With regard to the effects of natural weathering, the initial decrease in  $T_g$  found for the A1 system corresponded to a rainy spring; this suggested that the plasticization effect took place as well as in the A2 and A3 systems. In this period,  $\Delta H_r$  ( $2.2 \pm 1.9$  J/g), still measurable on the A1 system before outdoor exposure as a consequence of incomplete crosslinking, was slightly reduced at about  $1.4 \pm 0.7$  J/g. On the other hand, a sudden increase in  $T_g$  was recorded during the summer. Moreover, in this warm season, no  $\Delta H_r$  was measured on the A1 samples subjected to natural exposure. It is likely that the temperatures recorded over the summer were

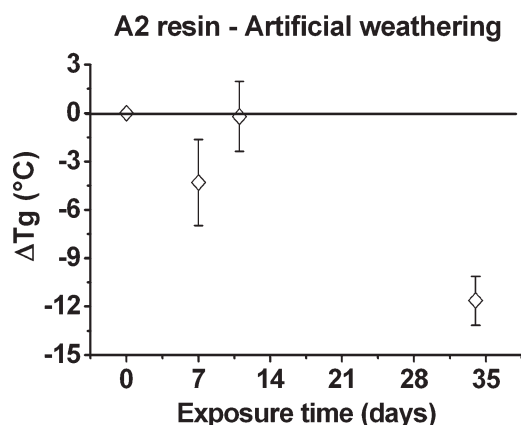


Figure 3 Variations in  $T_g$  ( $\Delta T_g$ ) of system A2 relative to the initial value calculated for unexposed specimens measured during artificial aging.

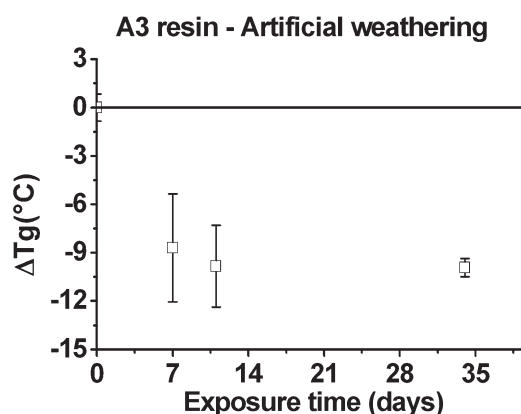
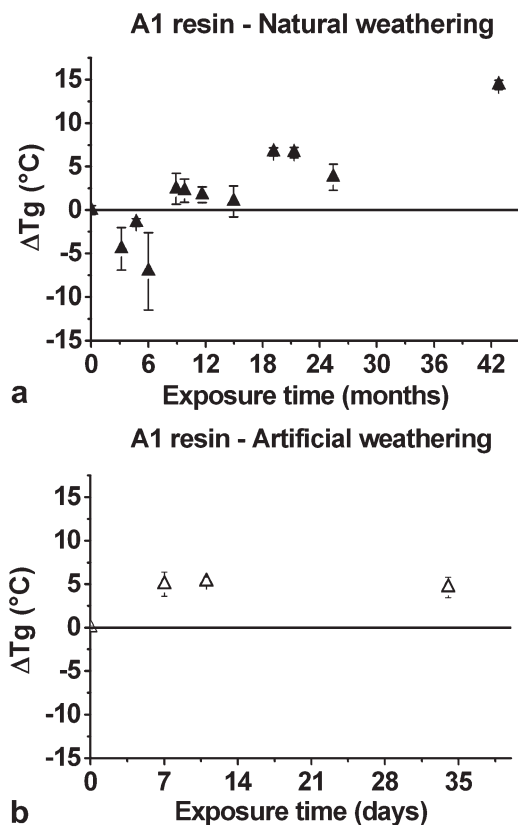


Figure 4 Variations in  $T_g$  ( $\Delta T_g$ ) of system A3 relative to the initial value calculated for unexposed specimens measured during artificial aging.



**Figure 5** Variations in  $T_g$  ( $\Delta T_g$ ) of system A1 relative to the initial value calculated for unexposed specimens measured during (a) natural weathering and (b) artificial aging.

high enough to promote both postcuring and the evaporation of the sorbed water; this led to a substantial increase in  $T_g$ .

For the artificial aging, a variation in  $T_g$  of about  $+5^\circ\text{C}$  was measured, regardless of the exposure time.

The decreases in  $T_g$  measured on all of the samples subjected to the artificial treatments, performed in a dark atmosphere, were evidence that the most significant effects on the thermal properties of these epoxy resins were due to the simultaneous exposure to high RH and mild temperature.

As previously stated, even though the A1 system was subjected to the thermohygroscopic treatment after 4.5 months of curing, it was not fully cross-linked. An exothermic peak due to the residual reactivity was, in fact, measured in the DSC thermogram, as listed in Table III. For the A1 system,  $\Delta H_r$  became null just after the beginning of artificial weathering (i.e., 7 days). We hypothesized that during the thermohygroscopic treatment, when the samples were kept at a temperature higher (i.e.,  $70^\circ\text{C}$ ) than the (ambient) temperature of curing, a postcuring process occurred: the crosslinking reactions started anew and complete, with a consequent increase in  $T_g$  and a decrease in the exothermic peak

related to the residual reactivity. This phenomenon yielded higher  $T_g$  values, which were able to counteract the decrease in  $T_g$  due to the plasticization effect of water, with a consequent certain increase in  $T_g$ .

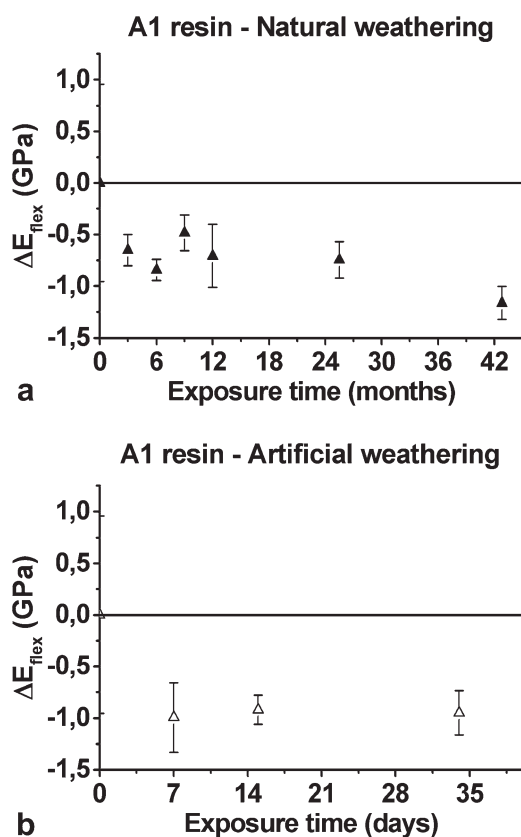
On the other hand,  $\Delta H_r$  calculated for the A2 and A3 systems and reported in Table III generally constantly decreased with increasing weathering time. An endothermic peak (centered at about  $127^\circ\text{C}$ ) was present in the DSC thermograms of the untreated A3 samples. This peak partially overlapped the peak of residual reactivity; therefore, for the A3 resin, it was impossible to calculate the zero time value of  $\Delta H_r$ . The disappearance of the endothermic peak in the analysis of the same samples in the DSC cell in a second scan and in the analyses performed after the thermohygroscopic treatments suggested that it was probably related to the evaporation of solvents. To assess any evaporation process, further investigations by means of thermogravimetric analysis are in progress. The exothermic peaks found for both A2 and A3 and due to the residual reactivity were still measurable, even after 34 days at  $70^\circ\text{C}$  and 75% RH. In these cases, the effect due to the postcuring process on  $T_g$  was less marked, whereas the effects of the plasticization and, mostly, of the degradation prevailed. Therefore, for A2 and A3, the whole effect of artificial weathering was a decrease in  $T_g$ .

With regard to the physical aging, because the resins were stored at a temperature lower than their  $T_g$  for a prolonged period (i.e.,  $23^\circ\text{C}$ ) before the artificial weathering, this phenomenon entirely took place. An endothermic peak was, in fact, always observed near the region of  $T_g$ , and the related  $\Delta H_{rel}$  was measured for all of the untreated samples (reported in Table III). Then, during the thermohygroscopic treatment, physical aging was erased because the systems were heated above their  $T_g$ ; hence,  $\Delta H_{rel}$  disappeared.

**TABLE III**  
 $\Delta H_r$  and  $\Delta H_{rel}$  Values of the Samples Subjected to Artificial Weathering

Resin	Weathering time (days)	$\Delta H_r$ (J/g)	$\Delta H_{rel}$ (J/g)
A1	0	$2.2 \pm 1.9$	$2.8 \pm 0.7$
	7	0.0	0.0
	11	0.0	0.0
	34	0.0	0.0
A2	0	$6.1 \pm 2.8$	$1.3 \pm 0.8$
	7	$4.4 \pm 1.5$	0.0
	11	$3.9 \pm 1.9$	0.0
	34	$1.7 \pm 0.6$	0.0
A3	0	Not determined <sup>a</sup>	$1.7 \pm 0.2$
	7	$7.5 \pm 0.2$	0.0
	11	$2.5 \pm 0.2$	0.0
	34	$2.8 \pm 1.2$	0.0

<sup>a</sup> $\Delta H_r$  for the untreated A3 samples could not be determined.



**Figure 6** Variations in the flexural modulus of elasticity ( $\Delta E_{flex}$ ) measured on system A1 relative to the initial value calculated for unexposed specimens measured during (a) natural weathering and (b) artificial aging.

It is well known that the presence of water in thermosets (plasticization) also erases physical aging (material rejuvenation). During natural weathering, the exposure of the systems whose  $T_g$  was already reduced by plasticization or degradation effects to possibly high temperatures partially erased the physical aging, and large decreases in  $\Delta H_{rel}$  were measured at intermediate exposure stages on all of the systems investigated. This phenomenon was able to start again when  $T_g$  increased, as shown by the new increase in  $\Delta H_{rel}$  measured at longer exposure times.

### Mechanical properties

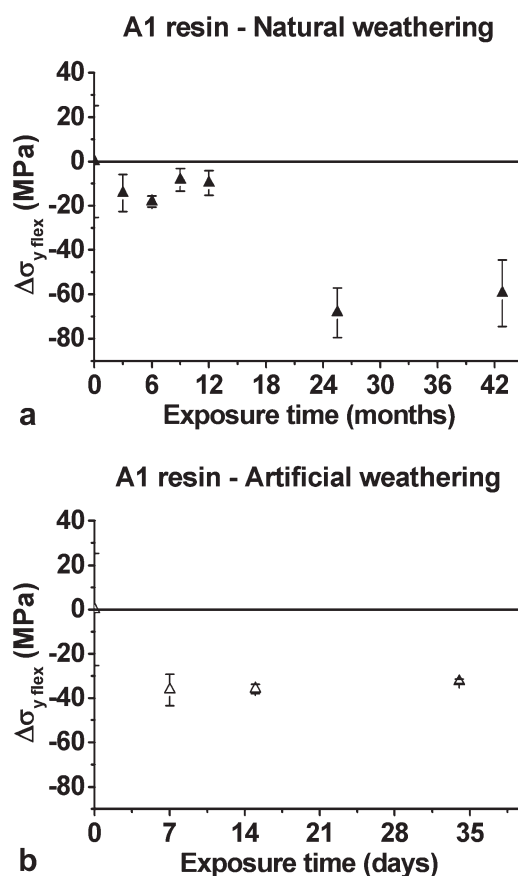
The artificial weathering procedure used also did not give rise to the same effects as the natural weathering procedure in terms of the mechanical properties.

In Figure 6(a,b), variations in the flexural modulus for system A1 as function of the exposure time of natural and artificial weathering, respectively, are reported. The flexural modulus measured for this system before any kind of exposure was 3.1 GPa. The effect of natural weathering was manifested as a gradual reduction in the flexural modulus up to 35%, which was obtained after a 43-month exposure.

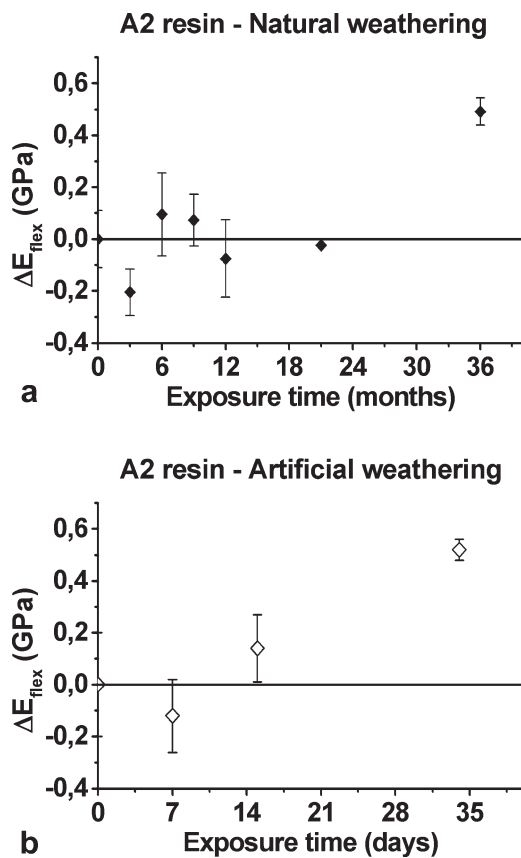
On the other hand, when the specimens were subjected to the artificial weathering procedure, a reduction in the flexural modulus of about 31% was always measured, regardless of the exposure time.

Analogously, in Figure 7(a,b), the variations in the maximum flexural strength measured for the A1 system as function of the exposure time for natural and artificial weathering, respectively, are reported. An initial maximum strength of 111.8 MPa was measured for unaged samples of A1. The natural weathering determined an average constant reduction in the flexural strength of about 11% throughout the 1st year of exposure, whereas after a more prolonged exposure, the flexural strength decreased severely (60%). The artificial weathering caused an average reduction in the maximum flexural strength of about 31%, which remained constant during the treatment. In this case, the effects of artificial weathering were more severe than those due to the early stage of natural weathering, but artificial weathering was not able to reproduce the effects of longer natural exposure times.

The marked decrease measured in the flexural characteristics, stiffness, and strength, were explained



**Figure 7** Variations in the maximum flexural strength ( $\Delta \sigma_{yflex}$ ) measured on system A1 relative to the initial value calculated for unexposed specimens measured during (a) natural weathering and (b) artificial aging.



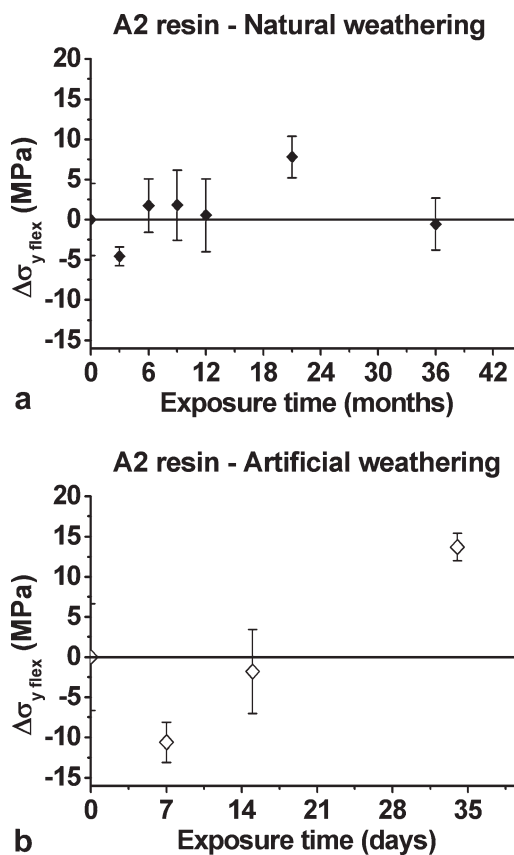
**Figure 8** Variations in the flexural modulus of elasticity ( $\Delta E_{flex}$ ) measured on system A2 relative to the initial value calculated for unexposed specimens measured during (a) natural weathering and (b) artificial aging.

in terms of a strong effect of the entering water, in accordance with the weight gain observed after both the natural and artificial procedures. The fluctuations in the mechanical properties observed during the natural exposure were in accordance with the fluctuations in weight reported in Figure 1(a).

With regard to the effects of the thermohygro-metric treatments, the results indicate that the plasticization process took place very fast because the variations in the mechanical properties were already measured on samples treated for 7 days. It was likely that the high temperature of exposure increased the rate of water absorption into the polymers, and therefore, this could decrease the time necessary to reach the saturation level. The permanence of specimens at a constant level of humidity, moreover, led to steady mechanical properties. We confirmed that these properties were mainly influenced by plasticization due to the absorption of water. Furthermore, the erasure of the physical aging, which took place because the resin was aged at a temperature higher than its  $T_g$ , contributed to the variations in the mechanical properties. The deaging process could have concurred to produce both the lowering of the flexural modulus and the maximum strength. In fact, these

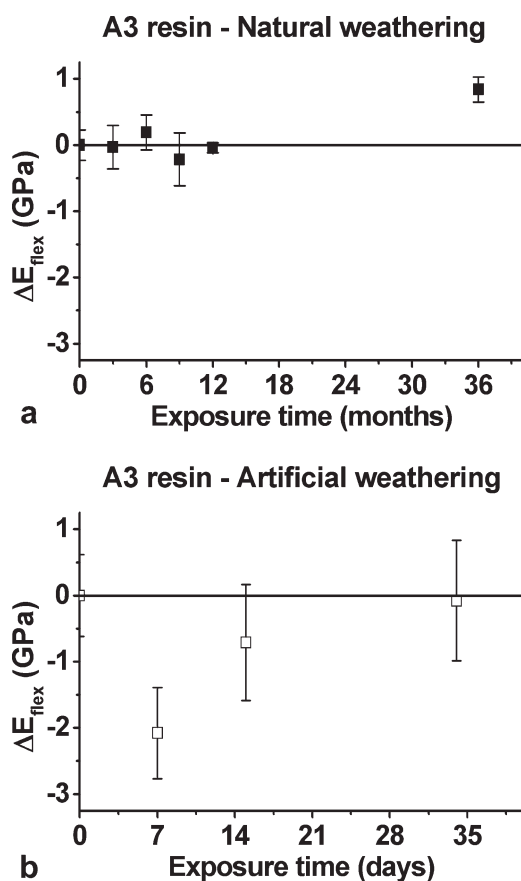
effects were more evident in samples that were artificially weathered, where no  $\Delta H_{rel}$  was measured.

In Figure 8(a,b), the variations in the flexural modulus of the A2 system as function of the exposure time for natural and artificial weathering, respectively, are reported. The flexural modulus measured on specimens cured for only 10 days, that is, before natural weathering, was 0.8 GPa, and due to the proceeding of curing, this property increased to 1.2 GPa after a curing time of 4.5 months, before the artificial aging. The stiffness of the specimens subjected to natural exposure fluctuated around an average value slightly higher (ca. 7%) than the initial one. This behavior was attributed to the meteorological conditions occurring just before the analysis of the samples, as already reported in a previous article.<sup>15</sup> At longer exposure times, a higher value for the modulus was measured and was associated with the postcure occurring at later times. Although this result was in agreement with the disappearance of the residual heat of crosslinking reactions, measured by the thermal analysis, it was somehow in contrast with the decrease in  $T_g$  when it was attributed only to plasticization effects. However, reductions in  $T_g$  have also been previously justified by chain scissions



**Figure 9** Variations in the maximum flexural strength ( $\Delta \sigma_{yflex}$ ) measured on system A2 relative to the initial value calculated for unexposed specimens measured during (a) natural weathering and (b) artificial aging.





**Figure 10** Variations in the flexural modulus of elasticity ( $\Delta E_{flex}$ ) measured on system A3 relative to the initial value calculated for unexposed specimens measured during (a) natural weathering and (b) artificial aging.

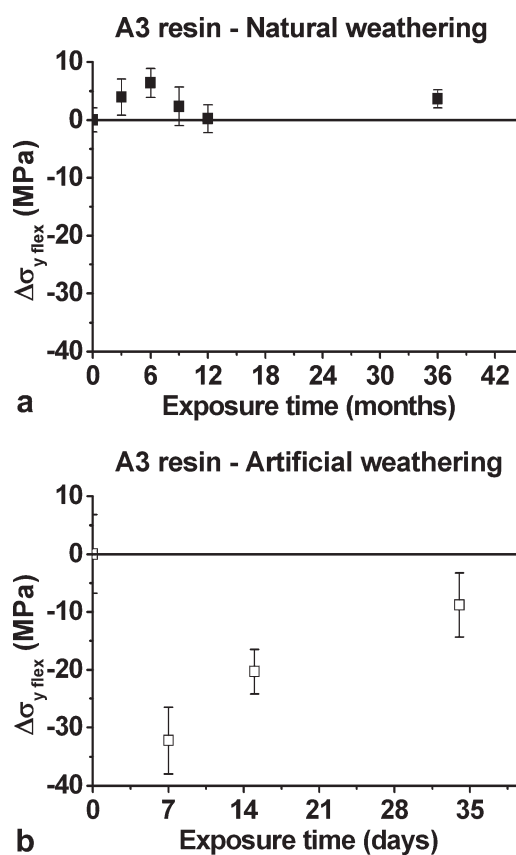
due to thermal or UV degradation; in this case, a higher elastic modulus along with a decrease in  $T_g$  were expected.<sup>18,23,26</sup>

The effects of artificial weathering were a sudden decrease in the flexural modulus, probably due to both the plasticization effect of the entered water and the erasure of the physical aging, followed by a new increase up to values much higher than the initial one (an increase of  $\sim 60\%$ ), in a manner that was similar to what was observed at the end of natural weathering. The increase in maximum flexural strength ( $\sigma_y$ ) observed at later aging times confirmed the occurrence of postcuring.

Figure 9 (a,b) reports variations in the flexural maximum strength of the A2 system as function of the exposure time for natural and artificial weathering, respectively. The flexural maximum strengths found for specimens cured for 10 days and 4.5 months were 27.1 and 41.6 MPa, respectively. Natural weathering produced a small average increase in the flexural strength of about 6%, with fluctuations of the flexural resistance around this average value. Artificial weathering produced an initial decrease in the maximum strength (ca. 25%) followed by a sub-

stantial increase at longer exposure times, up to 33%. The same explanation just proposed for the flexural modulus behavior could be extended to the flexural strength behavior.

In Figure 10(a,b), variations in the flexural modulus measured for the A3 system as function of the exposure time for natural and artificial weathering, respectively, are reported. The flexural modulus values measured for specimens cured for 10 days and 4.5 months were 1.6 and 3.3 MPa, respectively. The stiffness of this system was only marginally influenced by the external exposure, with an average increase of about 9%, and the fluctuating values were due to the external meteorological conditions. As already discussed for the A2 system, long exposure times were able to yield high flexural modulus values also for A3 (with an increase up to 52%). The effect of artificial weathering on the flexural stiffness was again similar to that observed for the A2 system. An initial decrease in the flexural modulus was due to both the plasticization effect of water and the erasure of physical aging; these effects were counteracted by the postcure taking place at longer weathering times, as the decreased  $\Delta H_f$  indicated.



**Figure 11** Variations in the maximum flexural strength ( $\Delta \sigma_{y,flex}$ ) measured on system A3 relative to the initial value calculated for unexposed specimens measured during (a) natural weathering and (b) artificial aging.

**TABLE IV**  
 $\Delta E$ 's of the Three Cured Resins Subjected to the Artificial Weathering

Weathering time (days)	A1	A2	A3
0	0.00	0.00	0.00
7	9.78	6.44	3.50
15	16.38	6.63	6.79
34	34.01	23.33	8.56

Figure 11(a,b) reports variations in the flexural maximum strength of the A3 system as function of the exposure time for natural and artificial weathering, respectively. Initial maximum resistances of 27.5 and 50.6 MPa were measured for unaged samples cured for 10 days and 4.5 months, respectively. Natural weathering produced a slight increase in the flexural strength of about 7%, whereas artificial weathering produced the already observed initial strong decrease followed by a substantial increase at longer exposure times. The same considerations discussed for the A2 system could be extended to the A3 system.

From the analysis of the flexural mechanical results, we concluded that natural weathering produced a general decrease in the mechanical properties of the three systems analyzed, with an average reduction in the flexural modulus of about 25%. More severe reductions were recorded for the maximum flexural strength at longer exposure times for the A1 system. The results of the test performed after natural exposure, moreover, were likely to have been strongly affected by the proceeding of curing reactions in the case of the A2 and A3 systems exposed when the curing process was still in progress and fluctuations in climatic conditions.

### Color measurements

The  $\Delta E$  values of the resins subjected to artificial weathering are reported in Table IV.

The results show that the treatment performed led to higher variations in A1 with respect to the other two systems. The lowest  $\Delta E$  values were generally calculated at any aging time for the A3 aged specimens, probably because of the presence of fillers in this system. Variation of color was not promoted by UV aging because the treatment was performed with-

**TABLE V**  
 $\Delta E$ 's of the A1 Resin Exposed to Natural Weathering

Weathering time (days)	A1
0	0.00
3	20.82
6	26.22
9	27.47
15	31.13
21	32.22

out light sources. The obtained results could, therefore, be ascribed to processes that were not activated by UV radiation, such as hydrolysis and/or thermooxidation.<sup>18,25,27</sup> The latter processes could have, in turn, severely affected the thermal and mechanical bulk properties of the systems, as already discussed.

In Table V, the  $\Delta E$  values of the A1 specimens exposed to natural weathering are reported. Greater variations in color were noticed in the first period of exposure. At longer times, an almost constant  $\Delta E$  value was achieved. By comparing the  $\Delta E$  values measured for the two different exposure regimes performed on the A1 system, we confirmed that artificial weathering affected the properties of the cold-cured resins more severely: in the latter case,  $\Delta E$  grew continuously and never reached a constant value, at least within the investigated aging time.

### CONCLUSIONS

The exposure to weathering of the cold-cured epoxy resins under study produced a general decrease in the properties of the systems. The changes in thermal and mechanical properties of the examined epoxy resins after natural weathering were, in part, reversible, according to the cyclic climatic conditions.

More severe effects were produced by artificial aging; these were attributed to the improved influence of single agents: the higher amount of water absorbed, which was able to produce the plasticization of the resins; the high temperature of exposure, which caused a more rapid postcure; thermooxidative processes; and the erasure of physical aging in the resins. Moreover, these levels remained constant during the artificial weathering treatment and were, therefore, more harsh and not even able to reproduce the fluctuations in external agents, which caused, in turn, fluctuations in the properties of the cured systems. However, variations in the properties due to natural exposure and artificial weathering were qualitatively similar.

Only limited effects were attributed to the UV aging because the most severe variations in properties were measured on the artificially aged systems, where no UV exposure was performed. On the other hand, UV exposure hurts and affects mainly the surface of a material, altering to a limited extent the bulk properties of thick specimens.

The behavior of the resins during natural exposure, finally, was also appreciably influenced by the progress of curing reactions, which were not completed before the exposure. We suggest, therefore, that any aging treatments should be performed on systems that have reached steady values of properties at the curing temperature chosen.

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## References

1. Amoroso, G. G.; Camaiti, M. *Scienza dei Materiali e Restauro*; Alinea: Firenze, Italy, 1997.
2. Selwitz, C. *Epoxy Resins in Stone Conservation; Research in Conservation 7*; Getty Conservation Institute: Los Angeles, 1992.
3. Griswold, J.; Uricheck, S. *J Am Inst Conserv* 1998, 37, 89.
4. Nagy, E. E. *J Am Inst Conserv* 1998, 37, 69.
5. Frigione, M.; Naddeo, C.; Acierno, D. *Mater Eng* 2000, 11, 59.
6. Roylance, D.; Roylance, M. *Polym Eng Sci* 1978, 18, 249.
7. Frigione, M.; Naddeo, C.; Acierno, D. *J Polym Eng* 2001, 21, 23.
8. Karbhari, V. M. *Reinf Plast* 2005, 49, 14.
9. Pimentel Real, L.; Gardette, J.-L.; Pereira Rocha, A. *Polym Degrad Stab* 2005, 88, 357.
10. Espí, E.; Salmerón, A.; Fontecha, A.; García, Y.; Real, A. I. *Polym Degrad Stab* 2007, 92, 2150.
11. Merlatti, C.; Perrin, F. X.; Aragon, E.; Margaiilan, A. *Polym Degrad Stab* 2008, 93, 896.
12. Wypych, G. *Handbook of Material Weathering*. ChemTec: Toronto, 1995.
13. ASTM D 756-93, Practice for Determination of Weight and Shape Changes of Plastics Under Accelerated Service Conditions. In *Annual Book of ASTM Standards*; American Society for Testing and Materials: West Conshohocken, PA, 1993.
14. Vauthier, E.; Abry, J. C.; Bailliez, T.; Chatetominois, A. *Compos Sci Technol* 1998, 58, 687.
15. Frigione, M.; Naddeo, C.; Acierno, D. *J Polym Eng* 2001, 21, 349.
16. ASTM D 790-92, Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials. In *Annual Book of ASTM Standards*; American Society for Testing and Materials: West Conshohocken, PA, 1992.
17. CIE Standard 014-4/E: 2007, Colorimetry-Part 4: CIE 1976 L\*a\*b\* Colour spaces, Commission Internationale de l'Eclairage: Vienna, Austria, 2007.
18. Barral, L.; Cano, J.; López, J.; López-Bueno, J.; Nogueira, P.; Abad, M. J.; Torres, A.; Ramirez, C. *J Appl Polym Sci* 2000, 77, 2305.
19. Kumar, B. G.; Singh, R. P.; Nakamura T. *J Compos Mater* 2002, 36, 2713.
20. Damian, C.; Espuche, E.; Escoubes, M. *Polym Degrad Stab* 2001, 72, 447.
21. Monney, L.; Belali, R.; Vebrel, J.; Dubois, C.; Chambaudet, A. *Polym Degrad Stab* 1998, 62, 353.
22. Bellenger, V.; Verdu, J. *J Appl Polym Sci* 1985, 30, 363.
23. Musto, P.; Ragosta, G.; Abbate, M.; Scarinzi, G. *Macromolecules* 2008, 41, 5729.
24. Piccirilli, N.; Shanahan, M. E. R. *Polymer* 2000, 41, 4077.
25. Musto, P.; Ragosta, G.; Russo, P.; Mascia, L. *Macromol Chem Phys* 2001, 202, 3445.
26. Delobelle, P.; Guillot, L.; Dubois, C.; Monney, L. *Polym Degrad Stab* 2002, 77, 465.
27. Buch, X.; Shanahan, M. E. R. *Polym Degrad Stab* 2000, 68, 403.