INFLUENCE OF POST-CURE ON CARBON FIBRE POLYIMIDE COMPOSITES WITH GLASS TRANSITION TEMPERATURES ABOVE 400°C

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ABSTRACT

The current communication present results from work on polymeric composites with extreme temperature performance. This study focuses on carbon fibre composites based on a new phenyl ethynyl terminated polyimide formulation NEXIMID® MHT-R (Nexam Chemicals AB, Sweden) based on hexafluoroisopropylidene bisphthalic dianhydride (6-FDA), 4-(Phenylethynyl)Phthalic Anhydride (4-PEPA) and ethynyl bis-phthalic anhydride (EBPA). In particular influence of post-cure conditions such as time, temperature and atmosphere on T_g of the composites is investigated. In addition to this monitoring and analyses of the consequences of post-cure on mass loss and occurrence of micro-cracks is carried out. Three different post-curing temperatures are considered in this study: 400°C, 420°C and 440°C. Two different atmospheres, air and inert by nitrogen, were also investigated. In summary the results reveal that remarkably high T_g, up to around 460°C, is achieved with only very limited mass loss. It was also observed that some, but limited amounts of, micro-cracks are developed within the laminates due to the inevitable high thermal stresses generated upon cooling from cure temperature.

1 INTRODUCTION

Although ceramic and metal matrix composites can be used at several thousand degrees, there is great interest in using fibre reinforced polymer composite in high temperature applications since they are more lightweight, have better fatigue properties and are more ductile [1]. There are traditional polymers that may be used for composites at relatively high temperatures such as epoxies, phenolics, cyanate esters, benzoxazines and bismaleimides (BMI) [2]. These resin systems are however only in rare cases suitable for continuous use at temperatures above 250°C due to e.g. insufficient thermal oxidative stability or glass transition temperatures (dry or wet). The current study is instead focused on polyimide resin composites. Polyimides are very temperature resistant and stable polymers, available either as thermoplastic or thermosets [3-4]. During the last years there has been significant development in the area of phenylethynyl-terminated imide (PETI) resins. They combine very high T_g with high toughness and low volatile generation during cure [5-7].

This study investigates how post-cure conditions (time, temperature and atmosphere) influences properties (thermal, mass loss after cure and occurrence of micro-cracks) of carbon fibre composites based on phenyethynyl terminated NEXIMID® MHT-R polyimide resin. The ultimate objective in the study is to obtain rational and scientific arguments that can be used for selecting most appropriate post-cure conditions of the composite. It is since previous established that a process ending with a 150 minutes cure at 370°C gives a T_g of 331-352°C [8]. It is anticipated that a post-cure at even higher

temperatures can further increase T_g. Besides changes of T_g the mass loss and the possible development of new micro-cracks within the laminate after post-curing is monitored. Three different post-curing temperatures are considered in this study: 400°C, 420°C and 440°C. Two different atmospheres, air and inert by nitrogen, were investigated.

2 MATERIALS

The resin used is a low molecular weight phenylethynyl terminated polyimide, NEXIMID[®] MHT-R prepared from a combination of 6F-dianhydride (6-FDA) backbone, 4-(Phenylethynyl)Phthalic Anhydride (4-PEPA) end-group crosslinker and ethynyl bis-phthalic anhydride (EBPA) main chain crosslinker. An 8-harness satin weave with surface weight of 380 g/m^2 prepared from Thornel T650/35 3K 309NTGP2 carbon fibers by Sigmatex was used as reinforcement. Quasi-isotropic laminates with $[(45/-45)/(0/90)]_{2s}$ layup and approximately 57% fibre volume fraction were manufactured by resin transfer moulding (RTM) in stainless steel tool using a flow and pressure controlled injection piston supplied by ISOJET. The following cure schedule was used: melt and homogenize resin in the piston at 240°C for 30 minutes; degass using vacuum at 240°C for 10 minutes; inject the resin at 290°C; increase temperature to 340°C at a heating rate of 1.7°C/min, cure at 340°C for 0.5 h; increase temperature to 370°C at a heating rate of 1.7 °C/min, cure at 370°C for 2 h, cool down to 80°C during 12 h and demould. A cure pressure of 12 bar was applied during the cure.

3 EXPERIMENTAL

The test program is graphically presented in Figure 1. All tests were conducted on specimens prepared in the size of 3 mm x 10 mm x 60 mm.
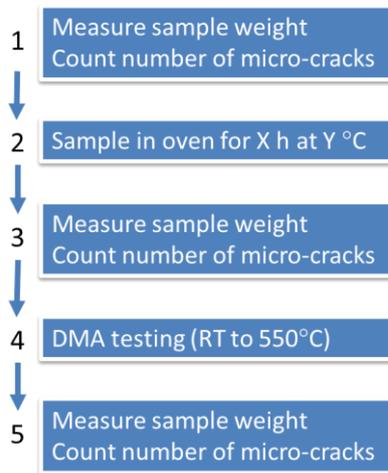

Figure 1 : Schematic representation of the test program

Specimen edges were polished prior to heat treatment in order to permit microscopy studies of possible crack development during tests and to minimize premature crack initiation due to edge defects. The post-cure time was fixed to two hours whereas three different temperature (400°C, 420°C and 440°C) and two different environments (in air and in nitrogen, N_2) were tested. Samples that were post-cured in air were placed on a steel grid inside the oven. Post-curing in nitrogen environment was conducted in the same oven but inside a 52 mm diameter steel tube with sealed ends, see Figure 2. The steel tube was connected to a nitrogen supply enabling continuous flushing with nitrogen during the post-cure. It should also be noted that no special precautions were taken to avoid thermal gradients during heating or cooling i.e. the samples were directly placed inside and removed from the oven.

A Mettler Toledo AE 240 precision scale was used for measuring mass of specimens. Initial mass, mass after post-cure and mass after DMTA measurements were recorded for all specimens. A TA Instruments Q800 equipped with 3-point bending fixture with a span length of 50 mm was the

equipment used for test. The measurements were conducted according to ASTM standard [9] with the exception that heating rate was set to 10°C/min in our tests. The T_g was determined from experiments as the intersection between the extrapolation of the inflectional tangent and the storage modulus tangent below the glass transition.

Figure 2 : Photograph of oven with steel tube used for post-curing in nitrogen environment

Optical microscopy was used for detection and quantification of occurrence and development of damage in the form of micro-cracks on the edges of the specimens. In the counting each laminate was divided into four sections, henceforth denoted as sub-laminates, through the thickness. Each section (or sub-laminate) is hence made up from two layers of satin weave i.e. a (45/-45)/(0/90)-stacking sequence is denoted as one sub-laminate. All micro-cracks within each sub-laminate over a length of 60 mm were summed together and normalized with respect to length to give a measure of the crack density (cracks per mm, [cr/mm]) in each sub-laminate.

4 RESULTS AND DISCUSSION

The results from DMA tests of T_g are presented in Figure 3. From the results it is evident that T_g increases with post-cure temperature. There is no apparent tendency of T_g reaching a maximum, hence it is possible that even higher T_g can be achieved with the current material system. The increased T_g is an indication of increased crosslinking at higher cure temperature due to reaction of the phenylethynyl group as have been observed in previous studies [10].
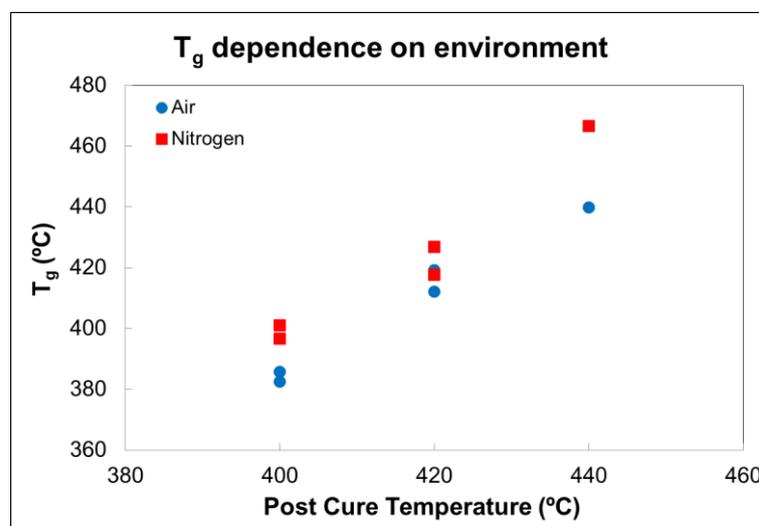

Figure 3 : Influence from temperature and environment on T_g after 2 hour post-curing.

The highest $T_g = 466°C$ was obtained after post-cure in nitrogen at 440°C. Curing in air at the same temperature gave a T_g of 440°C which is 25°C lower than when nitrogen was used. The same trend applies to the other two post-cure temperatures i.e. post-curing in the more inert N_2-atmosphere gives approximately 5-15°C higher T_g as compared to curing in air.
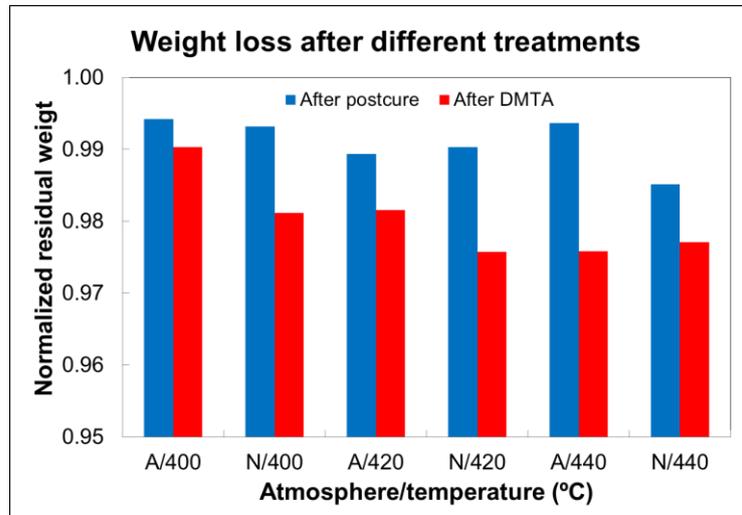

Figure 4 : Average changes in relative mass after different treatments

Relative mass losses on samples after different treatments are graphically presented in Figure 4. An immediate observation when comparing the blue bars is that there is some, but limited mass loss after all post-curing operations. These relative mass losses range from 0.5% to a maximum of 1.5% relative loss. Drying tests on as-manufactured samples revealed that approximately 0.4% of the weight loss can be attributed to moisture and hence explains the majority of the mass loss after post-cure. We also observe a weak tendency that increased post-curing temperature gives slightly higher mass loss. Any influence from the environment, air vs. nitrogen, is harder to establish. There appear to be a difference in mass loss between air and nitrogen atmosphere when post-curing at 440°C. At this temperature the mass loss is higher for samples cured in nitrogen environment. No influence is however noticed for the two lower temperatures, 400°C and 420°C.

When comparing mass loss after DMTA tests (red bars) in Figure 4 one notices a similar tendency as descried above, that samples cured at higher temperature lose more mass. The relative mass loss in this second treatment (i.e. mass difference between first post-cure treatment and DMA) is again remarkably low for a polymer composite and is of the same order of magnitude as the first treatment i.e. around 0.5% to 1.5%. The tests with DMA are conducted in air up to 550°C at a heating rate of 10°C/min. The samples are immediately cooled down to ambient temperature by the DMA test-machine once the maximum temperature was reached. This implies that the samples are exposed to temperatures higher than the original post-cure at 370°C for about 15-20 minutes in these tests. The original purpose with following the mass loss after DMA was to investigate if post-curing conditions have any significant influence on the thermal stability of the composite. Our results indicate that short term thermal stability at temperatures above the curing temperature in essence remains largely unaffected regardless of temperature and environment. The exposures in the current tests are however too short to provide meaningful information about longer term thermal stability.

Optical microscopy was performed on the polished edges before and after the different treatments. Typical examples of micrographs are shown in Figure 5(a)-(c). The uppermost graph shows the as-manufactured laminate whereas middle and the lower micrograph show the same specimen after post-cure and DMA respectively. The microscopy study revealed that there was damage present already in the as-manufactured samples. The damage was in the form of micro-cracks that extends within fiber bundles along the fiber direction and through the thickness of an individual ply. This type of damage is typical for plies subjected to tensile loading in transverse direction. For the current materials these

loads and stresses are clearly due to the thermals stresses generated during the manufacturing and subsequent cooling from cure temperatures. It is trivial to understand that no cracks if this type can be observed in layers with fibers aligned in parallel with the sample edge.

Figure 5 : Micrograph of the laminate as-manufactured (a), after post-curing at 420ºC in air (b) and after DMTA (c).

Results from quantification of the amount of micro-cracks are presented in Table 1. It can be noticed that the amount of initial micro-cracks in sub-laminates varied between 0.03 to 0.60 cr/mm (average is 0.31 cr/mm). Even though 0.60 cr/mm is a comparably high value for crack density, it should be noted that this value represents the accumulated number of cracks in the three plies of sub-laminate which contain visible cracks (+45º, -45º, 90º).

T [°C]	Environment	Average micro-crack density [mm^{-1}]					
		Initial		Post-PC		Post-DMA	
		inner	outer	inner	outer	inner	outer
400	Air	0.03	0.26	0.04	0.26	0.05	0.28
	N$_2$	0.08	0.56	0.10	0.63	0.22	0.80
420	Air	0.19	0.48	0.23	0.54	0.47	0.79
	N$_2$	0.19	0.53	0.24	0.60	0.29	0.68
440	Air	0.20	0.49	0.25	0.65	0.32	0.90
	N$_2$	0.16	0.60	0.21	0.65	0.28	0.71

Table 1 : Average micro-crack densities obtained from count of cracks on specimen edges in different sub-layers after different treatments.

Another observation from the first column in Table 1 is that the two outer sub-laminates have more initial cracks than the inner sub-laminates. Crack density in outer sub-laminates ranges between 0.26 to 0.60 cr/mm, whereas the corresponding range for inner sub-laminates is 0.03 to 0.20 cr/mm. Without any further analysis this observation provides the motivation to treat inner and outer sub-laminates separately. Another observation is that the samples subjected to post-cure at 400°C contained comparably small amounts of initial cracks. Since samples were selected for different treatment without any preferred order, currently there is no explanation for this phenomenon.

The crack density after post-cure increase with 0.01 to 0.05 cr/mm for inner sub-laminates and up to 0.16 cr/mm for outer sub-laminates, hence it is clear that the new cracks are created during the post-cure treatment. Values of the actual crack densities after post-cure from Table 1 are presented in graphical form in Figure 6. The graph shows and reinforces the conclusion that outer sub-laminates contain more cracks than inner ones. The graph also illustrates how samples post-cured at 400°C contain significantly fewer micro-cracks. These samples however contained low amount of cracks already to start with. It is not possible to distinguish and state any significant difference between neither post-cure temperatures nor environment on the crack density or the generation of new cracks, partially because the scatter of crack number in untested specimens is too high.
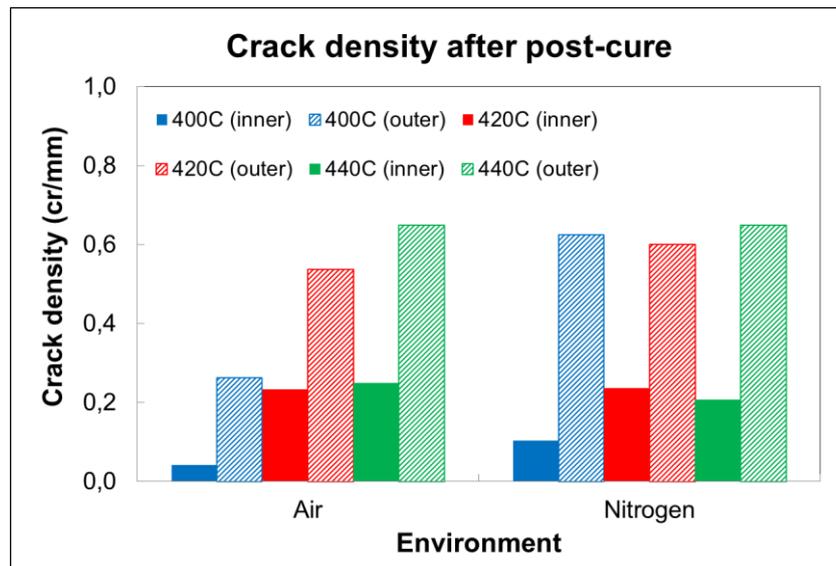

Figure 6 : Graphical representation of crack densities after post-cure for different treatments.

5 CONCLUSIONS

The results obtained in the study can be summarized with a number of statements: it is confirmed that 2h post-cure at temperatures in the range between 400°C and 440°C increase the T_g of NEXIMID MHT-R up to temperatures between 380°C and 461°C. It can be also stated that curing in nitrogen environment gives higher T_g. Some weight loss both associated with moisture and thermal degradation was observed. The weight loss after post-cure was about 0.5% to 1.5 % and is hence very limited. Moreover, a post-cure results in an increase of damage in the form of micro-cracks in the laminate. Cracking was consistently more severe (even before post-cure) in the outer layers compared to inner plies.

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