

Mechanical Properties of Epoxy Resin Modified with Polycarbonate and Reactive Polybutadiene

M. Bakar, J. Kobusińska, J. Szczerba

Plastics Department, Radom University of Technology, Chrobrego 27, 26-600 Radom, Poland

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ABSTRACT: Epoxy resin Epidian 5 cured with triethylene tetramine was modified with hydroxyl-terminated polybutadiene (PB) and polycarbonate (PC). Compositions with different amount of modifiers were obtained and tested for their impact strength, flexural strength, as well as resistance to crack propagation. The latter was assessed by evaluating the critical stress intensity factor under three-point bending mode using single-edge notched specimens. Scanning electron microscopy was used to analyze the fractured sample surfaces. The obtained results revealed that the mechanical properties of epoxy resin were improved due to the formation of heterogeneous phase with rubber particles, which arrest the propagation

of cracks. Moreover, synergism effect was observed with the hybrid composition containing 10% PC and 2.5% of reactive PB. The impact strength was higher by $\sim 15\%$ than the sum of impact strength of compositions containing only one modifier. Another hybrid composition with 2.5% PB and 2.5% PC also exhibited synergism effect with the flexural strain at break, the energy at break under flexure, as well as the brittle fracture energy estimated from the critical stress intensity factor measurements. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2892–2897, 2007

Key words: epoxy resin; polybutadiene; polycarbonate; fracture toughness; impact strength; flexural strength

INTRODUCTION

Epoxy resins are widely used as matrices for high performance composite materials, surface coatings, and adhesive joints due to their excellent resistance to solvents, processing characteristics, adhesion to metals and other materials. However, because of their highly crosslinked density, these materials exhibit low impact strength, poor resistance to crack propagation, and small elongation at break, i.e., they are inherently brittle. The brittleness has significantly limited their widespread fields of applications.¹

In the last few decades, more emphasis has been focused on the improvement of the fracture toughness and elasticity of epoxy resins. Approaches to improve epoxy resins toughness included the incorporation of ductile thermoplastics such as polysulfones,² polyethersulfones,³ polyetherimide,⁴ polycarbonate (PC),⁵ polyimides.⁶ Engineering thermoplastics were used to overcome the drawback of the loss of thermal properties induced by the incorporation of reactive liquid rubbers such as butadiene–acrylonitrile copolymers terminated with carboxyl, amine, hydroxyl, or epoxy groups.^{7–14}

Abbate et al. modified a highly crosslinked thermosetting epoxy resin with bisphenol A PC by means of

a reactive blending process. The authors used FTIR spectroscopy to analyze the curing process of epoxy resin with methyl anhydride with a tertiary amine as accelerator and confirmed that PC as modifier has no effect on the overall curing process of epoxy resin.¹⁵ In an independent work, Li et al. investigated the reaction mechanism of epoxy blend cured with an aliphatic amine and modified with PC.¹⁶ They used several hot melt and dissolution methods to prepare the epoxy/PC blends and analyzed the differences between the obtained products in terms of content of crosslinker and chain ends. However, it has to be mentioned that the effect of PC addition on the mechanical properties of epoxy resin were not investigated in these investigations.

The critical stress intensity factor, the critical strain energy release rate, and the glass transition temperatures were evaluated by Chen et al. for diglycidyl ether of bisphenol A (Epikote 828) cured with diethylenetriamine and modified with different amounts of PC.¹⁷ Their mechanical properties associated with structure morphology analysis showed that the obtained blends were miscible and the two fracture toughness parameters increased upon the addition of PC.

Hydroxyl-terminated polybutadiene (PB) rubber containing epoxy groups was used by Bussi and Ishida to investigate the cure process and the mechanical properties of epoxy resin.¹⁸ The results showed that the critical stress intensity factor value was enhanced only upon prereaction of the rubber with an excess of diepoxide monomers due to the incor-

Correspondence to: M. Bakar (mbakar@wp.pl).

poration of the rubber into the epoxy network. However, the absence of the rubber prereaction conducted to a faster gelation process of the epoxy resin forming thus only weak chemical bonding between the rubber particles and the polymer matrix.

More recently, Ozturk et al. used hydroxyl-terminated PB (HTPB) to investigate the mechanical and thermal properties of a brittle epoxy resin.¹⁹ They found that both tensile and impact strength were enhanced with 1% of HTPB and 2% of silane coupling agent. The strain at break was also increased due to the decrease of crosslinking density. Using scanning micrographs, they attributed the mechanical properties improvement to rubber deformations.

On the other hand, block copolymer of PB obtained from isocyanate-terminated PB and carboxyl-terminated PB was used by Barcia et al. to modify diglycidyl ether of bisphenol A.²⁰ The differences in the morphological features were attributed to the differences in gelation times as well as to the structure of block copolymers. Moreover, it was noticed that the best flexural and tensile properties improvement was obtained with the carboxyl-terminated PB-based block copolymer, whereas the block copolymer based on isocyanate-terminated PB exhibited higher flexibility.

The purpose of the present study was to modify epoxy resin Epidian 5 using PC and PB, terminated with epoxy and hydroxyl groups, aiming at improving its fracture toughness and elasticity.

EXPERIMENTAL

Materials

The following ingredients were used in the present work:

Diglycidyl ether of bisphenol A: Epidian 5 $M_w = 381$ g/mol from Sarzyna, Poland;

Curing agent: triethylene tetramine (trade name Z1) from Sarzyna, Poland;

Polycarbonate: Lexan from General Electric, Poland;
Polybutadiene poly bd 605E from Sartomer Company, France, with a viscosity of $\sim 16,000$ mPa s at 30°C.

Preparation of the formulations

Polycarbonate (PC) was first completely dissolved in dichloromethane to obtain a 15% solution, then added to epoxy resin. The formulations containing different amounts of PC were mixed at a temperature of 40°C for 20 min, then degassed under vacuum at 110°C for 2–3 h, finally cooled slowly to room temperature. The curing agent was added (in the proportions of 12 parts for 100 parts of resin) and mixing was carried out for an additional

10 min. The formulations were then poured into teflon-coated aluminum plates with required geometries. The curing of the obtained compositions was achieved at room temperature for 24 h, followed by postcuring for 3 h at 120°C. Compositions containing 0–30 phr of PC were prepared and tested for their mechanical and thermal properties.

Different amounts of polybutadiene (PB) were added to epoxy resin and mixed at a temperature of 40°C for 20 min. The formulations were then allowed to cool to room temperature prior to the incorporation of the curing agent as above. The mixing was continued for an additional 10 min before pouring the formulations into the plates. The curing and postcuring were realized as for PC.

Hybrid composites (i.e., containing both PC and reactive rubber) were obtained based on the best mechanical properties of composites with one modifier. They were prepared by first adding a specific amount of PC to the epoxy resin and mixing in a water bath at 40°C for 10 min using an electric stirrer. The mixture was then degassed in a vacuum oven at 110°C until a clear mixture is obtained. When the mixture has cooled to about 40°C, PB was added and mechanical mixing continued for an additional 10 min. Then the hardener was gently incorporated to the mixture after its temperature has decreased to about 20°C. Curing and postcuring of the obtained composites were conducted as for composites containing one modifier.

Properties evaluation

Impact strength was measured according to Izod method on notched samples using Zwick 5012 impact tester using Polish norm PN-87/C-89,050.

The flexural strength, the strain at break, and the energy at break were estimated under three-point bending on samples having 8 cm in length, 1 cm in width, and 4 mm in thickness and with a distance between the spans of 6 cm. The tests were performed at room temperature using an Instron machine with a crosshead speed of 5 mm/min.

The critical stress intensity factor K_{IC} was estimated under three-point bending mode on samples having 1 mm of crack length and the following geometries 8 cm \times 1 cm \times 0.4 cm using ASTM-E 399 according to the following equation¹:

$$K_{IC} = \frac{3PL\sqrt{a}}{2tw^2} Y\left(\frac{a}{w}\right)$$

where P is the load at fracture (N); L is the distance between the spans (m); a is the crack length (m); w is the sample's width (m); t is the sample's thickness (m); and Y is the geometrical factor, dependent on the fracture mode and $\frac{a}{w}$, expressed as follows:

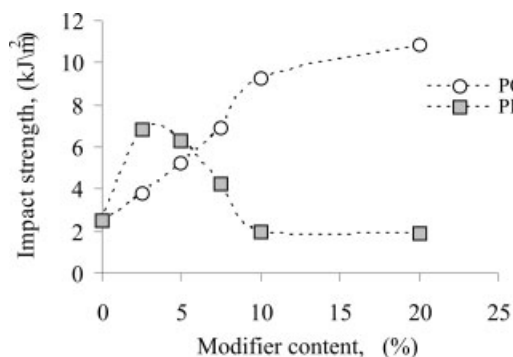


Figure 1 Impact strength as function of polybutadiene and polycarbonate content.

$$Y\left(\frac{a}{w}\right) = 1.93 - 3.07\left(\frac{a}{w}\right) + 14.53\left(\frac{a}{w}\right)^2 - 25.11\left(\frac{a}{w}\right)^3 + 25.80\left(\frac{a}{w}\right)^4$$

The brittle fracture energy was evaluated from the load–displacement curve during the crack propagation process and K_C estimation.

Five specimens were used for each data point.

Scanning electron microscopy was used to analyze the fracture surfaces and assess the toughening mechanism. The specimens obtained from the impact tests were prepared and examined using a Philips XEL30 Scanning Electron Microscope.

RESULTS AND DISCUSSION

Figure 1 represents the effect of PC and PB terminated with reactive groups on the impact strength (IS) of epoxy resin. It can be seen that IS increases, then decreases with increasing amount of PB. Maximum increase of about 175% in comparison with IS of cured nonmodified epoxy resin was obtained with 2.5% PB modified composition.

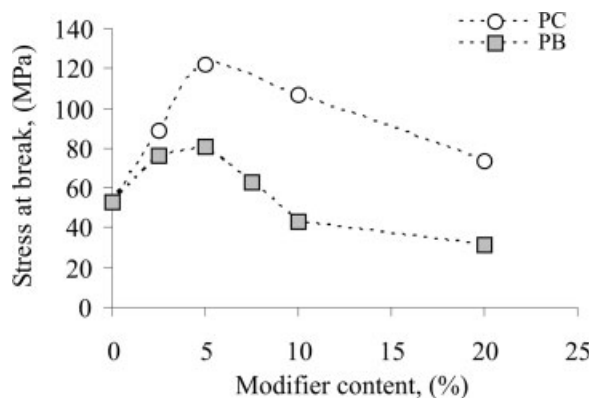


Figure 2 Effect of polybutadiene and polycarbonate on the flexural strength of epoxy-based compositions.

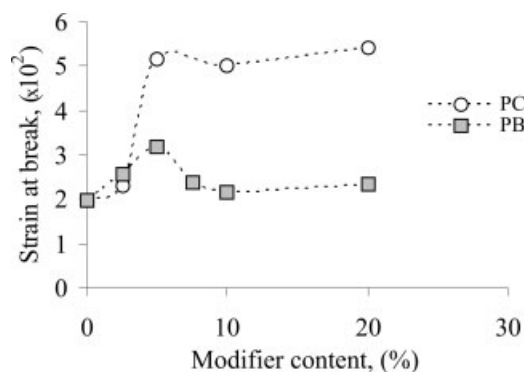


Figure 3 Effect of polybutadiene and polycarbonate on the strain at break under three-point bending.

The relatively lower impact strength improvement with reactive PB can be attributed to the longer gel time, leading most probably to lower crosslink density of the composition. With 2.5% PB, the gel time of the formulation has increased by more than 50%.

However, the addition of PC to epoxy resin resulted in a continuous increase of impact strength. We notice about four-fold increase when adding 10 or 20% of PC in relation to system resin–hardener. The improvement of impact strength can be directly related with the high IS of PC, which is generally attributed to its large β transition. It is well understood that a broad secondary transition is linearly proportional to the energy absorbed by the sample before its fracture.

The evolution of the stress at break estimated under three-point bending as function of modifier content is shown in Figure 2. It increases, then decreases as the modifier (PC or PB) content increases. Maximum tensile strength improvement is attained with 5% PC or 5% PB and it represents ~ 30 and 50% improvement respectively, in comparison with neat epoxy.

One can explain the increase of the flexural strength by the quite high strength of PC on one hand and the high elasticity of the rubber particles as well as their good adhesion with polymer matrix.

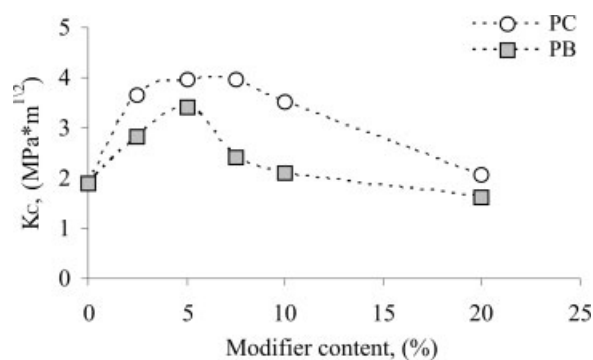


Figure 4 Effect of polybutadiene and polycarbonate on the critical stress intensity factor K_C .

TABLE I
Properties of Hybrid Compositions Containing 2.5% of Polybutadiene

Polycarbonate content (wt %)	Impact strength (kJ/m ²)	Flexural strength (MPa)	Flexural strain at break (10 ²)	Energy at break (kJ/m ²)	K_C (MPa m ^{1/2})	Energy of brittle fracture (kJ/m ²)
0/0 ^a	2.5 ± 0.2	53 ± 4	2.0 ± 0.1	3.5 ± 0.2	1.9 ± 0.1	4.3 ± 0.2
0	6.8 ± 0.4	76 ± 2	2.6 ± 0.2	6.2 ± 0.5	2.8 ± 0.2	4.8 ± 0.3
2.5	3.5 ± 0.3	64 ± 4	4.1 ± 0.2	12.5 ± 0.4	2.7 ± 0.3	5.8 ± 0.4
5	6.3 ± 0.3	63 ± 4	2.9 ± 0.1	9.2 ± 0.3	3.5 ± 0.3	7.4 ± 0.5
10	4.1 ± 0.2	66 ± 5	2.7 ± 0.3	6.7 ± 0.3	2.6 ± 0.2	4.3 ± 0.3

^a Composition with no modifier.

From Figure 3, one can notice that the addition of either PC or reactive PB leads to the improvement in strain at break.

With the addition of 5% of PB, the strain at break measured under three-point bending was maximally increased by 60% in relation to that of nonmodified epoxy resin. However, strain at break was further enhanced by 5% of PC (i.e., 160%). This can be attributed to the relatively high strain at break of PC, which is more than 100% at room temperature. Moreover, we can associate the composition strain at break improvement due to PB, also to the additional free volume provided by the modifier, which acts as plasticizer.²¹

The critical stress intensity factor K_C of epoxy resin as function of PC and PB content is represented in Figure 4. The resistance of epoxy-based compositions to crack propagation attained maximum values at 5% wt of either modifier. K_C was improved by ~ 80 and 100% respectively, for PB- and PC-based compositions. It has to be mentioned that all PC-modified compositions exhibited higher K_C values than the neat epoxy resin.

The improvement of K_C parameter of compositions with PB might be explained by the formation of a significant plastic zone around the propagating crack tip, which constitutes a source of additional energy absorption. The enhancement of crack propagation resistance in rubber-modified compositions can also be associated with the formation of a second phase in the system epoxy resin–modifier, which induces more energy absorption during the crack propagating process.²²

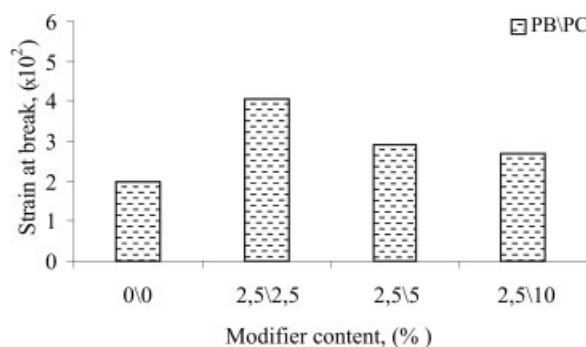


Figure 5 Effect of polycarbonate on the strain at break of epoxy composition modified with 2.5% of polybutadiene.

However, for epoxy compositions containing the thermoplastic modifier, K_C improvement can be explained by crack propagation arrest by the modifier particles, leading to the formation of more surfaces and thus the energy needed for surface formation is increased. The increase of K_C can also result from the enhanced compatibility between the polymer matrix and the modifier.

The effect of PC content on the properties of epoxy compositions containing 2.5% of reactive PB is shown in Table I. It shows that hybrid compositions containing 2.5% PB and 5% PC exhibit the highest impact strength, which is ~ 155% higher than that of cured epoxy with no modifier and is within experimental error equal to the sum of impact strength of compositions with only one modifier (i.e., composition with only 2.5% PB and composition with 5% PC).

The flexural strength under three-point bending, the energy at break as expressed by the area under the load–displacement curve, and the brittle fracture energy estimated from the load–displacement curve of the critical stress intensity factor measurements were also improved by the addition of PC or reactive PB.

The strain at break of hybrid compositions assessed by the strain at break under three-point bending conditions is shown in Figures 5 and 6. The addition of both PC and PB gave compositions with enhanced strain at break in relation to epoxy resin composition without modifier. Approximately 100% strain at break

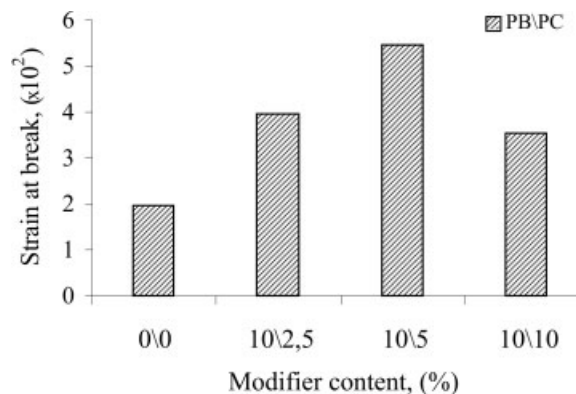


Figure 6 Effect of polycarbonate on the strain at break of epoxy composition modified with 10% of polybutadiene

TABLE II
Properties of Hybrid Compositions Containing 10% of Polybutadiene

Polycarbonate content (wt %)	Impact strength (kJ/m ²)	Flexural strength (MPa)	Flexural strain at break (10 ²)	Energy at break (kJ/m ²)	K_C (MPa m ^{1/2})	Energy of brittle fracture (kJ/m ²)
0/0 ^a	2.5 ± 0.2	53 ± 4	2.0 ± 0.1	3.5 ± 0.2	1.9 ± 0.1	4.3 ± 0.2
0	2.0 ± 0.1	43 ± 4	2.2 ± 0.2	3.4 ± 0.2	2.1 ± 0.1	3.9 ± 0.3
2.5	5.9 ± 0.4	80 ± 3	4.0 ± 0.1	10.3 ± 0.4	2.4 ± 0.1	4.5 ± 0.2
5	4.5 ± 0.4	65 ± 3	5.5 ± 0.3	19.9 ± 0.5	2.9 ± 0.3	5.6 ± 0.4
10	4.1 ± 0.5	71 ± 5	3.5 ± 0.3	8.5 ± 0.3	2.1 ± 0.1	3.5 ± 0.3

^a Composition with no modifier.

increase was noticed for the hybrid composition having 2.5% PB and 2.5% PC. Moreover, this strain at break is, within experimental error, comparable to the sum of strain at break values of compositions with one modifier. Moreover, the best strain at break improvement (175% in relation with neat epoxy resin) was obtained for the composition containing 10% PB and 5% PC. This content of PC seems to be the optimum amount of modifier to be added for maximum strain at break enhancement.

It is however important to add that the critical stress intensity factor K_C expressing the fracture toughness of the tested compositions reached a maximum value for the composition with 2.5% PB and 5% PC. The resistance to crack propagation is enhanced by ~ 80% with respect to K_C of the neat epoxy resin. Moreover, it is worth mentioning that all modified compositions have higher K_C values than the unmodified epoxy composition. As with K_C values, the energy of brittle fracture estimated from the area under the load–displacement curve is also maximum for the mentioned composition and it was higher by about 70% than that of unmodified polymer matrix.

The properties of the compositions obtained with 10 wt % of reactive PB and different amount of PC is shown in Table II. It is observed that hybrid compositions containing 10% PB/2.5% PC have the highest impact strength. However, the hybrid composition containing 10% PB and 2.5% PC has an impact strength, which is ~ 140% higher than that of neat epoxy resin and 15% higher than the sum of the impact strength of composition with 10% PB or composition with 2.5% PC, indicating that synergism effect has occurred. It has to be mentioned that such phenomenon has always been the goal of hybrid compositions production.

Synergism effect is generally attributed to a good homogeneous dispersion of the modifier within the matrix, as well as a good compatibility between the blends components.

The critical stress intensity factor K_C , which measures the resistance to crack propagation of the tested compositions, reached maximum values for the composition with 10% PB and 5% PC and was enhanced by 50% with respect to K_C of unmodified epoxy resin.

Comparing the two modified compositions (i.e., with 10 wt % PB and 2.5 wt % PB), one can confirm that this latter exhibits higher resistance to crack propagation (expressed by a higher K_C value) when 5% of PC is added.

Fracture surface morphological studies

Scanning electron micrograph of unmodified epoxy composition fracture surface shown in Figure 7 indicates a regular uninterrupted crack propagation near the crack tip.

However, micrographs of hybrid composition containing 2.5% PB and 5% PC shown in Figure 8 indicate an homogeneous and denser structure, resulting from a good bonding between the modifiers and the polymer matrix. Furthermore, the features show some plastic deformation due to the matrix, which will lead to a higher energy absorption during the crack propagation process.

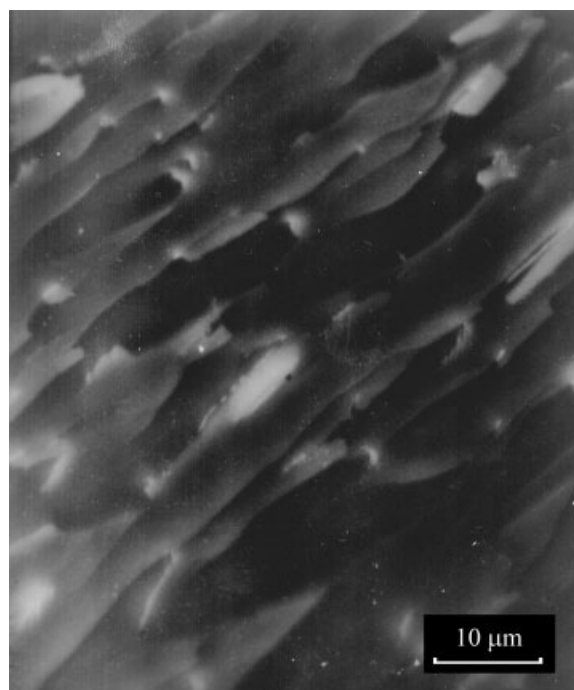


Figure 7 SEM micrographs of unmodified epoxy resin (magnification, ×1000).

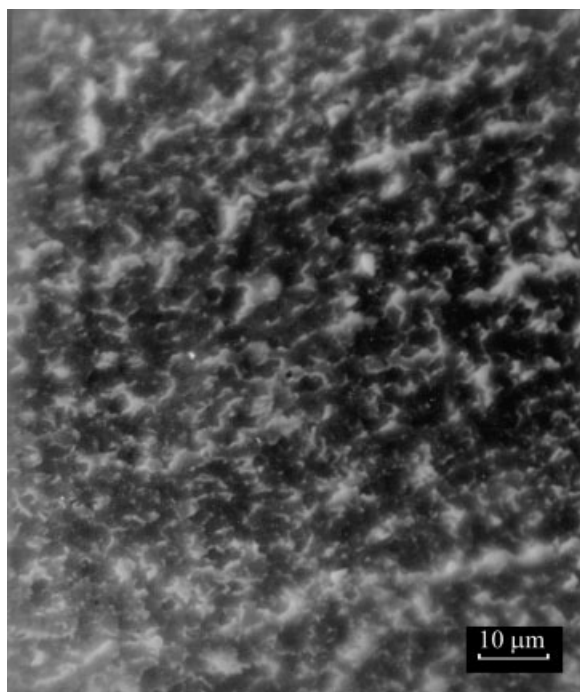


Figure 8 SEM micrographs of hybrid composition with 2.5% polybutadiene and 5% polycarbonate (magnification, $\times 1000$).

CONCLUSIONS

From the obtained results, we can make the following conclusions:

Compositions containing different amount of PC and reactive PB exhibited different mechanical properties. The addition of PC and hydroxyl-terminated PB separately or together improved the impact strength, the flexural strength under three-point bending, the resistance to crack propagation expressed by the critical stress intensity factor K_{IC} , as well the strain at break of the epoxy resin. The improvement in mechanical properties was mainly attributed to plasticizing effect of PB and higher toughness at room temperature in the case of PC.

Synergism effect was observed with the impact strength of hybrid composition based on epoxy

resin modified with 2.5% of reactive PB and containing 5% of PC. The impact strength was $\sim 15\%$ higher than the sum of impact strength of compositions containing only one modifier due to the homogeneous structure of the obtained composition as well as the compatibility between the modifier and the polymer matrix. One has to add that properties such as the strain at break (hybrid composition with 2.5% PB and 2.5% PC), the energy at break, and the fracture energy estimated from the critical stress intensity factor measurements attained the synergism limit.

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