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PHOTOINDUCED FRONTAL CATIONIC POLYMERIZATION OF EPOXY-CARBON FIBER COMPOSITES

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ABSTRACT: UV-activated FP was exploited for the preparation of epoxy-carbon fiber composites. The curing process was investigated showing the frontal behaviour and the final properties of UV-cured composites were compared with the same composites obtained by thermal curing in the presence of amine as hardener. The best curing formulations were designed, defining photoinitiator: thermal initiator ratio, which was 1.5:1.5. It was observed that the presence of the carbon-fibers induced an acceleration of the front velocity. By comparing the thermal-mechanical properties of the composite thermal cured and the same composite crosslinked by frontal process, we could observe that the last one showed higher T_g value and lower σ_f. This was attributed to the formation of a different polymeric network structure.

Keywrods: UV-activated frontal polymerization, carbon fibers composites, epoxy matrix.

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1. INTRODUCTION

Polymeric materials are reinforced with high modulus fibers to yield higher strength, higher stiffness, better toughness, and good dimensional stability [1]. Epoxy-carbon fibers composites are very important in different fields among which sport, automotive, aerospace, naval industry [2].

Epoxy-carbon composites are generally thermal crosslinked by using amine or anhydride as hardener. On the other hand, the UV-induced epoxy curing is an interesting alternative, achievable in the presence of a suitable cationic photoinitiator [3-5]. The UV-activation is particularly attractive since the crosslinkable formulations are solvent free, the production rates are high, and the energy required is much less than thermal curing [6].

Nevertheless, there is a strong limitation in UV-curing for thick composites due to an exponential decrease of light intensity towards the thickness of the photocurable formulation, as well as for the competitive light absorption by fillers or fibers, that could further hinder the light penetration to the deeper layers of the composite [7]. A suggested strategy to overcome this limitation, is the use of UV-activated Frontal Polymerization (FP) technique [8]. The frontal polymerization is a process that allows to convert monomer to polymer by exploiting the exothermicity of polymerization reaction [9-14] The result is a localized thermal reaction zone that propagates through the photocurable formulation as a thermal wave; a hot propagation and self-sustaining front can be observed.

The use of FP to produce composites is already reported in literature. Fiori et. Al reported the frontal polymerization of polyurethans containing silica fillers [15]. Mariani et. Al reported the preparation of epoxy-montmorillonite nanocomposites obtained by FP [16]; the materials showed similar or even better properties than those obtained by conventional polymerization routes.

Frontal cationic curing of epoxy resin was reported by Scognamillo [17] in which BF_3-amine was used to activate the cationic ring-opening polymerization of epoxy resin in the presence of kaolin and silica fillers. In previous paper [18] we reported the use of cationic photoinitiator together with benzoyl peroxide to activate epoxy curing using UV-light to ignite the reaction. Crivello [19] also reported the radical induced cationic frontal polymerization (RICFP) to obtain the UV-crosslinking towards the thickness of the photocurable formulation. In a more recent paper, we have reported the possibility to cure bulk pristine epoxy formulations [20, 21] containing SiO_2 by RICFP; the influence of the filler content on frontal propagation was investigated, showing a decrease of front velocity and front starting time by increasing the filler content [22]. We have also reported the UV-crosslinking preparation of epoxy-glass fibers composites via a RICFP. The proceeding of reaction is assured by the heat front propagation and the crosslinked composites obtained by frontal process showed even slightly better properties by comparison with the same composites thermally cured [23]

By pursuing these investigations, in this paper, for the very first time, we reported the use of UV-activated FP for the preparation of epoxy-carbon fiber composites. The curing process was investigated showing the frontal behaviour and the final properties of UV-cured composites were compared with the same composites obtained by thermal curing in the presence of amine as hardener.

2. EXPERIMENTAL

2.1 Materials

The epoxy resin and Ampreg26 amine hardener was supplied by Gurit Switzerland. The epoxy resin consists of a blend of bisphenol A (50–100%), bisphenol F (25–50%) and 1,6-hexanedioldiglycidylether (2.5–10%), while the hardener is a blend of amines (polyoxyalkyleneamine (25–50%), 2,2′-dimethyl-4,4'methylenebis (cyclohexylamine) (10–25%), 4,4′-methylenebis (cyclohexylamine) (10–25%) and 2,2'iminodiethylamine (2.5–10%)). The thermal initiator 1,1,2,2-tetraphenyl-1,2-ethandiol (TPED) was supplied from Alfa Aesar, the cationic photoinitiator (p-octyloxyphenyl) phenyliodonium hexafluoroantimonate (PAG) from ABCR. Carbon fabric was supplied by Toray Tokyo, T300 fibers are woven in 200 gsm Twill 2x2 balanced configuration, which ensures the same mechanical properties along the two main directions.

2.2 Epoxy-carbon fibers composites preparation and characterization

The composites were manufactured using carbon fabric T300 200 gsm Twill 2x2 and neat epoxy resin Ampreg26 (without amine hardener) containing 1,5 %wt of TPED as thermal initiator and 1,5 %wt of cationic photoinitiator. Four plies of carbon fiber were laminated into a silicone mould with a sample dimension of 12×60 mm and with a thickness of 3 mm. Each ply was 0.15 g and 0.5 g of total epoxy formulation was added.. After impregnation the corner of the mould was irradiated with a UV-lamp, Lightning Cure™ LC8, Hamamatsu, equipped with an optical fiber for 10 s, to activate the thermal front which allowed the completeness of polymerization in less than a minute.

As comparison, the same epoxy resin was added with the Ampreg26 amine hardener (epoxy/hardener ratio 100:33) and thermally cured at 80 °C for 3 h.

Epoxy conversion was evaluated, after curing, by DSC analysis measuring the exothermicity. Analysis were performed by using a Mettler Toledo DSC instrument. Samples having masses of approximately 10mg were insert in a 100 μl aluminium pans with pierced lids in a nitrogen atmosphere. The applied heating rate was 5 °C min^{-1} in a nitrogen atmosphere (rate 40 ml min^{-1}).

The polymerization front was detected by an optical camera Nikon D5500 and a thermal camera FLIR ONE microUSB. Temperature data were collected as a function of time. The reaction is initiated by UV irradiation on the surface of the formulation through an optical fiber for 10 s at a distance of 3 mm with an irradiated power output of 4000 mW cm^{-2}. Dynamic thermal-mechanical analysis (DMTA) were performed with a Triton Technology TT-DMA. The measurements were run with a heating rate of 3 °C min^{-1} in three-point bending mode. Mechanical tests were performed according with ISO14125 regulation, with an Instron 3366 in four-point bending mode using 12mm diameter roller, 45 mm outer span, 15 mm inner span and a 2 mm min^{-1} crosshead speed. All the specimens were equipped with strain gauges 3/350 LY48 supplied by HBM. Force and displacement data were collected on pc with Instron BlueHill software and strain data with HBM Spider8 amplifier data acquisition system, both at sampling frequency of 10 Hz.

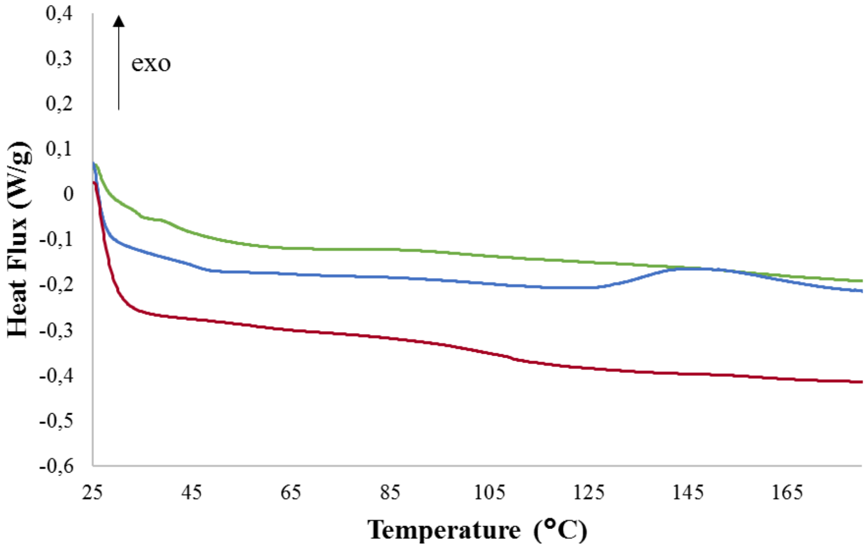
3. RESULTS AND DISCUSSION

The aim of this work was to investigate the possibility to crosslink epoxy-carbon fibers composites by using the UV-activated radical induced cationic frontal polymerization (RICFP).

It was demonstrated in previous papers [20-23] that the FP is started by the dissociation of a radical thermal initiator promoted by the heat released during surface UV-initiated cationic ring-opening polymerization. Subsequently, the carbon-centered radicals are oxidized to carbocations by the presence of the iodonium salt towards a radical induced cationic mechanism. The principle of the process was already demonstrated, and it was concluded that the ability to sustain a heat-front is strongly dependent on the heat dissipation of the material. For this reason, it is important to investigate the effect of the carbon fibers.

The first step of the investigation was the determination of the proper photoinitiator/thermal initiator ratio to maintain the thermal front and achieve the highest epoxy group conversion. The pristine epoxy based formulations investigated contained respectively 0.5:1.5 wt/wt, 1.5:1.5 wt/wt and 2:1 wt/wt photoinitiator:thermal initiator ratio. The epoxy cured formulations obtained in the presence of 0.5:1.5 wt/wt ratio, showed in the DSC thermogram a flex point at around 100 °C, attributable to the Tg of the polymeric network, but an important exothermic peak centred at around 150 °C. The peak can be attributed to the residual non-reacted epoxy functionalities. The other investigated formulations did not show any exothermic peak after irradiation, suggesting a complete epoxy group conversion during curing (see Figure 1).

Figure 1: DSC curves of the UV-irradiated epoxy formulations containing 0.5:1.5 (blue curve), 1.5:1.5 (green curve) and 2:1 wt/wt photoinitiator:thermal initiator ratio (red curve).



The epoxy formulation selected for the next investigations was the one containing 1.5:1.5 wt/wt photoinitiator: thermal initiator ratio. The front starting time was calculated to be 10 seconds. Following, thermal data (front velocity and maximum temperature reached) were collected by using a thermal camera. In Figure 2 the advancement of the thermal front registered by the camera is reported. It is evident a thermal front which propagates towards the length of the sample reaching very high temperature. The temperature profiles are collected, in the same Figure 2, for three different distances (respectively 10, 30, 50 mm distance from the light source). The time at which the temperature departs from the baseline is taken as the front time. By reporting the distance of the front as a function of the highest temperature reached in the sample, it should be possible to obtain the front advancement along the axial direction [8]. Indeed, the polymerization front propagates at constant speed, and this linear behaviour is strongly supporting the suggested front propagation mechanism.

The same measurements were performed for the same epoxy formulations (containing 1.5:1.5 wt/wt photoinitiator: thermal initiator ratio) in the presence of 4 carbon fabric plies (Figure 3). The starting time, front velocity and maximum temperature reached are collected in Table 1. It is possible to observe that the composite formulation was characterized by the same starting time of 10 seconds of irradiation. A higher front velocity and a slightly higher maximum temperature reached was measured for the composite's samples. This was attributed to the good thermal conductivity of the carbon fiber which facilitate the thermal front propagation. This behaviour is in agreement with previous data reported in iterature by Goli et. Al. [24].

Figure 2: Thermo-optical frame sequence of the thermal front advancement during the pristine resin polymerization (left); temperature-time evolution at three positions along the specimen at 10 mm (blue), 30 mm (red) and 50 mm (green) from the trigger point (right).

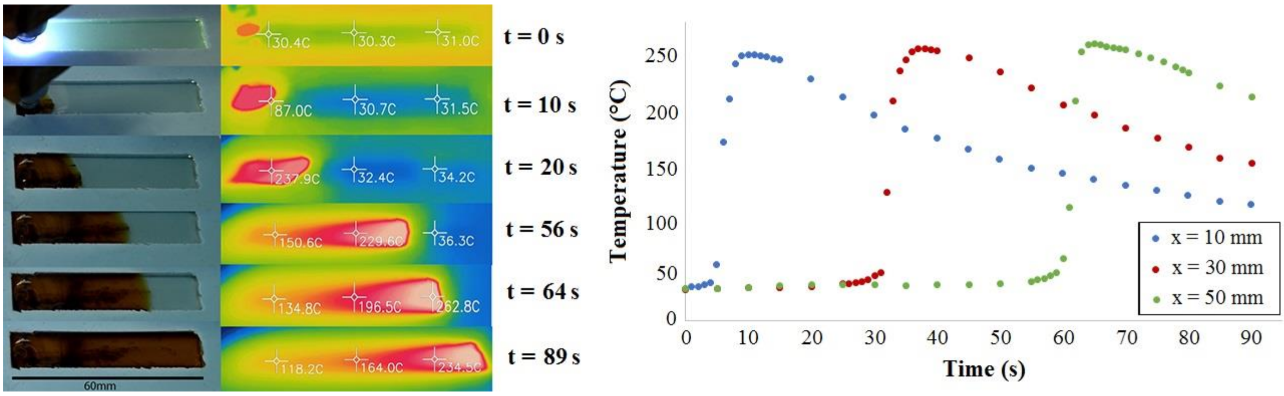


Figure 3: Thermo-optical frame sequence of the thermal front advancement during the composite polymerization (left); temperature-time evolution at three positions along the specimen at 10 mm (blue), 30 mm (red) and 50 mm (green) from the trigger point (right).

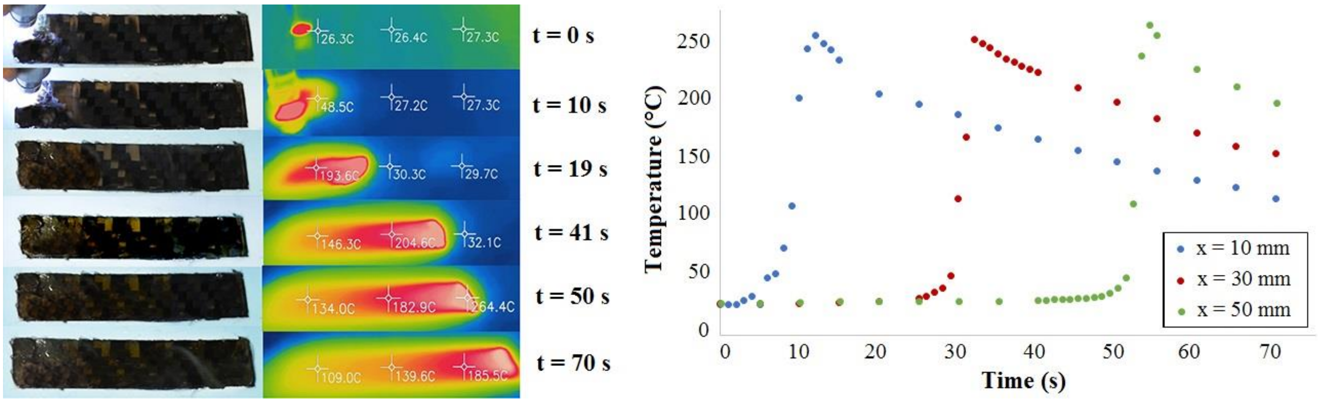
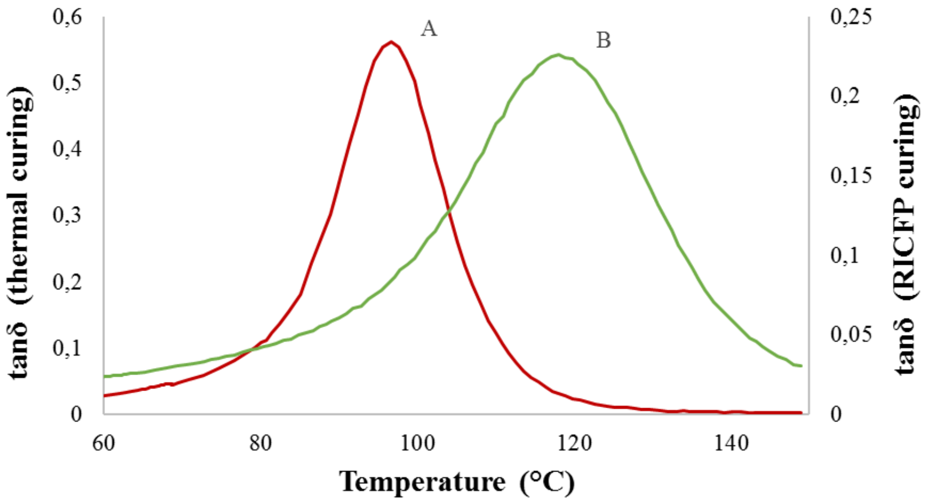


Table 1: Induction time, mean front velocity and highest temperature registered with thermo-optical test on pristine epoxy and epoxy composite.

Sample	**$t_{starting}$ (s)**	**Front Velocity (cm/min)**	**Max. T (°C)**
Pristine Epoxy	10	4,0	263
Epoxy Composite	10	5,1	264

The thermo-mechanical properties of the epoxy-carbon fiber composites obtained by UV-activated frontal curing was compared with the same composites thermally crosslinked. The tanδ curves recorded for the 2 different samples are reported in Figure 4.

Figure 4: Tanδ curve obtained by DMTA analysis of the crosslinked epoxy-carbon fiber composites obtained via thermal curing (curve A) and via RICFP (curve B).



It is possible to observe that the epoxy composites obtained via frontal polymerization showed a higher T_g values. Similar behaviour was observed in the previous investigation reported for glass-fiber reinforced composites [23] and the difference was explained based on the formation of a different polymeric network. In fact a highly flexible long chain amine is used when the composite is thermally cured and this will introduce important flexibilization on the crosslinked network with a lower Tg.

The final mechanical performance of the composites obtained by the two different process, were compared. The average stress-strain curves are reported in Figure 5 and the data are collected in Table 2.

Figure 5: Stress-strain average curves of the crosslinked epoxy-carbon fiber composites obtained via thermal curing (curve A) and via RICFP (curve B).

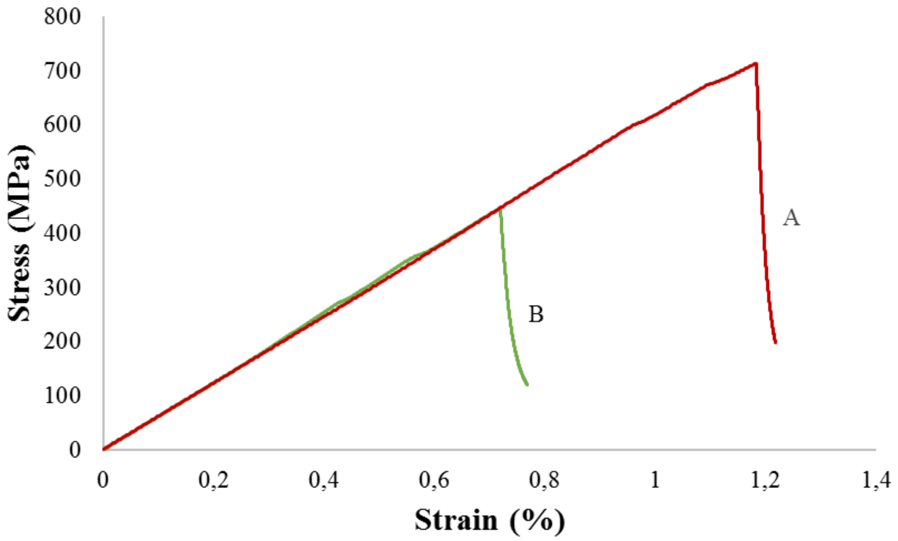


Table 2: Mechanical properties of the crosslinked epoxy-carbon fiber composites obtained by thermal curing and via RICFP.

Sample	**E (GPa)**	**σ_f (MPa)**
Thermal Cured Composites	61±5	715±54
Frontal Cured Composites	61±4	447±81

The mechanical analysis shows the achievement of the same rigidity for the composites obtained via RICFP and via thermal curing, while the strength σ_f is compromised in the case of RICFP. This is probably due to the higher rigidity, as previously discussed due to the formation of a different network.

4. CONCLUSIONS

In this paper we reported the successful UV-initiated frontal polymerization of an epoxy-carbon fiber composite. The best curing formulations were designed, defining the best photoinitiator: thermal initiator ratio, which was 1.5:1.5. These formulations allowed to reach a complete epoxy group conversion and showed the sustainability of the heat front along the distance of the sample. The thermal front propagation was assessed by using a thermal camera and a starting time of 10 second of irradiation was measured. By comparing the front velocity and the maximum temperature reached among the pristine epoxy formulation and the composite epoxy formulation, it was observed that the presence of the carbon-fibers induced an acceleration of the front velocity. This was attributed to the high thermal conductivity of the reinforcing fiber which could facilitate the thermal front propagation. By comparing the thermal-mechanical properties of the composite thermal cured and the same composite crosslinked by frontal process, we could observe that the last one showed higher T_g value and lower σ_f. This was attributed to the formation of a different polymeric network structure. In fact, the thermal cured composites network is strongly influenced by the amine hardener which flexibilizes the final structure. As previously reported for glass-fiber reinforced composite, the important advantage of the UV-frontal activated polymerization process is related to the very fast polymerization compared with thermal curing, which allows to get high productivity, maintaining the good thermo-mechanical properties of the epoxy composites.

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