IMPACT TOLERANCE OF THERMOPLASTIC AND THERMOSET EPOXY CARBON TEXTILE COMPOSITES

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ABSTRACT

Recently, a thermoplastic epoxy resin (TP-EP) was developed with both advantages of thermoset and thermoplastic resins. The TP-EP has the good workability of TS and the formability and recyclability of TP. The present study aims to assess the impact tolerance of the TP-EP carbon textile composite (CFRTP) compared to the thermoset epoxy resin (TS-EP) counterpart. Drop weight impact test, with a hemispherical striker tip were performed for different molecular weight (Mw) of the TP-EP matrix. An impact energy of 30J was selected for comparison. The impact damage extension was visualized by a thermal-camera and by laser microscope measurements. The residual mechanical strength after impact was measured by compression tests. The highly polymerized CFRTP had higher maximum impact force, lower energy absorbed ratio, lower residual dent and smaller damaged surface, meaning a better impact tolerance.

1 INTRODUCTION

Nowadays, industry is experiencing many benefits from implementing fibre reinforced composites. These are widely used in the aerospace, automotive, marine, wind power, defence and civil engineering industries. Long and continuous fibre reinforced composite materials have been used in several industrial applications having excellent potential for reducing not only the weight but also lifetime maintenance costs owing to their corrosion and fatigue resistance. However, composites are costly and difficult to repair when exposed to impact damage [1]. Composite materials are sensitive to impacts, and it is a serious threat for composite structures because impact could produce large internal damages (such as delamination, matrix cracking, and fiber/yarn breakage) while leaving a small indent on the impact surface [2]. Hence, understanding the characteristics of these materials and their dissipation energy capacity are the major concerns for improving the impact resistance and damage tolerance of composite structures.

Impact resistance and damage tolerance of composite materials are affected by several factors, which are divided into primary and secondary factors [2]. The primary factors are reinforcement architecture and resin system. The latter is the topic of this paper for understanding the effect on the impact tolerance of carbon textile composite materials.

Secondary factors are hygrothermal conditions, stacking sequence, fiber hybridization, matrix hybridization, repeated impact, etc. [2].

As for the primary factors, on one hand, many studies were conducted to improve the impact resistance by changing the reinforcement architecture, e.g. 3D composites were developed which have through the thickness reinforcement ([3], [4]).

On the other hand, the attention was focused on developing resin systems with improve toughness (eg. [5], [6], [7]). Thermoset resin systems were extensively used for manufacturing composites components due to their ease manufacturing and improved mechanical/thermal properties. However, their non-recyclability, due to the irreversible exothermic chemical reaction during curing, draw the attention of the composite industry to use thermoplastic resin systems.

The main advantage of thermoplastic resins (TP) compared to thermoset (TS) counterpart are: increased toughness, better recyclability due to the physical change in the shape upon heating, and mainly the ability to deliver fast manufacturing processes. However, available TP resins have higher melt viscosity than TS ones. Due to high viscosity, the infusion process with conventional TP resins could lead to inappropriate impregnation of the fiber bundles.

Recently, a thermoplastic epoxy resin (TP-EP) was developed with both advantages of thermoset and thermoplastic resins [8]. The TP-EP has the good workability of thermoset resins and the formability and recyclability of thermoplastic systems.

In previous studies, the TP-EP was adopted for manufacturing textile carbon fiber reinforced thermoplastic epoxy composites (CFRTP), and to study the effect of the weight-average molecular weight (Mw) on quasi-static and fatigue mechanical performance [9]. The results highlighted the better properties of high Mw CFRTP with improved tensile strength and longer tensile-tensile fatigue life. Moreover, the CFRTP had an enhanced fracture toughness compared to the TS counterpart, namely a thermoset epoxy resin (TS-EP) reinforced with the same carbon textile (CFRTS) having almost the same fiber volume fraction. The enhanced toughness of TP vs TS epoxy composite was measured by mode I and mode II tests, as detailed in [10].

The latter suggests an improved damage resistance of the composite driven by the properties of the TP-EP matrix, which could provide a better retention of the mechanical properties after impact. Hence, the present study aims to assess the impact tolerance of the TP-EP carbon textile composite compared to the TS-EP counterpart. Drop weight impact test was performed on two different Mw of the TP-EP matrix. An impact energy of 30J was selected for comparison to the CFRTS. The impact damage extension was visualized by a thermal-camera and by laser microscope measurements. The residual mechanical strength after impact was measured by compression tests.

2 MATERIALS AND MANUFACTURING

Plain weave carbon fiber fabric (Mitsubishi Rayon TR3110MS) was used as reinforcement (yarn TR30S 3L, linear density 1.79 g/cm^3, pick and end counts 12.5 per inch, areal weight 200 g/m^2).

Thermoplastic epoxy resin (Denatite XNR 6850A, Accelerator XNH 6850B; supplied by Nagase ChemteX Corporation, Japan) [8] was used as matrix (T_g was approximately 100 °C).

Thermoset epoxy resin (JER828, Mitsubishi Chemical Corporation) and amine (JER113, Mitsubishi Chemical Corporation) were used as resin and curing agent, respectively.

Plain weave CFRTP prepreg was made by the following procedure. The resin, ‘XNR 6850A’, was heated by an electric oven at 120 °C. When the temperature of the resin reached 105 °C, the accelerator ‘XNH 6850B’ was added to the resin with stirring. The plain weave carbon fabric was impregnated with the thermoplastic epoxy resin by hand lay-up.

CFRTP prepreg impregnated with the thermoplastic epoxy resin in the state of oligomer was polymerized at a given temperature in an electric oven. The molecular weight of prepreg was finally controlled by a predetermined time and temperature sequence.

The obtained prepreg was dried at 50 °C for 12 hours. CFRTP laminates were prepared with 20 layers by hot-press molding at 175~195 °C and 6~12 MPa. The CFRTP laminates had fiber volume fraction and thickness of approximately 45 % and 4 mm, respectively.

The same plain weave carbon fiber fabric was used as reinforcement of the thermoset resin. The CFRTS plates with 20 layers were laminated by hand lay-up impregnation. The mold was cured in a hot press at 80 °C for 1 hour and then at 150 °C for 3 hours. The CFRTS laminates had approximately 45 % fiber volume fraction and thickness of 4 mm, as the CFRTP ones.

3 FEATURES OF THE EXPERIMENTAL MEASUREMENTS

The weight-average molecular weight of the TP-EP matrix was measured for each batch by the gel permeation chromatography (GPC), adopting a CLASS-LC10 (Shimadzu Corporation) and a GPC column (Styragel HR4E, Styragel HR5E: waters). Tetrahydrofuran (THF) was used as solvent. The calibration curves were drawn based on the retention time and the Mw of standard polystyrene.

Drop weight impact test was according to ASTM D7136 [11], with a hemispherical striker tip of 20 mm diameter. The adopted impact device was CEAST FractoVis 6789. For the sake of comparison, an impact energy of 30 J was selected, setting the impactor mass of 6.153 kg and impactor drop height of 0.497 m. The specimen (100 × 60 mm^2) was clamped by a system with an inner hole diameter of 40 mm, and impacted at the center. The recorded impactor velocity at time of initial contact was 3.1227 m/s. The rebound catcher system was enabled to stop the impactor during its second descent. Three specimens for each material and Mw were used for impact test and after impact measurements. Two specimens were considered for compression strength before impact due to the reduced quantity of available materials.

To assess the damage imparted during impact, the morphology of the impacted surface was detected by a shape measurement laser microscope KEYENCE VK-X210. Moreover, an infrared thermo camera TESTO 890 (accuracy 0.1°C) was adopted to monitor the evolution of the temperature on the specimen surface opposite to the heating source. The heating source was applied for a period of 5 seconds using an infrared lamp (electric power of 2.5 kW) positioned at a distance of about 20 cm from the specimen. Images (resolution 640 x 480 pixels) were continuously recorded for 12 seconds, with a frequency of 20 Hz, from the beginning of the heating, to have the heterogeneous evolution of the thermal front into the material as results of the impact damage. The specimen was set in a 4 cm thick frame of expanded polystyrene during heating and temperature recording.

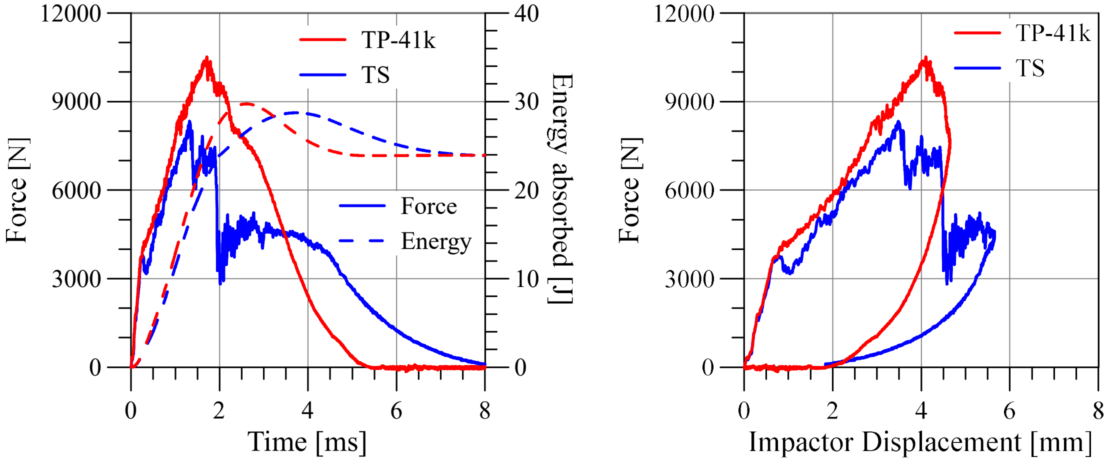
Compression strength, before and after impact, was measured according to ASTM D7137 [12], by a Shimadzu universal material testing machine (load cell 50 kN), cross head speed of 1 mm/min.

4 RESULTS AND COMPARISONS

In previous study ([9], [10]), the effect of the weight-average molecular weight (Mw) on mechanical properties of the same carbon textile composite highlighted the better properties for Mw higher then 60k (k means thousand). Therefore, in the present study, two molecular weights of TP-EP were selected to assess the effect on the impact performance compared to the thermoset counterpart, namely 41k and 68k (lower and higher the transition level).

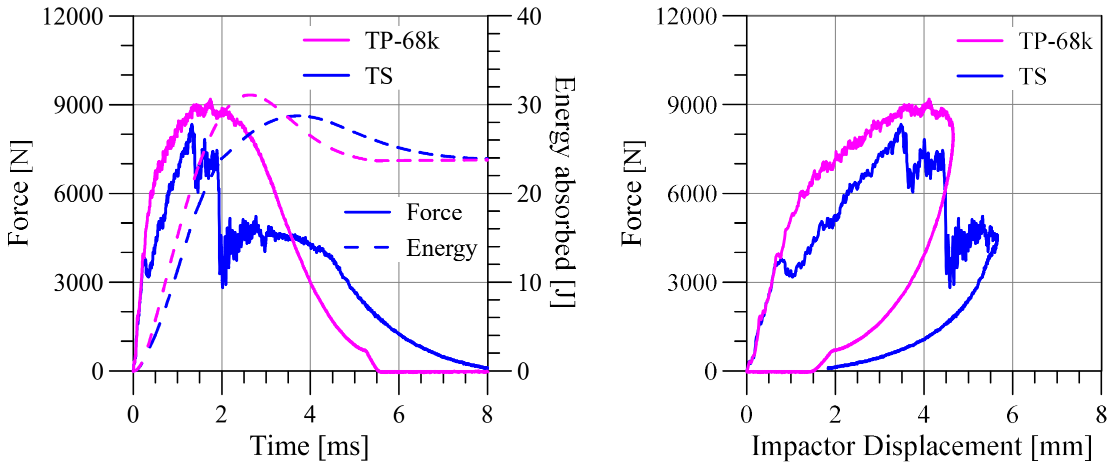
The selected impact energy (30 J) did not lead to perforation, for all considered materials. It allowed measurement of the residual compression strength.

A comparison of the force and energy evolution during impact of the thermoplastic and thermoset reinforced composites shows considerable differences (see Figure 1a for Mw=41k, and Figure 2a for Mw=68k). The TP-EP composites of both Mw had different shapes of the force versus time curve at the first discontinuity of the slope (F_1). The TS material had a reduction while the TP had continuous increase of the load, meaning a different extension of the damage initiation area (matrix cracking). Differences are also visible for the maximum recorded contact force (F_{max}) and impact duration. Higher maximum force and lower impact duration for the TP-EP reinforced composites. Moreover, oscillations of the force in the descending branch become more serious for the TS, indicating that a more serious damage occurs (several unstable delamination) in the CFRTS than in the CFRTP laminates.



(a) (b)

Figure 1: Impact response of CFRTS and CFRTP with TP Mw=41k: (a) Force and Energy vs. Time; (b) Force vs. Impactor displacement.



(a) (b)

Figure 2: Impact of CFRTS and CFRTP with TP Mw=68k: (a) Force and Energy vs. Time; (b) Force vs. Impactor displacement.

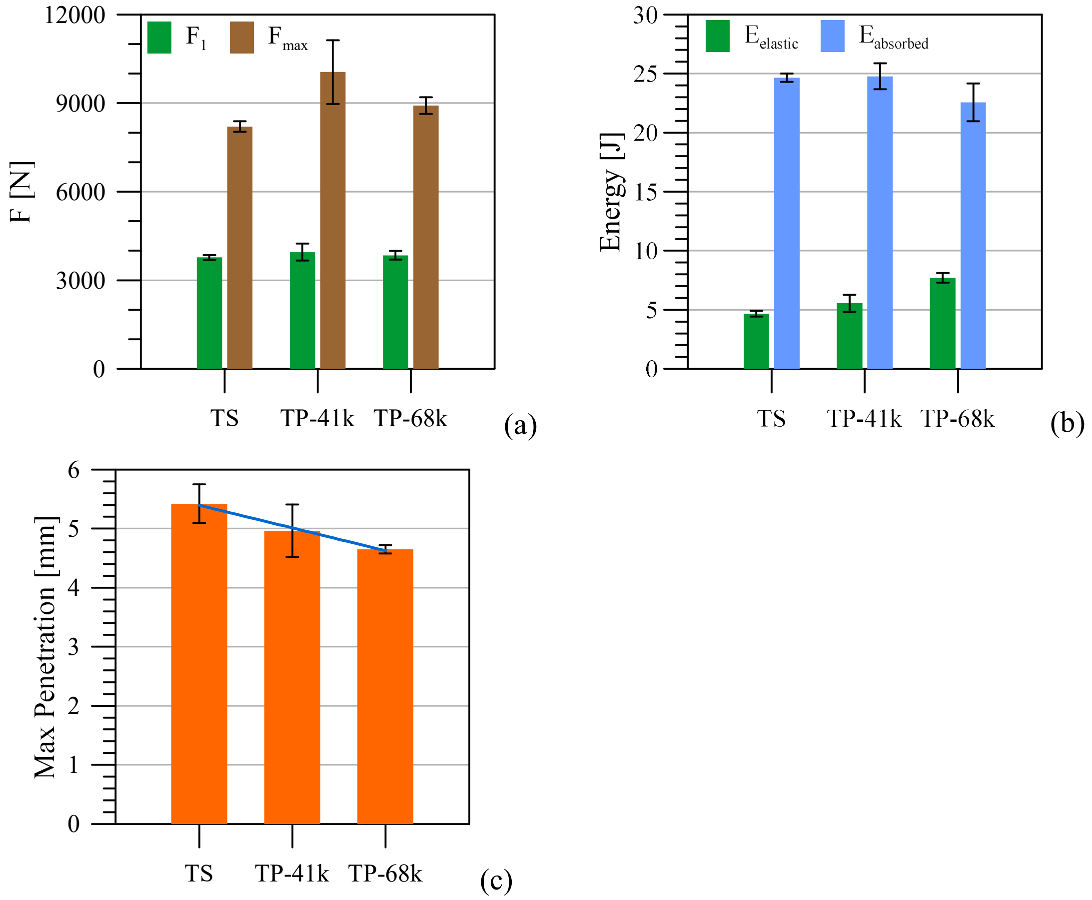
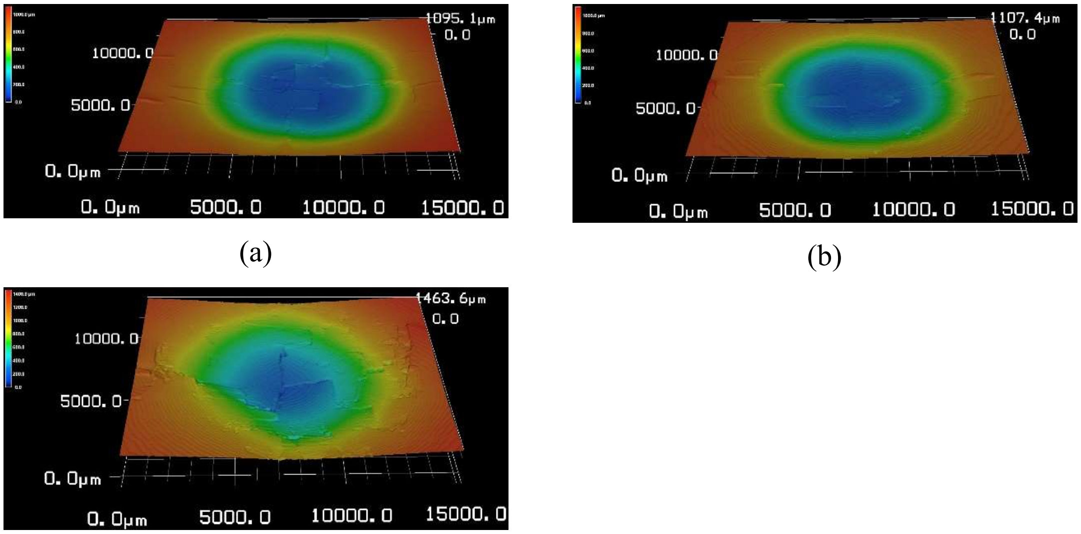


Figure 3: Comparison of (a) force at slope change (F_1) and max force (F_{max}); (b) elastic energy ($E_{elastic}$) and absorbed energy ($E_{absorbed}$); (c) max penetration of impactor. Average and standard deviation (error bars) of three samples.

Similar observations can be deduces extracting some significant quantities from the impact curves (as in Figure 1 and Figure 2). The force at the first discontinuity of the slope (F_1) had quite similar values for the considered materials, while the average maximum force (F_{max}) recorded for the TP-EP composites shows an increase in the range 9-22% with respect to the TS-EP counterpart (Figure 3a). It means that the TP composites are more impact resistant than TS one.

Figure 3b compares the elastic and absorbed impact energies. The average absorbed energy for the composite with TP-EP Mw=68k is lower (~10%) than TS-EP composite. Assuming the absorbed energy proportional to imparted damage (see e.g. [13]), the TP matrix suggests a composite more damage tolerant then the one with TS. It is confirmed considering the energy absorbed ratio. It was 0.81, 0.75 and 0.85 for composite with TP-EP 41k, TP-EP 68k and TS-EP, respectively. It indicates a more significant damage imparted in the TS composite which had the higher energy absorbed ratio.

From the force vs impactor displacement curves (as in Figure 1b and Figure 2b), the average maximum deflection measured during impact (maximum impactor displacement) shows a linear decreasing tendency from the TS to the TP with increasing Mw (see Figure 3c, correlation coefficient R = 0.99). The maximum deflection of the TP-EP 68k was almost 15% lower than the TS-EP composite. It is consistent with the residual dent measured by the laser device on the impacted surface of the specimens (Figure 4 and Figure 5). The permanent indentation is a predictive mark to evaluate the residual mechanical capabilities of the composite. The dent compared in Figure 5 indicates that the TP-EP reinforced materials are less prone to permanent indentation, meaning predictable better mechanical behaviour after impact.



(a) (b)

(c)

Figure 4: Laser shape measurements of the sample impacted surface (15 mm × 10 mm): (a) CFRTP with TP Mw=41k; (b) CFRTP with TP Mw=68k; (c) CFRTS.

The damaged surface morphology shows a more diffuse damage pattern with longer and denser cracks on the surface of the thermoset composite (Figure 4c). This is reflected on the thermal behaviour of the impacted composites. To eliminate the influence of environment interference and sensitivity of apparatus on thermal measurements, the subtracting method is here adopted (see e.g. [14]), namely the temperature distribution at time zero (beginning of heating) was subtracted to that of each image caught at any recording time. It provides the variation of temperature (ΔT) maps with respect to the first image. The variation of temperature maps on the impacted surface, detailed in Figure 6, are after 10 seconds since the beginning of the heating (heating time was 5 seconds). The heat flux propagates in the material creating a heterogeneous distribution due to the difference of thermal conductivity between the undamaged and damage material. Hence, the infrared thermography highlights the temperature on the specimen surface related to the local damage after impact.

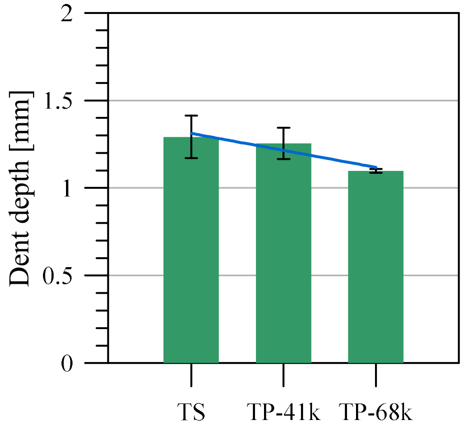
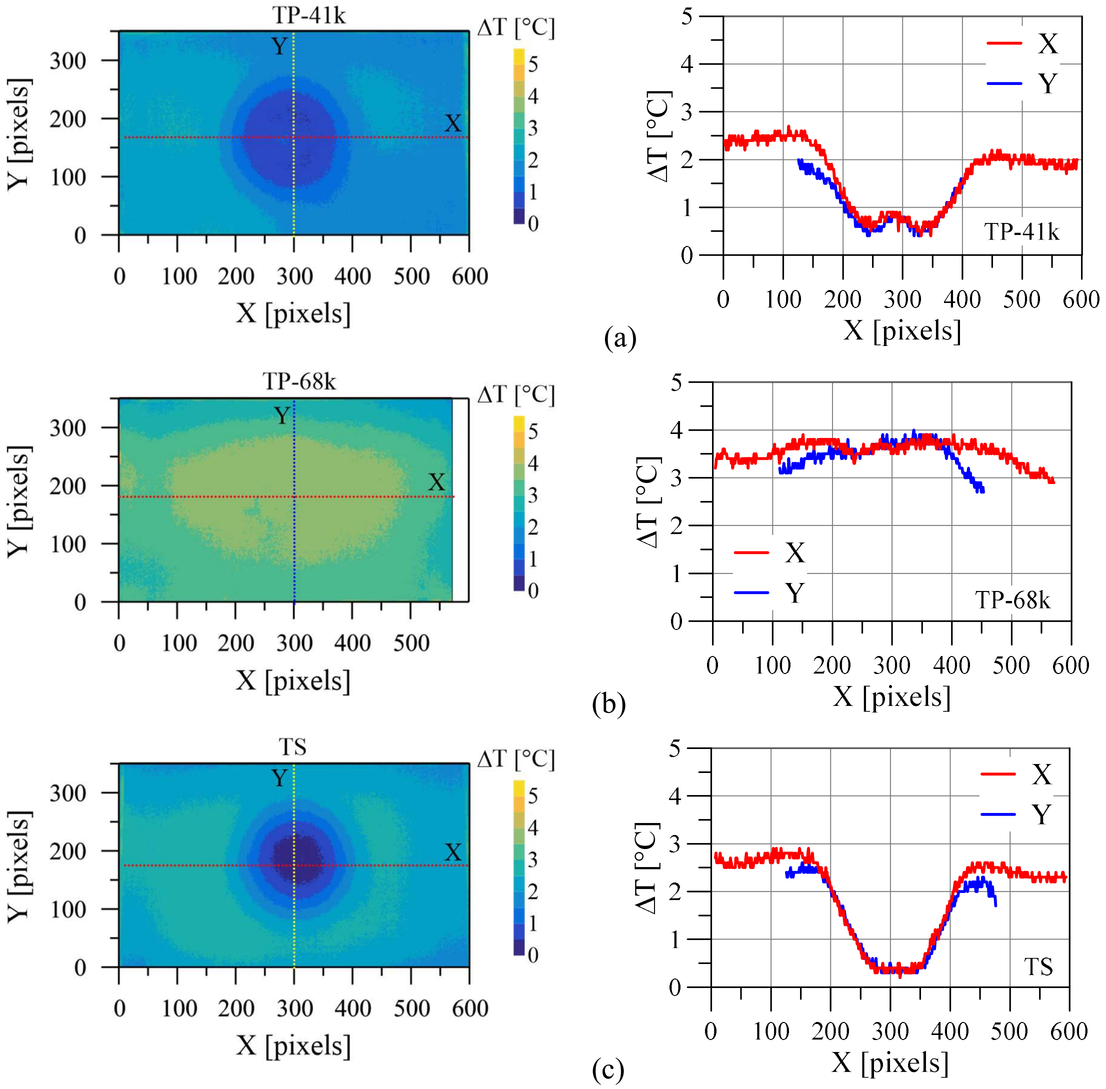


Figure 5: Residual dent depth after the impact by laser measurements.



(a)

(b)

(c)

Figure 6: Thermography after impact: (left) variation to time zero of temperature map; (right) variation of temperature profile along the centerlines X and Y. (a) CFRTP with TP Mw=41k; (b) CFRTP with TP Mw=68k; (c) CFRTS.

The discontinuities created by the imparted cracks in the damaged area slow the heat flux, while it is faster in the undamaged material. All maps distinguish the damage and undamaged portion of the specimens by different ΔT, showing the expected damaged circular area as imparted by the spherical impactor. However, a rough estimation and comparison of the damaged surface highlight considerable difference between the composites. The TS and TP Mw=41k reinforced composite had the wider damaged surface (Figure 6c,a), slightly smaller for the latter, while the TP Mw=68k had a relatively different damaged surface (Figure 6b). It is visible by the small variation of temperature along the two considered paths almost 1°C (see right diagram in Figure 6b), while it was 2.5°C and 2°C for the TS and TP Mw=41k counterparts. The thermal measurements confirm the above understanding and the previous findings on better toughness of the TP composite with a Mw higher than 60k. The high molecular weight of the TP-EP matrix enhances the impact damage tolerance of the carbon textile composite in comparison to the TP-EP with low Mw and, mainly, to the thermoset epoxy.

The impact damage tolerance is reflected in the retention of the mechanical properties after impact. Here the compression strength was measured and compared to the measurements before impact (Figure 7). The elevate damage imparted during the impact on the CFRTS created a reduction of the strength of almost 49%. The two TP-EP composites experienced a lower extension of the damage and probably different damage modes mainly governed by the matrix plasticization which allowed for a retention in the range 73÷94% of the pre-impact compressive property (Figure 7).

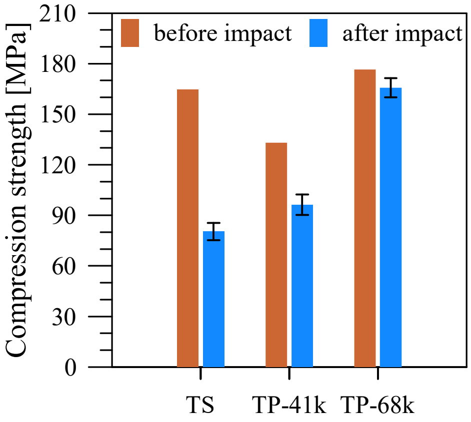


Figure 7: Comparison of the compression strength before and after impact. Average and standard deviation (error bars) of three specimens (two specimens if no bars).

5 CONCLUSIONS

The recently developed thermoplastic epoxy resin (TP-EP) with both advantages of thermoset and thermoplastic resins was adopted to assess the impact tolerance of carbon textile reinforced composites. The enhancement of the mechanical performance, e.g. fracture toughness, of the highly polymerized thermoplastic epoxy composite, detailed in previous study, was also measured by impact tests. The Mw=68k TP-EP composite had higher maximum impact force, lower energy absorbed ratio and lower residual dent. Moreover, the laser and thermographic measurements showed for the TP composite different morphology and smaller damaged surface. This resulted in a better impact tolerance of the TP-EP composite, which was emphasized by compression after impact strength. The TP-EP matrix allowed for a retention of the almost 94% of the pre-impact strength, compared to the 50% of the conventional thermoset epoxy reinforced composite.

Considering those results, two are the future studies: local observations of the impact damage morphology to better understanding the different damage mechanisms in the composite with TP epoxy and conventional TS one; nano-enhanced TP epoxy resin systems to delay the matrix damage initiation and then extend the fatigue life and improve the impact tolerance of carbon reinforced composites.

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