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# An Innovative Approach for Restoring the Mechanical Properties of Thermoplastic-Matrix Nanocomposite by the Use of Partially Polymerized Cyclic Butylene Terephthalate

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**Abstract:** This work is focused on the production of a smart material from cyclic butylene-terephthalate (CBT), characterized by the built-in capability to recover its damage, through the catalyzed ring opening polymerization (ROP) of its oligomers; in particular, molten CBT, after filling the damaged zone, can be converted into poly-butylene terephthalate (PBT), thus promoting a join of the broken surfaces and fixing the crack. To obtain a material with self-healing potential, the production of a partially polymerized system is required. For this purpose, two solutions were studied: the first one involved the use of two catalysts with different activation times, whereas the second solution implied the intercalation of the faster catalyst inside the nanoclay lamellae. Since the intercalation allowed slowing the activation of the catalyst, residual CBT can be converted in a second step. Mechanical properties of partially reacted PBT samples and their healing ability were checked by flexural analyses; in order to promote the healing process, samples were notched to simulate partial damage and left in oven for different times and temperatures, to allow the activation of the unreacted catalyst with the consequent ROP of the residual CBT; flexural tests on samples after healing showed a good recovery of mechanical properties.

**Keywords:** nanocomposites; self-healing; ring opening polymerization; CBT; mechanical properties

## 1. Introduction

Nowadays, polymers and composites are widely used in several applications, like automotive, aerospace, sport, electronics, and civil engineering [1]. Although these materials present very good properties, they can be damaged during their use for mechanical, chemical, thermal, or UV exposition [2,3]. The damage can be located inside the structure, making detection and external intervention difficult or impossible [4]. Non-destructive techniques for the detection of damages and repairing methods of visible cracks [5,6] do not allow for repairing microcracks inside the polymer or composite structure. To overcome this limit, in the 1980s [7] the concept of self-healing material was introduced with the aim of healing invisible microcracks inside the material and extending the working life of the components [8]. The ability of a self-healing polymeric material is that of recovering its properties after damage, both autonomously or with a specific stimulus, such as heating or radiation, thus avoiding external repair and reducing costs and maintenance [9]. When self-healing materials are subjected to a rupture, they can show the ability to restore different properties, such as tensile strength, elongation at break, barrier and surface properties [10]. Many self-healing techniques, such as molecular interdiffusion [11], thermally reversible crosslinks [12], hollow fiber approach [13], chain rearrangement [14], or microencapsulation [15], are already employed for the recovery of

polymers and composites [16,17]. Nevertheless, these techniques require specific methods to be carried out, which involve difficult implementation in the traditional polymer processes. Also, these approaches for self-healing make use of particular classes of polymers, which have quite a narrow field of application in common polymer technology; generally, thermoset polymers are employed for self-healing, which in turn have a limited series of applications compared to thermoplastics.

Therefore, this work aims to develop a nanocomposite with self-healing potential based on a commodity thermoplastic matrix, polybutylene terephthalate. The nanocomposite developed in this work is based on a commodity thermoplastic matrix, polybutylene terephthalate, suitable for many industrial applications because of its outstanding combination of engineering properties, which make it very attractive in different sectors of polymer technology. The matrix was obtained starting from cyclic butylene-terephthalate (CBT), which, through a catalyzed ring opening polymerization, can be converted to poly-butylene terephthalate (PBT) [18,19]. Before the healing process, the matrix will be composed of a mixture of PBT, cyclic CBT, and active catalyst. When damage occurs, a crack is formed on the surface or in the bulk of the material. Heating of the material at about 150 °C allows for melting of the CBT, which reaches very low viscosity (about 10 Pa\*s) [20] and diffuses inside the crack, filling it. At higher temperature, during the healing process, the presence of residual CBT and active catalyst induces a thermal activated ring opening polymerization (ROP) which, through the conversion of CBT to PBT, allows welding the surface of the crack, restoring the original load-bearing characteristics. The whole healing process takes place at temperatures lower than melting of PBT (about 220 °C), to retain the mechanical properties and dimensional stability of the material.

The proposed approach has a series of advantages compared to other approaches: the thermoplastic matrix developed has already a self-healing ability, although its properties could be improved by the presence of a nanofiller; also, the healing reaction can be tailored by modifying the catalyst type and amount, and the healing ability is preserved for a very long time at room temperature. Finally, the healing agent produces a polymer which is the same polymer used for the matrix, no gas is evolved during the reaction, and no temperature increase takes place, due to the fact that the ROP is athermal.

## 2. Materials and Methods

The CBT 100 resin used in this work is a cyclic oligomer of PBT produced by Cyclics Corporation and distributed by Pflex in pellet form. The catalysts for ROP are Fascat 4101 (Butyltin Chloride Dihydroxide, by Sigma-Aldrich, St. Louis, MO, USA), a solid catalyst characterized by a lower activation temperature (between 140 °C and 190 °C), and Fascat 4102 (Butyltin Tris (2-Ethylhexoate), by Sigma-Aldrich), characterized by a higher activation temperature (210–240 °C). Both catalysts, during ring opening polymerization, do not supply end groups and remain built into the polymer, obtaining a very high molecular-weight macrocycle [21]. Figure 1 shows the mechanism of CBT ring opening polymerization with the incorporation of the cyclic stannoxane catalyst into the macrocyclic structure.

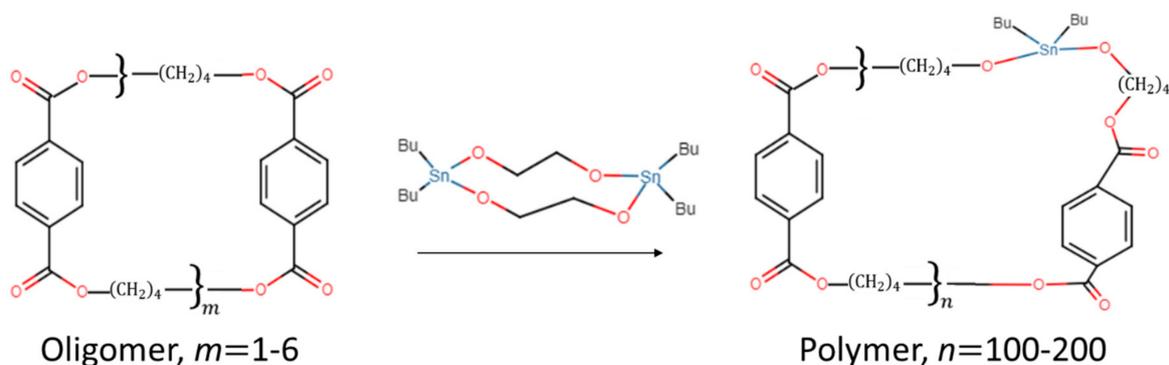


Figure 1. Incorporation of tin into a macrocyclic structure via the cyclic stannoxane.

The nanofiller is a montmorillonite (MMT) powder without any organic modifier (Dellite HPS, by Laviosa Chimica Mineraria S.p.A, Livorno, Italy).

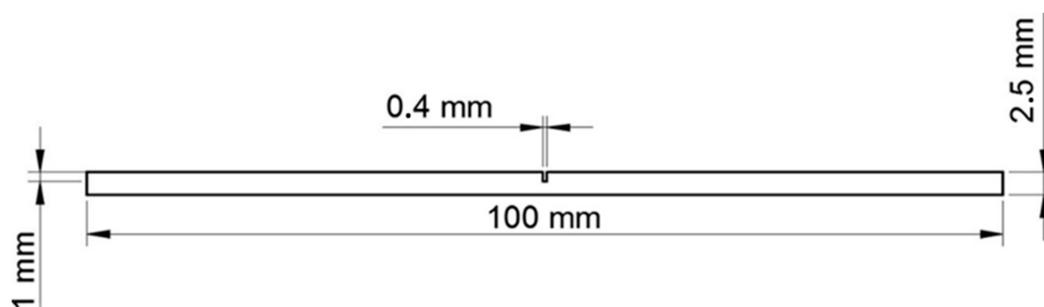
The intercalation of the catalyst in the MMT lamellae was obtained by the addition of 400 mg of MMT and 100 mg of Fascat 4101 in 100 ml of water. The suspension was kept stirring for 24 h and then maintained at 60 °C until the complete evaporation of the water was reached. In a previous work [8] it was found that intercalation of the catalyst inside MMT lamellae significantly reduces the catalyst activity, and has the same qualitative effect of adding a slower catalyst. A thermoplastic epoxy resin (ELANTECH by Elantas Europe S.R.L, Altana division, Hamburg, Germany) was added at 4% wt. to the mixture as toughening agent, in order to reduce the brittleness of the material [22].

The production of PBT samples was reached by the melting of pre-dried [23] CBT in a Vaseline bath at 160 °C. The complete melting of CBT was followed by the addition of the catalysts (free or intercalated) and the toughening agent. After stirring for 3.5 min, the mixture was poured in a Teflon mold and placed in a forced convection oven. The mold was extracted when the temperature, monitored with a thermocouple, reached 190 °C, thus allowing a partial polymerization of CBT into PBT, involving the presence of both PBT and residual unreacted CBT oligomer inside the sample. A temperature of 190 °C was chosen since it made it possible to obtain good mechanical properties, still retaining an adequate amount of residual CBT and slower catalyst, or intercalated catalyst in the case of the nanocomposite. All the compositions of the mixtures produced are shown in Table 1. Sample F1\_F2 was characterized by the presence of two catalysts, whereas sample F1\_F1MMT was characterized by the presence of the faster catalyst, which was however, partially intercalated in the nanofiller.

**Table 1.** Composition of the mixtures produced in wt.%.

Sample	CBT	Elantech	Fascat 4101	Fascat 4102	Intercalated Fascat 4101	MMT	Healing
F1	95.5	4	0.5	0	0	0	-
F1_F2	95.5	4	0.25	0.25	0	0	195 °C, 30 min 200 °C, 20 min
F1_F1MMT	94.5	4	0.25	0	0.25	1	160 °C, 24 h 180 °C, 24 h

The prepared samples were subjected to a notch with a milling disc, to simulate the presence of partial damage. In particular, as shown in Figure 2, the notch was characterized by a width of 0.4 mm, which was constant throughout the thickness. Afterwards, notched samples were heated at temperatures ranging between 160 °C and 200 °C, in order to activate the slower catalyst or the intercalated catalyst, thus promoting healing of the notched samples. Temperatures and times used for the healing process are shown in Table 1. In particular, two strategies were chosen: samples with two catalysts were healed using shorter maintenance in oven (from 20 min to 40 min) and higher healing temperatures (195 °C and 200 °C); samples with intercalated catalyst were healed using longer maintenance in oven (24 h) and lower temperatures (160 °C and 180 °C).



**Figure 2.** Geometry of the notched samples.

Rheological tests were performed on unreacted CBT samples after mixing at 160 °C, on an Ares Rheometric Scientific rheometer, with parallel plate geometry, and diameter of the plates 25 mm. Dynamic temperature ramp tests were performed, with a preheating at 130 °C, followed by a ramp from 130 °C to 250 °C at 5 °C/min, 1 mm initial gap, a frequency of 3.14, and 1% strain. The partial polymerization of the system was evaluated by a DSC1 Star System by Mettler-Toledo, with a heating scan from 25 °C to 270 °C at 10 °C/min; the presence of residual CBT was then confirmed by the presence of its melting peaks.

As prepared, notched and repaired samples were subjected to flexural tests, using LLOYD LR5K dynamometer by LLOYD Instruments, according to ASTM D790-00.

Initially, the efficiency of healing was evaluated by considering the deformation at break as the control property. Therefore, the parameter  $\eta_{healing,\epsilon}$ , was estimated as [24]:

$$\eta_{healing,\epsilon} = \frac{\epsilon_{Rh} - \epsilon_{Rn}}{\epsilon_{Ru} - \epsilon_{Rn}}, \tag{1}$$

where  $\epsilon_{Rh}$ ,  $\epsilon_{Rn}$ , and  $\epsilon_{Ru}$  are the deformation at break of healed samples, notched samples, and unnotched samples, respectively. The value of  $\eta_{healing,\epsilon}$  ranges between 0 and 1, being  $\epsilon_{Rh} > \epsilon_{Rn}$ ; its value increases as  $\epsilon_{Rh}$  approaches  $\epsilon_{Ru}$ , thus allowing to completely restore the deformation at break of unnotched PBT. On the other hand, during healing, a modulus increase was also observed for PBT; in view of a potential application of the developed material, this increase of the modulus could be detrimental. Therefore, a second healing efficiency parameter,  $\eta_{healing,E}$  was considered:

$$\eta_{healing,E} = \frac{E_{Ru} - E_{Rn}}{E_{Rh} - E_{Rn}}, \tag{2}$$

where  $E_{Rh}$ ,  $E_{Rn}$ , and  $E_{Ru}$  are the flexural modulus of healed samples, notched samples, and unnotched samples, respectively. As in Equation (1), the efficiency parameter of Equation (2) ranges between 0 and 1; being  $E_{Rh} \geq E_{Ru}$ , its value is maximum when no change of the modulus occurs, and goes to 0 as  $E_{Rh}$  increases.

Finally, a total healing parameter was obtained as the product between the two healing parameters:

$$\eta_{healing,tot} = \eta_{healing,\epsilon} \eta_{healing,E} = \frac{\epsilon_{Rh} - \epsilon_{Rn}}{\epsilon_{Ru} - \epsilon_{Rn}} \frac{E_{Ru} - E_{Rn}}{E_{Rh} - E_{Rn}}, \tag{3}$$

which makes it possible to contemporarily account for the restoring of the deformation at break and increase of the modulus.

Samples before and after restoring the notch are shown in Figure 3.



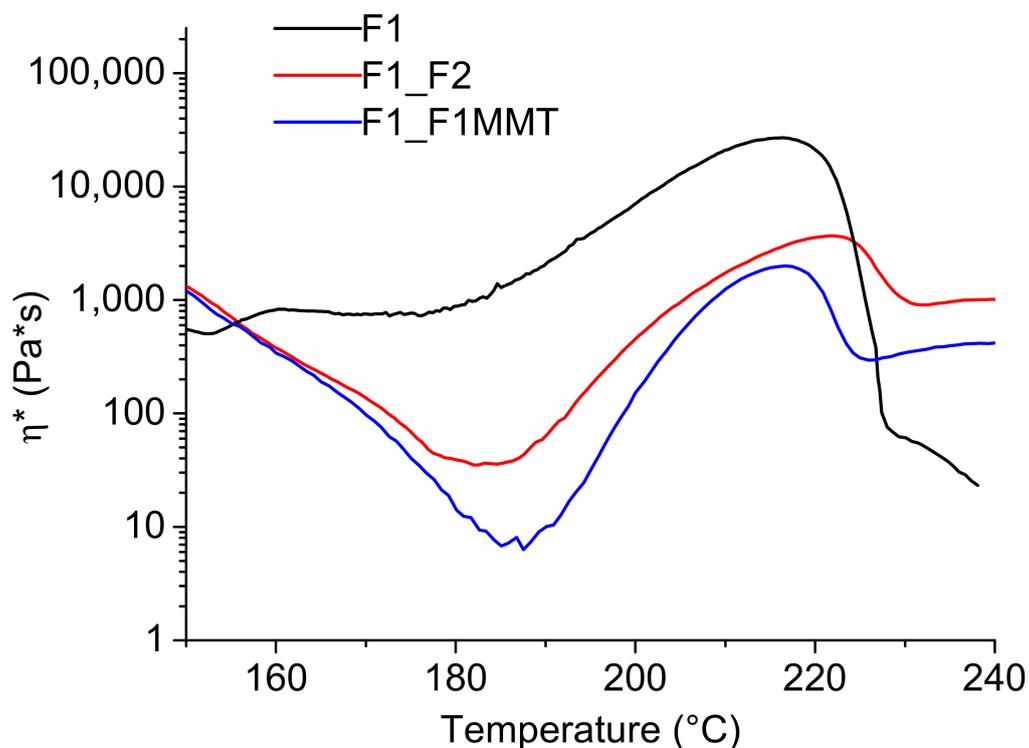
Figure 3. Notched samples before and after healing.

### 3. Results and Discussion

#### 3.1. Viscosity Evolution

The evolution of the viscosity of CBT mixtures with the increase of temperature is shown in Figure 4. When the Fascat 4101 catalyst was used, the viscosity remained constant until 180 °C; this step

was followed by a sharp increase of viscosity because of the growth of molecular weight due to the ROP. Then, after reaching a maximum value at about 215 °C, the viscosity rapidly decreased due to PBT melting. The choice of using two catalysts made it possible to obtain two steps of reaction: in the first step, starting at about 180 °C, Fascat 4101 was activated; after reaching a maximum at about 220 °C, the viscosity decreases, which was again due to PBT melting; however, the viscosity decrease was much slower than in the case of the single catalyst system; in addition, viscosity increased in the range between 230 °C and 240 °C. This was attributed to the activation of Fascat 4102, which involves a second step of polymerization and further increase of viscosity, and counterbalances the viscosity decrease due to melting. When using partially intercalated Fascat 4101, the viscosity evolution was similar to that observed for the two-catalyst system. However, in this case, the second step of polymerization was attributed to the presence of intercalated catalyst, which, as reported in a previous work, shows much higher activation temperature compared to a free catalyst [13,25].



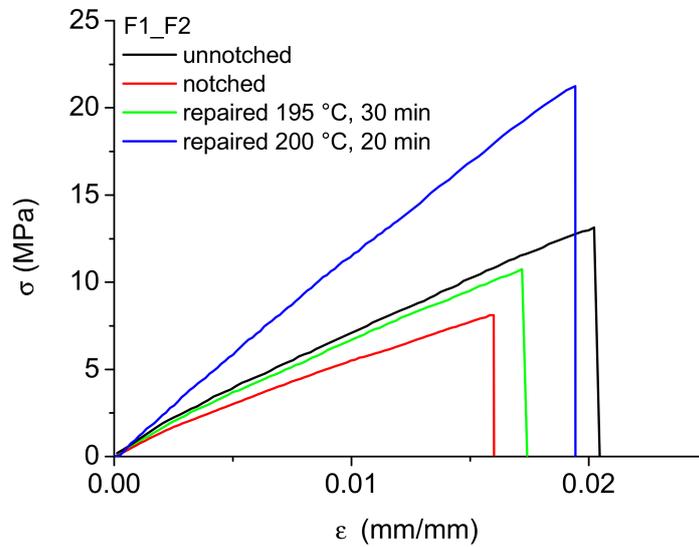
**Figure 4.** Dynamic temperature ramp tests on cyclic butylene-terephthalate (CBT) samples.

### 3.2. F1\_F2 System

#### 3.2.1. Mechanical Characterization of F1\_F2 System

Typical stress–strain curves of PBT with two catalysts, tested as produced, after notching and after healing, are reported in Figure 5. The values of flexural strength, modulus, and deformation at break are reported in Table 2, where each value was obtained as the average of six measurements. Compared to as-produced samples, notching involved a significant decrease in flexural strength (−44%) and deformation at break (−19%), and a less significant reduction in the modulus (−8%); however, healing of the samples allowed partial or complete restoration of the mechanical properties. In particular, healing at the lower temperature involved a partial recovery of the flexural strength (−19% with respect to the initial value of the as produced sample) and deformation at break (−13%), with a negligible change of the flexural modulus (+2%), compared to as-produced sample. On the other hand, healing at the higher temperature involved an almost complete recovery of the deformation at break (−3%), which was, however, associated with a significant increase of the flexural strength (+39%) and modulus (+31%). According to the results reported in a previous work, the increase of the flexural strength

and modulus compared to as produced samples is attributed to lamellar thickening effects occurring during healing of the material [13].



**Figure 5.** Flexural curves of poly-butylene terephthalate (PBT) without notch, notched, and healed with different recovery conditions.

**Table 2.** Flexural results on PBT samples before and after healing with different recovery conditions.

F1_F2 System	$\sigma_R$ (MPa)	$\epsilon_R$ (mm/mm)*10 <sup>-2</sup>	E (GPa)
Unnotched	15.4 ± 6.63	1.97 ± 0.122	0.91 ± 0.39
Notched	8.59 ± 0.82 (-44%)	1.59 ± 0.259 (-19%)	0.84 ± 0.24 (-8%)
repaired, 195 °C 30 min	12.5 ± 3.48 (-18%)	1.70 ± 0.604 (-14%)	0.93 ± 0.37 (+2%)
repaired, 200 °C 20 min	21.4 ± 4.25 (+39%)	1.90 <sup>2</sup> ± 0.707 (-3%)	1.20 ± 0.17 (+31%)

In fact, as reported in Table 3, for the sample healed at 195 °C, the increase of the melting peak temperature was found to be about 7 °C compared to as produced samples, whereas for the sample healed at 200 °C the increase was found to be almost 12 °C, whereas the crystallinity of the samples was found to be independent of the healing conditions. On the other hand, a residual amount of CBT ( $x_{CBT}$ ), obtained as the ratio between the melting enthalpies of CBT and total melting enthalpy of CBT and PBT, was found for lower healing temperatures

**Table 3.** Melting enthalpies and residual amount of CBT before and after healing of F1\_F2 system.

F1_F2	$\Delta H_{m-CBT}$ (J/g)	$T_{m-PBT}$ (°C)	$\Delta H_{m-PBT}$ (J/g)	$x_{CBT}$
Before healing	6.85	205.7	21.3	0.32
Healing at 195 °C for 30 min	1.89	212.8	44.6	0.04
Healing at 200 °C for 20 min	0	219.3	44.9	0

### 3.2.2. Healing Efficiency of F1\_F2 System

The healing efficiency of PBT samples recovered at different temperatures and times was calculated according to Equations (1) and (2) from the data in Table 3. According to Equation (1), as the deformation at break increases, the healing efficiency increases as well. Referring to results of Figure 6, a rise of the healing temperature involves a higher deformation at break, and therefore a higher healing efficiency,  $\eta_{healing,\epsilon}$ . In contrast, according to Equation (2), an increase in flexural modulus involves a reduction of the healing efficiency  $\eta_{healing,E}$ . Therefore, a growth of the healing temperature, with consequent

higher flexural modulus, also involves a decrease of  $\eta_{healing,E}$ , as clearly observed in Figure 6. In turn, the increase of the flexural modulus can be attributed to a growth of lamellar thickness which occurs at the higher temperature, and is highlighted by higher melting temperature (Table 3).

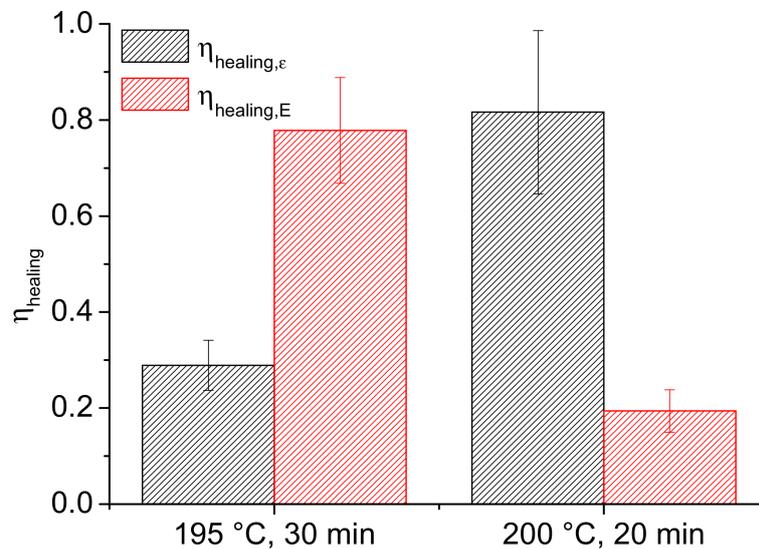


Figure 6. Healing efficiency at different healing times and temperatures for toughened PBT.

### 3.3. F1\_F1MMT System

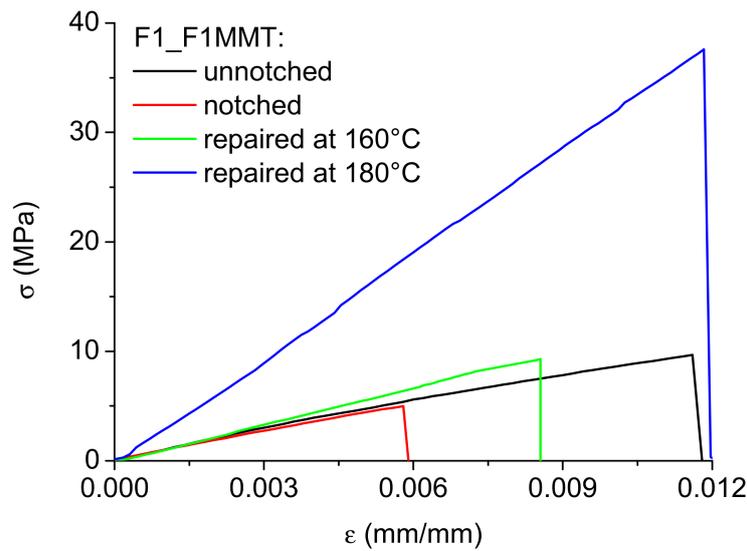
#### 3.3.1. Mechanical Characterization of F1\_F1MMT System

Stress–strain curves for PBT obtained with the partially intercalated catalyst are reported in Figure 7, and the corresponding values of the flexural properties are reported in Table 4. Comparison of the results of Tables 2 and 4 indicates that the nanocomposite was characterized by a lower flexural strength and deformation at break, with respect to the two catalysts system, whereas the modulus was not changed by the addition of the nanoclay. The difference between the two samples can be explained by two different factors:

- The addition of the nanoclay, which is known to reduce the ductility of the materials;
- The higher amount of residual CBT for the nanofilled system compared to the two-catalyst system, as highlighted by DSC analysis reported in a previous work [13].

Table 4. Flexural properties of nanofilled PBT, repaired at different temperatures.

F1_F1MMT System	$\sigma_R$ (MPa)	$\epsilon_R$ (mm/mm)*10 <sup>-2</sup>	E (GPa)
Unnotched	10.9 ± 1.96	1.55 ± 0.565	0.92 ± 0.27
Notched	5.59 ± 1.37 (−48%)	0.667 ± 0.194 (−57%)	0.87 ± 0.11 (−5%)
Repaired at 160 °C	9.35 ± 2.11 (−14%)	1.00 ± 0.435 (−35%)	1.07 ± 0.20 (+16%)
Repaired at 180 °C	34.9 ± 6.01 (+220%)	1.36 ± 0.305 (−12%)	2.86 ± 0.16 (+210%)



**Figure 7.** Flexural stress–strain curves on PBT nanocomposites before and after healing.

The results of Table 4 show that, as in the case of the two-catalyst system, notching of the PBT nanocomposites involved a significant decrease of the flexural strength (−48%) and deformation at break (−56%), whereas the decrease of the modulus was much less substantial (−5%). After healing, the PBT showed a significant increase of the elongation at break and tensile strength and an increase of the flexural modulus, which significantly depends on the healing temperature. In particular, healing at 160 °C allowed partial restoration of the deformation to break (−35%) and flexural strength (−14%) with a modulus increase of about 16%. Healing at 180 °C allowed almost complete restoration of the deformation at break (−12%), but the modulus and the strength of the material increased by a factor of 3. As in the case of the two-catalyst system, significant lamellar thickening effects were observed during healing of the partially intercalated catalyst system: healing at 160 °C and 180 °C involved an increase of the melting temperature peak by 3.5 °C and 37 °C, respectively (Table 5).

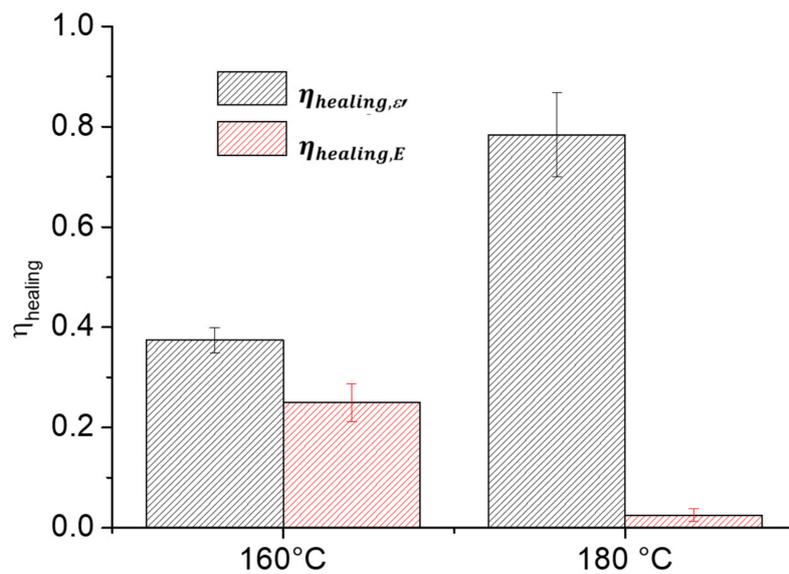
**Table 5.** Melting enthalpies and residual amount of CBT before and after healing of F1\_F1MMT system.

F1_F1MMT	$\Delta H_{m-CBT}$ (J/g)	$T_{m-PBT}$ (°C)	$\Delta H_{m-PBT}$ (J/g)	$x_{CBT}$
Before healing	14.4	192.6	10.9	0.57
Healing at 160 °C for 24 h	8.94	196.0	27.7	0.32
Healing at 180 °C for 24 h	0	229.7	71.9	0

Moreover, in the case of healing of the nanocomposite, the very long times of isothermal at high temperature also involved significant recrystallization, as highlighted by the increase of the melting enthalpy by a factor of 3 and 7, compared to as produced samples, for the healing at 160 °C and 180 °C, respectively (Table 5). Again, as for F1\_F2 system, some residual CBT was observed only for the sample healed at lower temperatures.

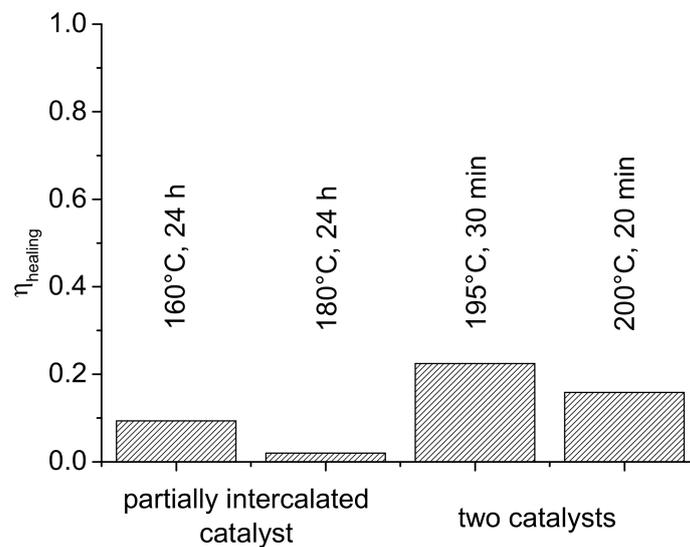
### 3.3.2. Healing Efficiency of F1\_F1MMT System

The healing efficiency of the material was then calculated according to Equations (1) and (2) from the data reported in Table 5. Results reported in Figure 8 for  $\eta_{healing,\epsilon}$ , indicate that the healing treatment at 180 °C made it possible to obtain the highest efficiency in terms of deformation at break, despite the significant increase of the modulus, as highlighted by the very low value for  $\eta_{healing,E}$ . In contrast, healing at 160 °C made it possible to obtain a lower value of  $\eta_{healing,\epsilon}$ , however still retaining a sufficiently high value of  $\eta_{healing,E}$ .



**Figure 8.** Healing efficiency at different healing temperatures for nanofilled toughened PBT.

The total healing efficiency, as defined in Equation (3), is finally reported in Figure 9, for the two-catalyst system and the partially intercalated system at different healing conditions. The results of Figure 9 highlight that, in general, a long healing treatment or higher healing temperatures involve a significant reduction of the efficiency; this is mainly due to the modulus increase which in turn results from lamellar thickening or recrystallization effects.



**Figure 9.** Total healing efficiency at different healing temperatures for nanofilled toughened PBT.

#### 4. Conclusions

In this work, the potential development of an innovative self-healing nanocomposite, based on a poly butylene-terephthalate (PBT) matrix, was studied. The material realized is characterized by a partial polymerization of CBT, therefore it is composed of cyclic-butylene terephthalate (CBT) and poly butylene-terephthalate, PBT, derived from the Ring Opening Polymerization (ROP) of CBT. In order to reduce the brittleness of the material, a thermoplastic epoxy resin was added to the system. The material was able to recover its damage through the filling of the crack with molten residual CBT and its subsequent conversion to PBT.

The partially polymerized system was obtained in two ways: first, two catalysts with different activation temperatures were used, then the faster catalyst was intercalated inside MMT galleries. In both cases, as confirmed by rheological analyses, two steps of reaction were achieved: the first one, due to the faster catalyst, which was activated at lower temperature, and the second one due to the slower catalyst, or the intercalated one in case of nanocomposite, which was activated at higher temperatures; moreover, the second step of reaction occurred at temperatures always lower than melting of PBT, thus retaining shape stability. The CBT/PBT mixture was obtained through the first step of the reaction, whereas healing was obtained through the second step of the reaction.

The presence of the cracks due to damage was simulated by inducing a well-defined notch geometry in the PBT samples. The second thermal treatment, aimed at restoring the load-bearing capability of the material, allowed an increase in the elongation at break to values which were comparable to the initial properties of the material before notching. In addition, the recovery of the elongation to break to the initial value was higher for healing treatments performed at higher temperatures. By properly tailoring the healing temperature, partial conversion of CBT to PBT can be exploited to allow for repeated healing of the material. However, a significant increase of the flexural modulus of the material occurred with higher healing temperatures, which can be, in some cases, unacceptable. Therefore, estimation of a healing efficiency parameter made it possible to highlight that:

- A healing cycle at lower temperatures and times (195 °C for 30 min for F1\_F2 system and 160°C for 24 h for F1\_MMT system) allows for partial recovery of the elongation to break, still retaining a stiffness comparable to the initial stiffness of the material. This cycle is desirable when the stiffness of the material is of utmost relevance, and any variation must be avoided;
- A healing cycle at higher temperature and times (200 °C for 20 min for F1\_F2 system and 180°C for 24 h for F1\_MMT system) allows a complete recovery of the elongation at break, despite a significant increase of the modulus. This cycle is desirable when the stiffness of the material is of secondary relevance, and variations of the modulus are acceptable.

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