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Self-Healing Properties of Epoxy Resins with Poly( $\epsilon$ -caprolactone) Healing Agent

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Abstract:

Thermally induced healing through thermoplastic poly( $\epsilon$ -caprolactone) (PCL), dissolved in 12.5, 25, 37.5 and 50 wt.%, respectively, in amine cured epoxy resins (EPs) was studied on compact tension (CT) specimens. Aromatic (hydrogenated diglycidyl ether of bisphenol A-type) and aliphatic (glycerol-triglycidylether) EPs were cured with the same amine (Jeffamine D 230) to receive EPs with different glass transition temperatures ( $T_g$ ).  $T_g$  values of the parent EPs were lower ( $T_g = 32$  °C) and higher ( $T_g = 90$  °C), respectively, than the melt temperature ( $T_m \approx 60$  °C) of the PCL. The curing-induced phase separation morphology of PCL was studied by light microcopy. Additional information on the phase structure was deduced from dynamic mechanical analysis (DMA). Blending with PCL reduced the  $T_g$  of the corresponding EPs. Fully broken CT specimens were repeatedly healed at 80 °C which was close to or higher than the actual  $T_g$  of the EP/PCL blend. It was found that the transition of PCL from disperse to continuous phase depends not only on the PCL amount but also on the EP type and its curing. EP/PCL systems with semi interpenetrating network structure (bi-continuous) exhibited markedly higher healing efficiencies compared to those in which PCL was present as disperse phase. The healing efficiency depended also on the temperature difference between the healing temperature and  $T_g$  of the EP with respect to  $T_m$  of PCL. When  $T_g > T_m$  then the related difference should be kept small while for  $T_g < T_m$  the temperature difference should be large to support healing. Accordingly, the segmental mobility within the crosslinked EP network is a key parameter for thermal mending, too.

Key words: epoxy (EP), polycaprolactone (PCL), self-healing, healing efficiency

## 1. INTRODUCTION

Mending, self-healing of polymer and related composites were always on the top of the wish list of researchers. Many concepts have been introduced for the healing of bulk polymers and their feasibility checked (1). The related approaches are differently classified. Classifying usually considers whether or not the healing requires an external stimulus. When no external stimulus is required then mending is termed as to autonomic, whereas its triggering with additional treatment (usually heat) is called to intrinsic. Note that in both cases the healing agents are available in the bulk material though in very different forms. Healing agents may be in reservoirs (capsules, capillaries) which break up upon external mechanical damage thereby initiating the healing reaction. When a catalyst is required, then it may be incorporated in the matrix polymer, available in one of the healing components in non-active or latent form, and the like. The chemical build-up of the healing agent may markedly differ from that of the matrix. Recent achievements on the healing with bulk materials are already transferred to the interphase of polymer composites, as reviewed recently (2).

Unlike thermosets, thermoplastics can be healed by molecular re-entanglement processes. Re-entanglements across the (broken) surfaces of thermoplastics are typically triggered by heat. The temperature, at least locally, should be higher than the glass ( $T_g$ ) or melting temperature ( $T_m$ ) depending whether the actual polymer is of amorphous or semicrystalline nature. This is also the basic principle of thermoplastics welding. Healing by re-entanglement in amorphous polymers was already performed in the 1980s, pioneered by the group of Kausch (3-4). Interestingly, already at this time fracture mechanical treatise was used to quantify the healing efficiency, which remained the dominant tool until now (5).

Both amorphous and semicrystalline thermoplastics are often used for the toughening of thermosetting resins. Their use started when it was recognized that the first generation tougheners, namely liquid functional rubbers, prominently reduce the  $T_g$  and stiffness of the corresponding thermosets, especially those of the epoxy resins (EP). Nonetheless, the development and working principle of liquid rubber and thermoplastics as toughening modifiers of EP are essentially the same. Both of them are soluble initially and undergo a reaction- (curing) induced phase separation. The resulting morphology may be very different. Considering just the amount of the modifier the morphology is varying between different disperse and continuous structures. It is the right place to mention that a co-continuous morphology composed of thermoplastic and thermoset phases, is termed to as semi interpenetrating network (semi IPN). Many different thermoplastics have been tried as potential tougheners in EP (6). The preferred morphology was micron-scale dispersion of the thermoplastic phase in the EP matrix. This is usually achieved with a thermoplastic content of less than 15 wt.%. In this case, the thermoplastic particle act as stress concentrators, induce cavitation/debonding (depending on the interfacial adhesion) which are supporting the shear deformation of the EP which is the major energy absorption mechanism.

It is intuitive that this thermoplastic phase, in whatever morphology present, may work for healing. One would expect that a semi IPN structure results in a better healing than a dispersed morphology. One would also surmise that such a thermoplastic should be selected as modifier the  $T_g$  or  $T_m$  of which is below that of the  $T_g$  of the EP. This requirement can be easily met by poly( $\epsilon$ -caprolactone) (PCL) having a melting temperature of about 60 °C (7). Moreover, PCL is a polyester that should have good solubility in EP. It is available commercially in different molecular weights which is a further tool to control its dissolution in EP. In fact, PCL has been tried as toughening agent in EPs from the 2000s (8). Attempts

were also made to control its reaction-induced phase separation through further additives, such as organoclay (9). Thermal mending of EP via thermoplastic PCL was first explored by Luo et al. [10]. The cited authors modified an aromatic amine cured diglycidyl ether of bisphenol A-based EP (DGEBA) with PCL, added up to 34.9 wt.%. They revealed that the morphology above 15.5 wt.% PCL content consisted of a continuous PCL phase in which interconnected EP spheres are dispersed. As a consequence, the PCL phase may serve for thermal mending of this high  $T_g$  EP that was proven, in fact.

It was recently reported that EP/PCL systems may show promising shape memory behavior, especially when a semi IPN structure is present. The latter was set either by infiltration of an electrospun PCL nanoweb with EP or by dissolving PCL prior to crosslinking the corresponding EP (11 and references therein). In this work it was also claimed that an EP/PCL system with semi IPN structure may exhibit the combination of shape memory and self-healing. This concept, i.e. dual functionalization through semi IPN structuring, has to be credited to Karger-Kocsis based on the following citation: "By creating a semi-interpenetrating network composed of a crosslinked thermoset and a thermoplastic, Karger-Kocsis considered that both shape memory and self healing functions can be combined" (12).", that appeared in 2008. This dual function, i.e. combination of shape memory and self-healing, was proved by the group of Leng on the examples of EP/PCL blends (with up to 23.3. wt.% PCL content) (13) and with EP infiltrated electrospun PCL web (14 wt.%) specimens (14) very recently. It has to be underlined that in all works, performed on studying the self-healing of EP/PCL systems (10, 13-14), the specimens were always only partly broken.

This work was devoted to study the self-healing of EP/PCL systems as a function of the PCL content (varied between 0 and 50 wt.%) and EP type. Two EPs with different  $T_g$  values (lying below and beyond the  $T_m$  of PCL) were involved in this study in order to get information on curing-induced morphology changes and their effects on thermal mending. Healing efficiency was tested on fully broken compact tension (CT) specimens. Their halves were slightly pressed against each other at the temperature of 80 °C, i.e. above the  $T_m$  of PCL. This temperature was close to or well beyond the  $T_g$  of the actual EP/PCL blends.

## 2. EXPERIMENTAL

### 2.1. Materials

PCL granule (grade CAPA 6400) having an average molecular weight of 37000 g/mol and  $T_m$  of 59 °C ) was supplied by Perstorp (Malmö, Sweden). An aromatic (IpoX ER 1010, hydrogenated DGEBA version, epoxy equivalent: 180-196 g/equ.) and aliphatic EP (MR 3012, glycerol-triglycidylether, epoxy equivalent: 134-154 g/equ.) resin (both from IpoX Chemicals, Budapest, Hungary) and Jeffamine D230 type polyetheramine (amine equivalent: 60 g/equ.) hardener (Huntsman, Bergkamen, Germany) were chosen in this work. Their curing in stoichiometric amounts (viz. resin/hardener in 100/32 and 100/40 parts for the aromatic and aliphatic EP, respectively) yielded EPs with  $T_g$  values (read at the maximum of the mechanical loss peak,  $\tan\delta$ ) of 90 °C and 32 °C, respectively (see later). These EPs are further denoted as to EP(H) and EP(L), respectively, considering whether the related  $T_g$  is higher (H) or lower (L) than  $T_m$  of PCL.

### 2.2. Specimen preparation

The required amount of PCL was added to the EP resin in a polypropylene beaker placed in water bath. The temperature of the water batch was set for 85 °C and the PCL was dissolved in the EP under

mechanical stirring for 30 minutes. The blend was cooled then to 65 °C where the stoichiometric amount of the amine hardener was introduced. After stirring and degassing, the final composition was poured into aluminum or polytetrafluoro ethylene molds to produce plaques of 1 and 4 mm thicknesses, respectively. The curing cycle was: 24 hours (h) at room temperature and 2 h at 80 °C. The PCL contents of the cured EPs were 0, 12.5, 25, 37.5 and 50 wt.%, respectively. Specimens for dynamic mechanical analysis (DMA) and compact tension (CT) specimens for healing were cut from the 1 and 4 mm sheets, respectively.

### 2.3. Morphology detection

Phase separation of PCL in the cured EP was inspected in a light microscope (LM, Olympus BX51M) using polished samples. EP/PCL samples were embedded in an EP resin, and after curing of the latter subjected to mechanical polishing with emery papers (Struers LaboPol5). LM pictures were taken from the polished surfaces in reflection mode.

### 2.4. Testing

DMA tests were conducted on 1 mm thick rectangular specimens (clamping length 12 mm) in a DMA Q800 device (TA Instruments) in tension mode. The heating rate, oscillation frequency and oscillation amplitude were 3 °C/min, 10 Hz and 0.05%, respectively. The DMA curves (storage modulus and  $\tan\delta$  as a function of temperature) served to determine the  $T_g$  and  $T_m$  values of the EP and PCL.

For crack healing CT specimens, cut from the 4 mm thick sheets, were used. Their dimension is depicted in Figure 1.

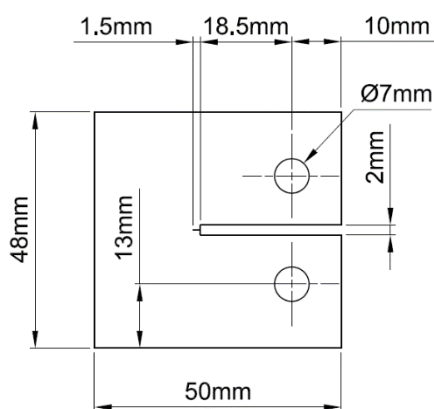


Figure 1. Dimension of the CT specimens used. Note: sawn notch was sharpened by a fresh razor blade in 1.5 mm depth

CT specimens were fully broken under tensile load (mode I crack tip opening according to fracture mechanical terms) at room temperature at a crosshead speed of 5 mm/min in a universal testing machine (Zwick Z020) equipped with a 1 kN load cell. The force-load line deformation curves (F-x) were registered. Healing was triggered by fitting the broken CT halves and holding them in position under slight pressure (ca. 400 kPa) via a home-made screw device prior to place them in a thermostatic oven at  $T=80$  °C for 30 min. After healing the CT specimens were fractured again thereby monitoring the F-x curves. This procedure was repeated, and thus each CT specimens was subjected to two healing cycles.

The healing efficiency, disclosed later, was determined in three parallel tests for each EP/PCL formulation.

### 3. RESULTS AND DISCUSSION

#### 3.1. Morphology

Figure 2 shows LM pictures taken from the EP(H) systems containing 12.5 and 50 wt.% PCL, respectively. One can see, that PCL appeared as dispersed phase at 12.5 wt.% PCL (cf. Figure 2a). By contrast, a quasi bi-continuous (semi IPN like) structure appeared at 50 wt.% PCL content (cf. Figure 2b). The nodular structure in Figure 2b may be similar to what was claimed by Luo et al. (10), viz. interconnected EP spheres dispersed in a continuous PCL matrix. Accordingly, at 50 wt.% PCL content phase inversion happened.

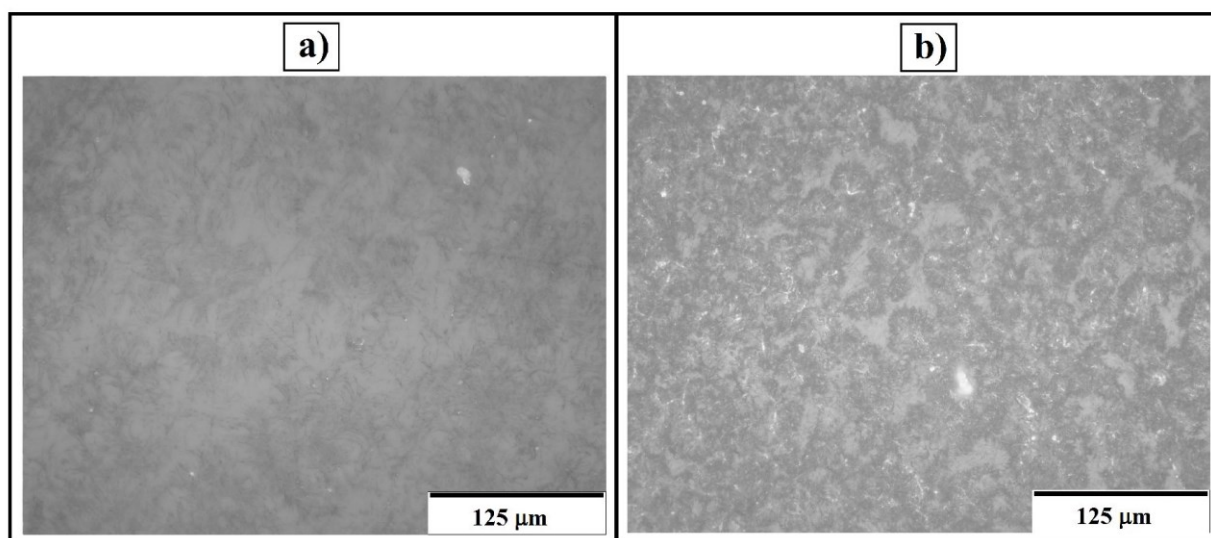


Figure 2. LM pictures taken from the polished surfaces of EP(H)/PCL systems containing 12.5 wt% (a) and 50 wt.% (b) PCL

The morphology of EP(L)/PCL is completely different from the EP(H)/PCL counterpart. PCL appears as discontinuous phase in large domains without any regularity when the PCL content is 12.5 wt.% (cf. Figure 3a). Thus, the PCL is still in form of disperse phase in EP(L)/PCL-12.5wt.% blend. The first indication for the onset of a semi IPN structure can be recognized at PCL amount of 25 wt.% (cf. Figure 3b).

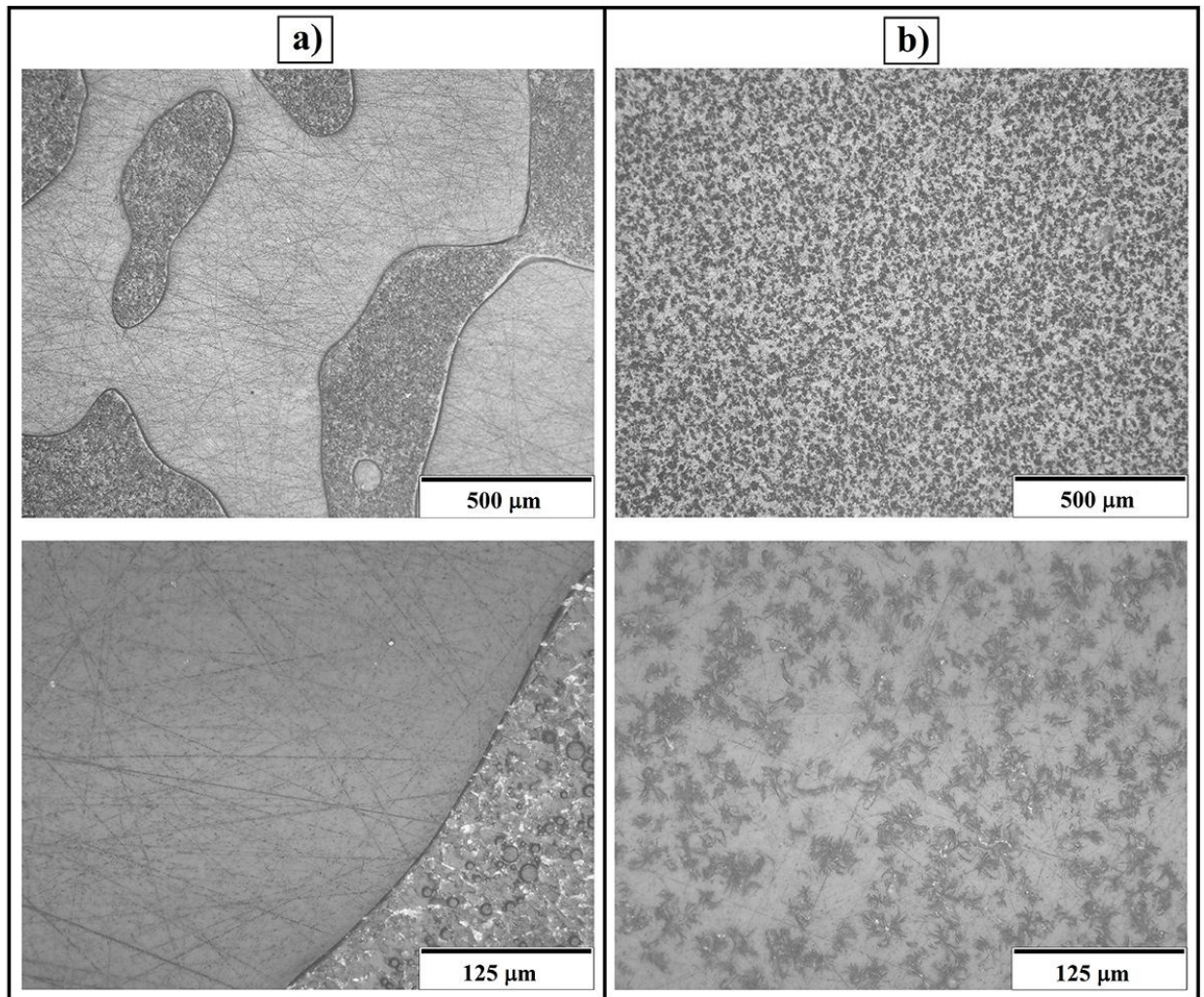


Figure 3. LM pictures taken from the polished surfaces of EP(L)/PCL systems containing 12.5 wt% (a) and 25 wt.% (b) PCL at different magnifications.

This confirms the reaction-induced phase separation, and thus the resulting morphology of the same thermoplastic in the cured resins strongly depends also on the molecular structures of the EP and hardener, their reactivity, and cure cycle used. Accordingly, no general rule of thumb can be deduced on the morphology development of a thermoplastic modifier in EP as a function of its amount.

### 3.2. DMA

The storage modulus ( $E'$ ) and  $\tan\delta$  as a function of temperature ( $T$ ) are depicted for the EP(H)/PCL systems in Figure 4a and b, respectively

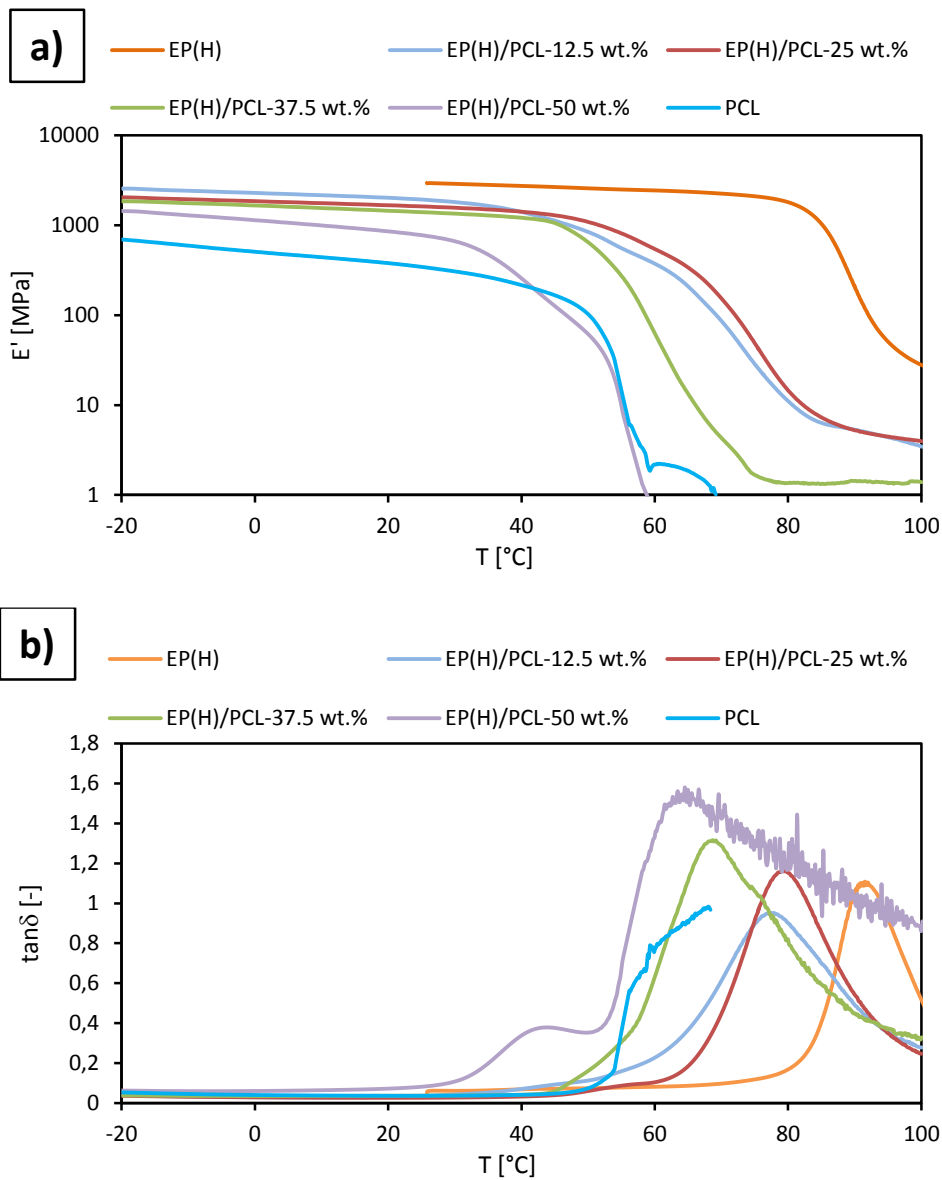


Figure 4.  $E'$  vs.  $T$  (a) and  $\tan\delta$  vs.  $T$  curves (b) for the EP(H)/PCL systems

Figure 4a shows that the glassy moduli of the EP(H)/PCL blends decrease with increasing PCL content. This is due to the fact that PCL is “softer” than EP(H), i.e. its glassy modulus is below that of EP(H) – see Figure 4a. One can also see that  $E'$  starts to drop at lower temperatures with increasing PCL amount. This drop, very close to the  $T_m$  of PCL, is most pronounced for EP(H)/PCL-50. In this system no rubbery plateau was observed up to  $E' = 1$  MPa meaning that the phase inversion was completed. This finding is in harmony with the information deduced from the LM microphotograph in Figure 2b. For all other EP(H)/PCL formulations the EP-related rubbery plateau is well resolved in Figure 4a. This confirms the presence of a continuous EP phase. The  $\tan\delta$  increases with increasing PCL content, as expected (cf. Figure 4b). Note that segmental motion is highly enhanced due to the fact that PCL is in the molten stage and its incorporation reduced the apparent crosslink density (that is well reflected by the decreasing rubbery plateau moduli in Figure 4a). At the same time, this peak was increasingly broadening and shifting toward lower temperatures with increasing PCL. The single but broad  $T_g$  peak indicates good compatibility between the EP(H) and PCL. Its shift toward lower temperature can be assigned to a reduction in the apparent crosslink density or increase in the free volume (9). Similar results were reported by other EP/PCL systems, too (9,14). The presence of PCL becomes, however,

clearly detectable only for EP(H)/PCL-50 where an additional peak at  $T \approx 45$  °C appears. The  $T_g$  values of our blends are tabulated in Table 1. It is noteworthy that PCL incorporation in EP does not necessarily reduce the  $T_g$ . Luo et al. (10), working with a different EP system (especially the hardener differed from ours) did not observe any change in the  $T_g$  of the EP/PCL blends.

The DMA response of the EP(L)/PCL systems are displayed in Figure 5.

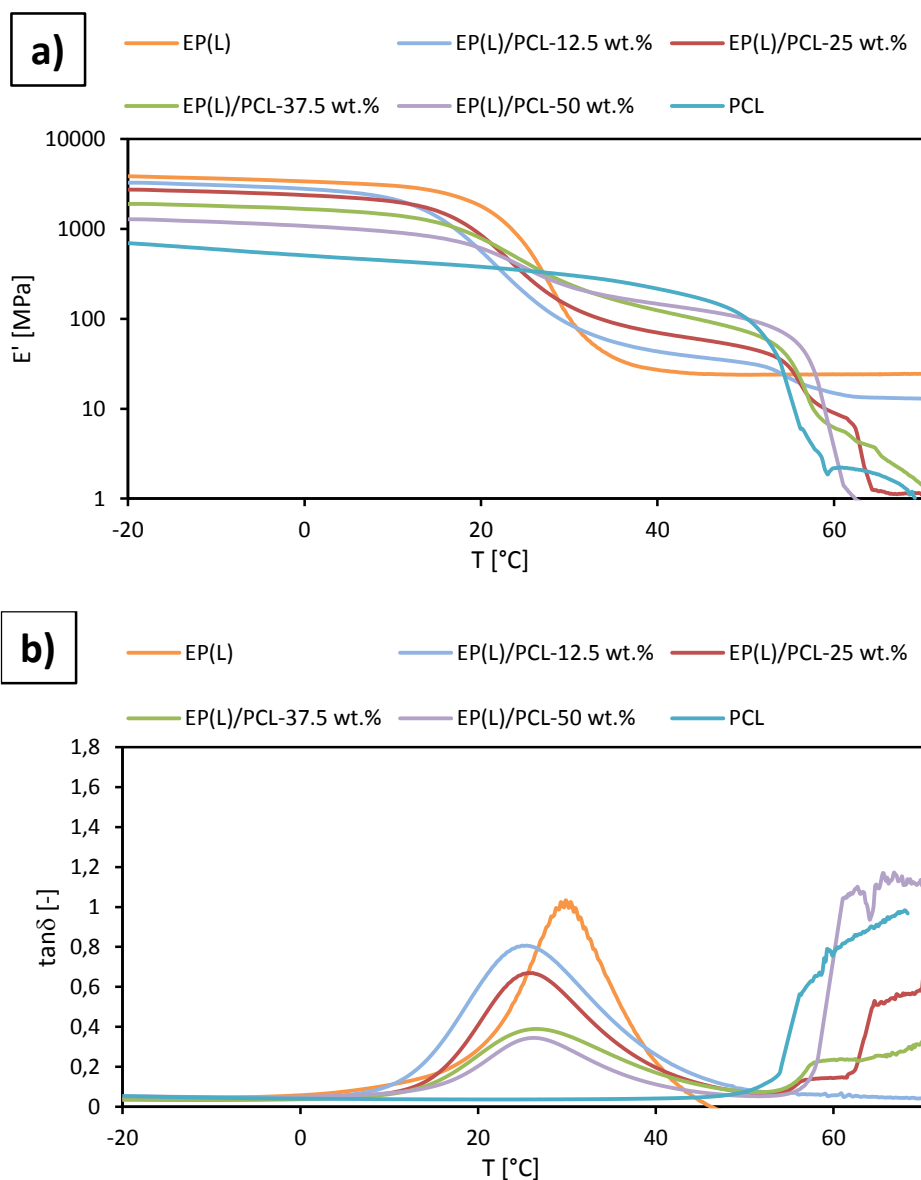


Figure 5.  $E'$  vs.  $T$  (a) and  $\tan\delta$  vs.  $T$  curves (b) for the EP(L)/PCL systems

By contrast to EP(H)/PCL in case of EP(L)/PCL we get a clear hint for the presence of semi IPN structure for all EP(L)/PCL combinations. Note that  $T_g$  of EP(L) is at ambient temperature based on the  $T_g$  step in  $E'$  vs.  $T$  (Figure 5a) and peak position of  $\tan\delta$  (Figure 5b, Table 1). Above the  $T_g$  a declining plateau range can be seen for the EP(L)/PCL blends in Figure 5a. Note that in this range the PCL is the stiffer phase than the EP – see Figure 5a. The slightly declining plateau in the  $E'$  vs.  $T$  traces above the  $T_g$  of EP confirms the presence of PCL as continuous phase. The  $E'$  decrease in this range is linked with the thermoplastic



feature of PCL which melts at  $T \approx 60$  °C. An EP-related rubbery plateau at  $T > 60$  °C can be found only for EP(L)/PCL-12.5 wt.%. This finding is in line with the related LM pictures in Figure 3a. In this blend the PCL is present in a large band-like structure but still forms the disperse phase. Attention should be paid on some peculiarities in the  $\tan\delta$  vs. T traces in Figure 5b. The  $T_g$  ( $\alpha$ -relaxation) peak is not splitting but broadening with increasing PCL content. This hints for good compatibility between the components again. Unlike to our blend system, the PCL presence may be well detectable in the  $\alpha$ -relaxation transition when different EP/hardener formulations are used (13). The  $T_g$  shift (cf. Table 1) toward lower temperatures for the EP(L)/PCL series is accompanied with an unexpected feature: the peak position of the  $T_g$  transition did not change but its height was monotonically reduced with increasing PCL contents. The latter suggests a clear reinforcing effect of PCL which, unlike to the EP(H)/PCL series, is solid at this temperature. Considering the  $T_g$  values of the EP(L)/PCL series no further change after the initial one (owing to the blending with 12.5 wt.% PCL) could be noticed with increasing PCL content. It has to be born in mind that PCL is very sensitive to cold crystallization due to the fact that its  $T_g$  is at about -50 °C and its  $T_m$  rather close to ambient temperatures (15). Thus, PCL may undergo a complex crystallization process after its curing-induced phase separation. This is well reflected by the peculiar runs of the  $E'$  vs. T and  $\tan\delta$  vs. T traces about  $T > 50$  °C for the EP(L)/PCL blends (cf. Figures 5a and b). To quantify the PCL melting the related  $T_m$  was read at the temperature where initially a steep increment in the  $\tan\delta$  vs. T trace occurred (cf. Table 1.)

Table 1.  $T_g$  and  $T_m$  data for the EP/PCL blends and for their PCL phase, respectively. Notes:  $T_g$  is given as the peak temperature of the  $\alpha$ -relaxation transition.  $T_m$  was read at the temperature linked to the steep increment, reflecting melting, in the  $\tan\delta$  vs. T trace. – not applicable

System	PCL content (wt.%)	Temperature (°C)	
		$T_g$	$T_m$ (PCL)
EP(H)/PCL	0	90	-
	12.5	77	-
	25	80	-
	37.5	69	-
	50	64	-
EP(L)/PCL	0	32	-
	12.5	26	-
	25	27	55
	37.5	28	55
	50	28	57
PCL	100	-	53

This is here the right place to underline that all EP(L)/PCL systems should show triple shape memory behavior (7,11), because  $T_m$  of PCL and  $T_g$  of EP(L), differing from one another markedly, may work as switch temperatures for programming of two temporary shapes. For the permanent shape the intermingled semi IPN structure is responsible (7). This triple shape memory function has been demonstrated in our former paper (11).

### 3.3. Self-healing

The F-x curves of the EP(H)/PCL systems indicated brittle fracture even when the PCL content was 50 wt.% - cf. Figure 6. This is the usual prerequisite of adopting the linear elastic fracture mechanical

treatise. Considering  $F_{max}$  the fracture toughness and fracture energy could be easily computed. This evaluation was not followed because the EP(L)/PCL systems exhibited a more ductile behavior as shown on the example of EP(L)/PCL with 37.5 wt.% PCL (cf. Figure 7).

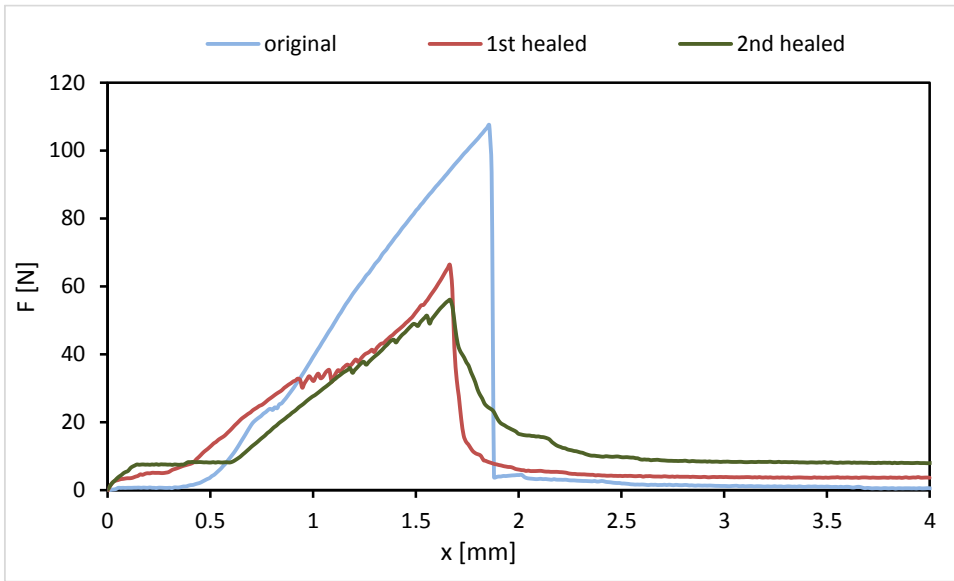


Figure 6. Representative F-x traces registered for a CT-specimen of EP(H)/PCL-50 in repeated healing steps

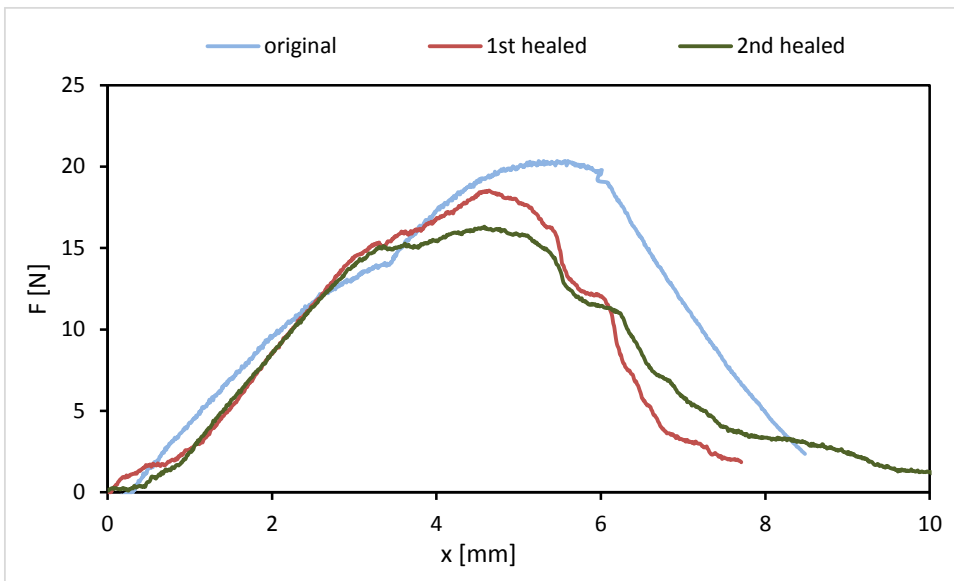


Figure 7. Representative F-x traces registered for a CT-specimen of EP(L)/PCL-37.5 in repeated healing steps

It is worth of mentioning that the overall ductility of the EP(L)/PCL blends decreased with increasing amount of PCL when considering the post-maximum range in the related F-x curves.

The healing efficiency was calculated by:

$$\text{healing efficiency (\%)} = \frac{F_{max,healed(i)}}{F_{max,original}} \quad (1)$$

where  $F_{\max, \text{healed}(i)}$  and  $F_{\max, \text{original}}$  denote the maximum load after the  $i$ -th (in this case up to two) healing and the maximum load registered on the virgin specimen, respectively

To consider the force ratio instead of computing the fracture toughness is widely used in the literature (10, 13). Results of the healing efficiency are tabulated in Table 2.

Table 2. Healing efficiency data for the EP/PCL systems studied. Note: average from three parallel tests. Designation: - not measurable

System	PCL content (wt.%)	Healing efficiency (%)	
		1st	2nd
EP(H)/PCL	0	-	-
	12.5	2±1	-
	25	11±1	-
	37.5	45±4	38±3
	50	62±15	52±5
EP(L)/PCL	0	-	-
	12.5	2±1	-
	25	80±4	52±5
	37.5	77±5	61±3
	50	82±4	67±3

Data in Table 2 suggest that the presence of a disperse structure, irrespective of its actual morphology, yields low thermal mending. This is even the case when a band-like quasi continuity may be present, as surmised for EP(L)/PCL-12.5. On the contrary, the formation of a semi IPN like structure prominently improves the healing efficiency. Moreover, the healing is strongly influenced by the network structure of the EP itself. Recall that healing was performed at a temperature (80 °C) which was at about the  $T_g$  of EP(H) but markedly above the  $T_g$  of EP(L) series – cf. Table 1. Accordingly, the temperature difference between the healing and the  $T_g$  of the actual EP/PCL blend may be a key factor. The  $T_g$  is controlled by network characteristics, including the molecular buildup of the EP and hardener themselves. Recall that in this study an aromatic (EP(H)) and an aliphatic (EP(L)) EPs were used with the same hardener to vary the  $T_g$ . On the other hand, healing is possible also when it is triggered above  $T_m$  of the PCL but below the  $T_g$  of the corresponding EP (13). Also in this case the actual temperature difference between the healing temperature (above  $T_m$  of PCL) and  $T_g$  should affect the thermal mending in large extent, which was found, in fact (13). Nevertheless, further works should address this issue. Even more important is however to figure out how the phase separation process can be controlled in order to get the most suited morphology for healing thereby not sacrificing the basic properties of the initial EP.

Finally, let us compare the present healing efficiency values with those published in the literature. The related data varied between 20 and 80 % for EP/PCL-23.3 wt.% (13). This scatter was a function of the temperature difference between  $T_g$  (=137 °C) and  $T_{\text{healing}}$  (84 – 144 °C): the smaller this difference the higher was the healing efficiency. Recall that this finding supports our results and the former claim on how to perform healing. Researchers using other thermoplastics than PCL, such as phenoxy polymers and poly(bisphenol A-co-epichlorohydrin), reported healing efficiency values in the range of 50-70% (16-17), which all are similar to our present ones.

#### 4. CONCLUSION

This work devoted to study the thermally induced healing via re-entanglement of molecules of the thermoplastic PCL phase formed by phase separation in EP resins upon their curing. PCL was dissolved in various amounts in EPs initially exhibiting higher (EP(H)) and lower  $T_g$  values (EP(L)) than the  $T_m$  of PCL. Healing was triggered at 80 °C which was at about to far beyond the above transition temperatures. Note that the  $T_g$  of the EPs varied with the EP/PCL compositions. Based on this study the following conclusions can be drawn:

- Unlike a disperse structure, the development of a bicontinuous, semi IPN like structure in EP/PCL strongly contributes to the thermally-induced healing, also when performed repeatedly. Further investigations are needed to clarify how the curing induced phase separation of PCL can be controlled in epoxy resins in order to get the most suited morphology for healing.
- The difference between the temperature of healing and  $T_g$  of the EP influences the healing efficiency whereby the actual position of  $T_m$  of PCL should also be considered. When  $T_g > T_m$  then the related difference should be small while for  $T_g < T_m$  the temperature difference should be large to get the best healing efficiency. This finding implies that the network characteristics of the EP are of key parameters also from the viewpoint of thermal mendability.
- Though shape memory assisted self-healing (11, 13-14) was not proven in this case, this behavior should be an inherent feature of EP(L)/PCL and easily checked even using CT specimens, however, only when partly broken.

#### Acknowledgements:

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