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Recycling of the Rodrun LC-5000 LCP/polycarbonate in situ composites

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Abstract

Two recycling routes were used for the investigation of the effect of the recycling on the properties of the Rodrun LC-5000 liquid crystalline polymer and polycarbonate composite. By comparing the virgin LCP/virgin PC binary composite with the recycled LCP/virgin PC binary composite, only a slight decrease in Young's modulus, but a significant decrease in the tensile strength and the tensile strain for the latter one was observed. In contrast to the effect of virgin LCP resin, the addition of multi-stage recycled LCP did not alter the viscosity of the composites of recycled LCP/virgin PC very much regardless of the number of recycling stages of the LCP. There is a significant decrease in Young's modulus of the recycled LCP/PC binary composite. Examination of the fracture surfaces indicates that the morphology of the composites changes with the number of stages of recycling. The fracture surface tends to be smooth and the transition between the skin layer and the core region becomes smaller after recycling with the increase of the recycling cycles.

Keywords: Liquid crystalline polymer; Polycarbonate; Recycling

1. Introduction

In situ composites of liquid crystalline polymers and thermoplastics have been extensively studied by many researchers over the last 20 years [1–3]. Topics of interest range from rheology [4–6] to reinforcing mechanisms [7–9] of the composites. Research results showed that the structure and properties of the LCPs and their in situ composites with thermoplastics matrix are strongly dependent on the conditions of the process [5,10]. Among LCP/TPs in situ composites, LCP/PC was the most popular system that has been extensively studied and the results showed that it exhibits the best LCP fibrillation [6,11]. In view of the growing interest in the applications of LCP/TPs, recycling of these composites should be an important issue of research. Reprocessing of neat LCP resin has been studied by Bastida et al. [12] and recently by the authors. Yet, extensive literature search indicates that published works on various aspects of recycling of LCP/TPs blends are extremely scarce.

This paper describes the results of recycling LCP/PC in situ composites.

2. Experimental details

Two recycling routes were designed and used for the investigation of the effect of multi-stage recycling on the properties of the LCP/PC composites. Melt flow rate (MFR) and tensile test were used to characterize the rheological and mechanical properties, respectively. The morphology development of the multi-stage recycled composites was examined by scanning electron microscopy (SEM).

3. Materials

An advanced type-3 LCP, Rodrun LC-5000 liquid crystalline polymer, was supplied by Unitika (Hong Kong) Ltd. This advanced type-3 LCP is a flexible semi-aromatic thermoplastic liquid-crystal copolyester resin which is synthesized from *p*-hydroxybenzoic acid (PHB) and poly(ehtylene terephthalate) (PET) with a molar ratio of 80/20. The melting point is 280°C.

Polycarbonate (7025A), bis-phenol A type, was supplied by Mitsubishi Engineering-Plastics Corp. This polycarbonate is a linear polyester of carbonic acid $(COOC_6H_5C(CH_3)C_6H_5O)_n$ in which dihydric phenols are linked through carbonate groups.

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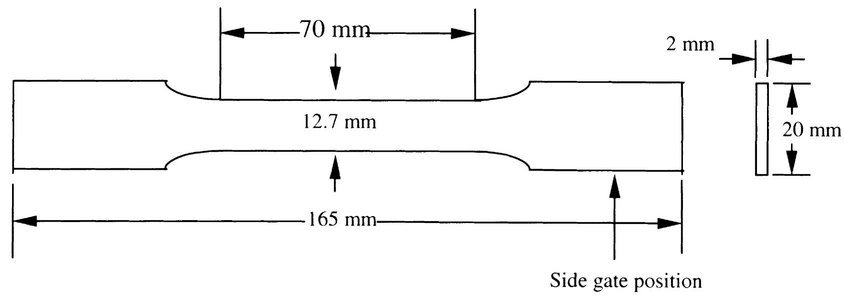

Fig. 1. Test specimen dimension and gate position.

4. Injection molding and recycling process

All the tensile bars were molded directly using a reciprocating screw injection molding machine (Jet master Mark II-C Injection Molding Machine, MKII, Chen Shong Machinery Co., Ltd, Hong Kong). The bar cavity was side-gated such that melt flow is along the direction of the long axis of the tensile bar. Product information from Unitika was used for the operation conditions of the LCP/TPs composites i.e.: injection temperature 280–295°C, mold temperature 40°C, injection time 5 s, injection pressure 900 bar. Before injection molding, all polymer pellets were dried in an oven with dry hot air at 100°C for at least 24 h. Fig. 1 shows the test specimen dimension and gate position.

A crushing machine was used to shred the injection molded tensile bars into pellets of irregular shape of approximately 5–6 mm^3 for subsequent mixing and reprocessing.

The multi-stage recycling process was carried out according to the schedule as shown in Fig. 2.

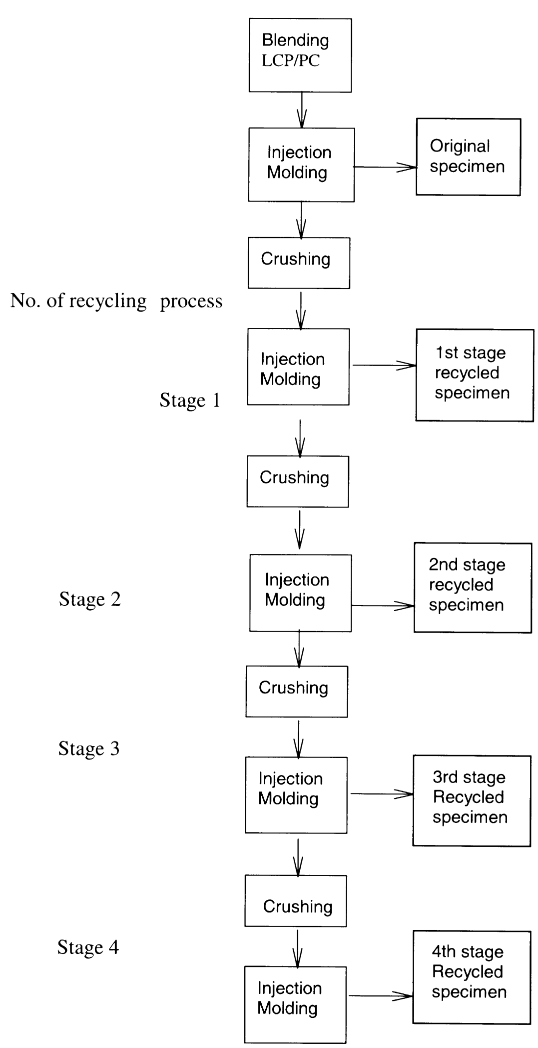

Fig. 2. Specimen production flow chart.

5. Properties evaluation

SEM on the tensile fracture surfaces of injection-molded tensile bar was performed using a Leica Stereoscan 440 (Leica Cambridge Ltd). The samples were sputter-coated with gold before SEM examinations. Low acceleration voltages (≤7 kV) were used in the SEM operation.

The tensile modulus and strength of the LCP/PC in situ composites were measured according to ASTM D638M-87B using an Instron tensile testing machine operated at both 1 and 10 mm/min. cross-head speed respectively. All strains were measured using an extensometer with a gauge length of 25 mm. Except for special cases, the thickness of all the specimens is 2 mm.

The MFR was taken at selected temperatures using the Melt Flow Rate Apparatus (Model 4, Daventest Ltd) according to ASTM D1238-79 and 2782 Method 105 C.

6. Results and discussions

The degree of improvement in the strength of the binary composites has been proved to be dependent apparently on the composition and the processing conditions such as viscosity ratio, temperature, flow rate etc. Thus, it is an interesting subject on how the morphology and mechanical properties develop during the multi-stage recycling processes.

Two recycling routes were used for the investigation on the effect of recycling upon the properties of the LCP/PC composites. One was reprocessing the LCP neat resin first

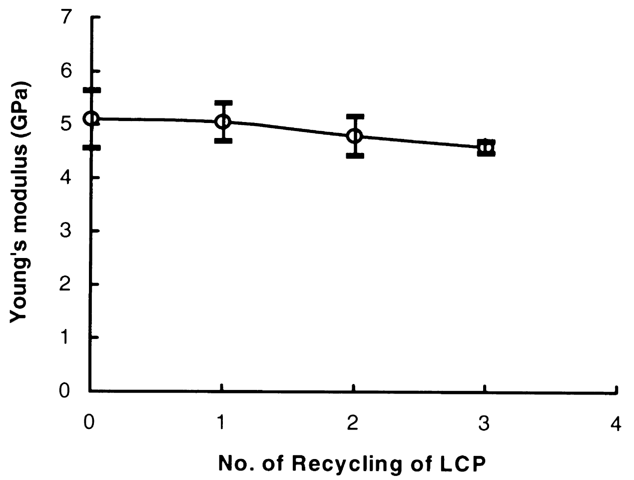

Fig. 3. Young modulus as a function of the number of recycling stage of LCP in the composite of recycled LCP/virgin PC.

and then put it into the virgin PC matrix; the other was reprocessing the composite of LCP/PC.

7. Composite of recycled LCP and virgin PC

7.1. Mechanical property development during recycling

The effect of multi-stage reprocessed LCP on the properties of the composites of reprocessed LCP and virgin PC with 30:70 weight ratio was investigated.

In comparing the virgin LCP/virgin PC binary composite with the recycled LCP/virgin PC binary composite, it was found that there is only a slight decrease in Young's modulus, (Fig. 3) but a significant decrease in the tensile strength (Fig. 4) and the tensile strain (Fig. 5). The trend for both the tensile strength and tensile strain of the composites with respect to the number of recycling stages are the same.

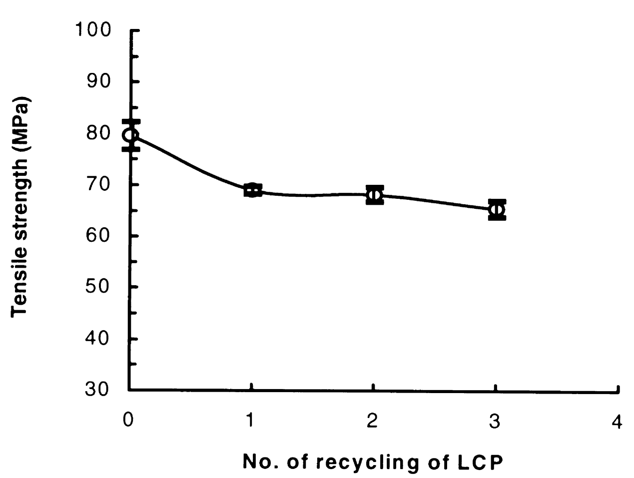

Fig. 4. Tensile strength as a function of the number of the recycling of LCP stage in the composite of recycled LCP/virgin PC.

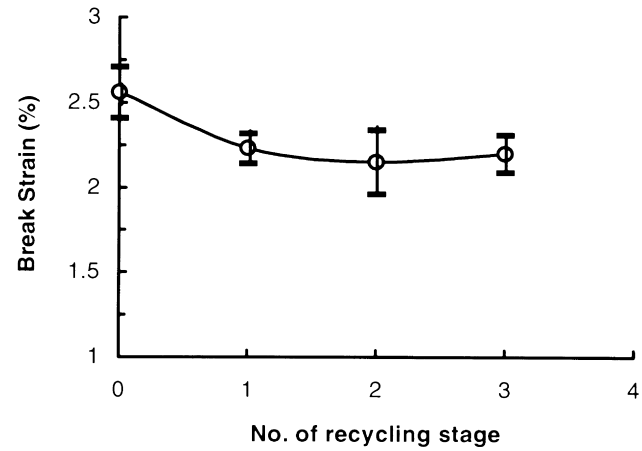

Fig. 5. Break strain as a function of the number of recycling of LCP stage in the composite of recycled LCP/virgin PC.

When the first stage recycled LCP was added to the virgin PC, the tensile properties of the composite decrease significantly as compared with that of the composite of the virgin LCP/virgin PC. However, composites made with recycled LCP and virgin PC have similar properties regardless the number of recycling stage for the LCP, as shown in Figs. 3–5.

7.2. Melt flow behavior during recycling

Fig. 6 shows the MFR of recycled LCP/virgin PC as a function of the number of stages of recycling of LCP at 285°C. In contrast to the increase in MFR of the recycled LCP near resin as shown in Fig. 7, the addition of multi-stage recycled LCP to the composite did not alter the viscosity of the composites of recycled LCP/virgin PC significantly regardless the number of recycling stage of the LCP.

Hashin [13] estimated the upper and lower bounds of the viscosity of non-Newtonian fluid mixtures:

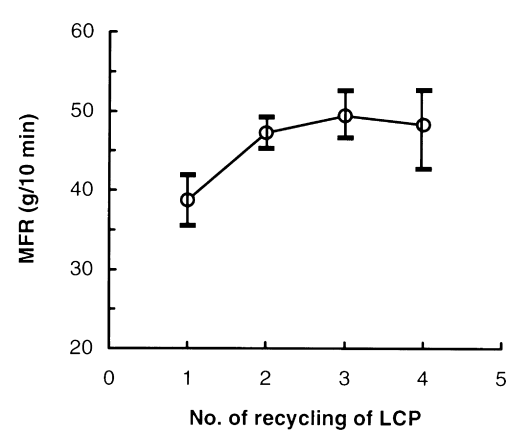

Fig. 6. MFR as a function of the number of recycling stage of LCP in the composite of recycled LCP/virgin PC.

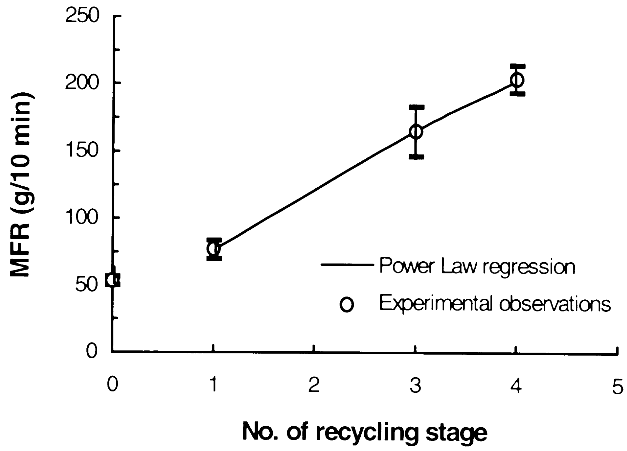

Fig. 7. MFR as a function of the number of reprocessing the LCP neat resin.

Upper bound

$$\eta = \eta_2 + \frac{\Phi_1}{\dfrac{1}{\eta_2 - \eta_1} + \dfrac{1}{2}\dfrac{\Phi_2}{\eta_2}} \tag{1}$$

Lower bound:

$$\eta = \eta_1 + \frac{\Phi_2}{\dfrac{1}{\eta_2 - \eta_1} + \dfrac{1}{2}\dfrac{\Phi_1}{\eta_1}} \tag{2}$$

where Φ_1 and Φ_2 are the volume fractions of components 1 and 2, respectively; ν_1 and ν_2 the viscosity of components 1 and 2, respectively, $\nu_2 > \nu_1$; ν is the viscosity of the composite.

Heitmiller et al. [13] derived an expression for the viscosity of a mixture with a morphology of n concentric layers of Fluid 1 in Fluid 2. When there are many layers, the

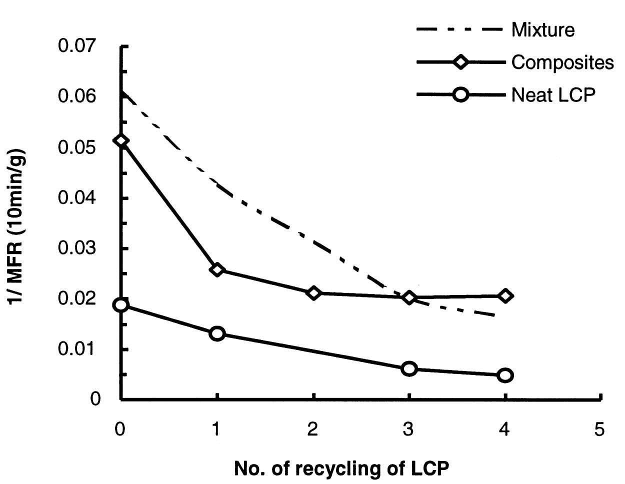

Fig. 8. Reciprocal of MFR as a function of the number of recycling stage of LCP in the recycled LCP/virgin PC. Rule of mixture line was calculated by Eq. (3).

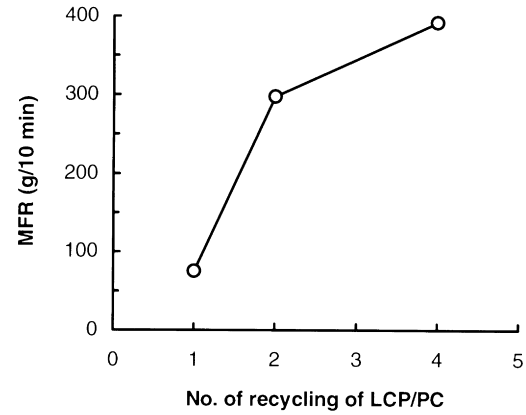

Fig. 9. MFR as a function of the number of recycling of the LCP/PC binary composite.

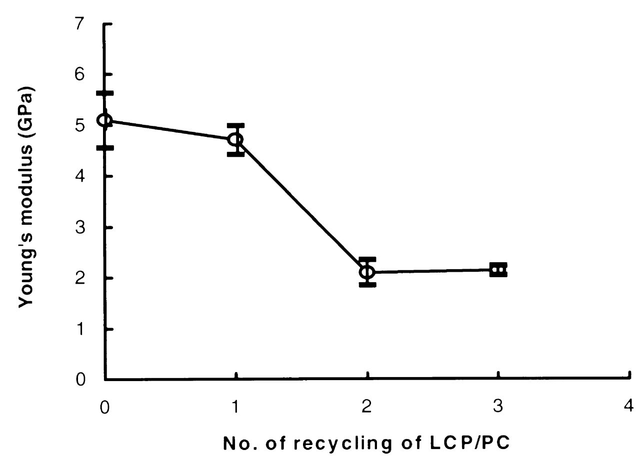

Fig. 10. Young modulus as a function of the number of recycling stage for LCP/PC binary composite.

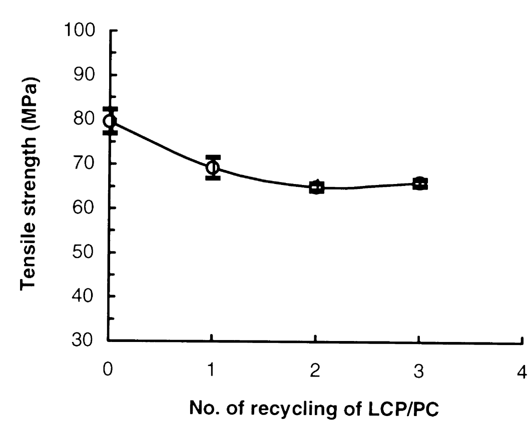

Fig. 11. Tensile strength as a function of the number of recycling stage for LCP/PC binary composite.

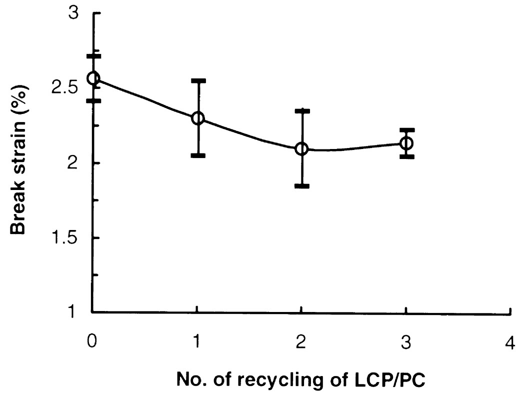

Fig. 12. Break strain as a function of the number of recycling for LCP/PC binary composite.

viscosity expression reduces to

$$\frac{1}{\eta} = \frac{W_1}{\eta_1} + \frac{W_2}{\eta_2} \qquad (3)$$

where W_1 and W_2 are the weight fractions of components 1 and 2, respectively

If the data of MFRs is rearranged and the reciprocal of the MFR value is taken to be directly proportional to the viscosity, based on the respective experimental data of the recycled LCP and virgin PC, the theoretical reciprocal MFR of the recycled LCP/virgin PC composite can be calculated using Eq. (3) and the results are shown in Fig. 8. Fig. 8 shows a significant decrease in the viscosity of the composite of recycled LCP/virgin PC when stage 1 recycled LCP was blended with virgin PC. There are no apparent changes in the viscosity of the composite when the number of recycling stages for LCP is greater the one.

MFR of the recycled LCP/PC binary composite, however, increased significantly with the increase of the number of the recycling, as shown in Fig. 9. This indicates that there is a significant decrease in the molecular weight of the component of PC in the case of recycled LCP/PC composite. The degradation of PC is most likely caused by the combined action of thermal degradation and the shear stress occurring during the repeating injection molding processes.

8. Recycling of the LCP/PC binary composite

8.1. Mechanical property development during recycling

In the case of the second recycling route, i.e. recycling of

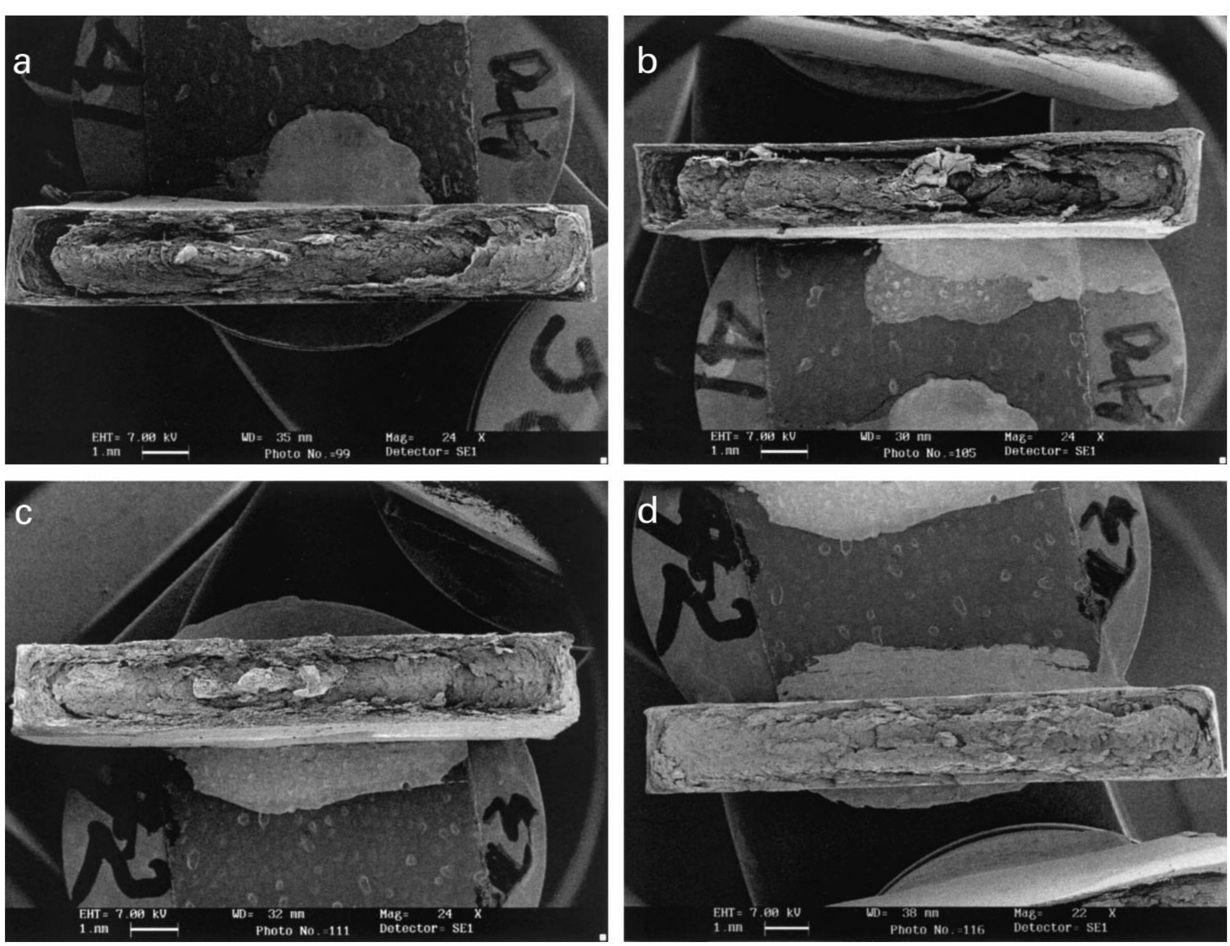

Fig. 13. Morphology development of the recycled LCP/PC in the cross section: (a) stage 1; (b) stage 2; (c) stage 3; and (d) stage 4.

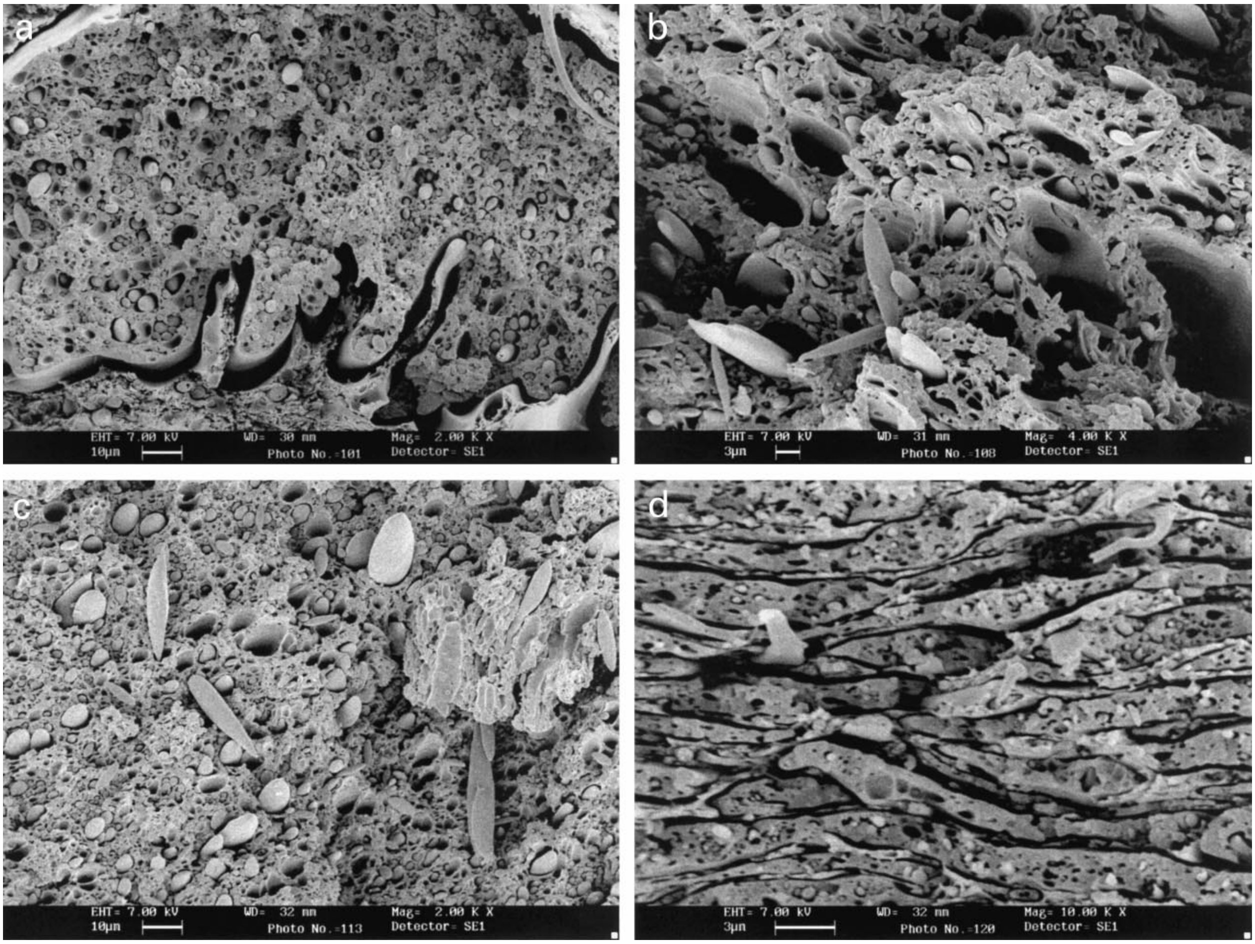

Fig. 14. Morphology development of the recycled LCP/PC in core area: (a) stage 1; (b) stage 2; (c) stage 3; and (d) stage 4.

the LCP/PC binary composite, there is a significant change in Young's modulus of the recycled composites, as shown in Fig. 10. As compared with Fig. 3, in which the decrease in Young's modulus is small when recycled LCP was added to virgin PC, Fig. 10 shows that the decrease in Young's modulus of recycled LCP/PC composite was quite significant. This can be attributed to the decrease in molecular weight of the recycled PC.

The trend in the decrease of tensile strength and break strain of the recycled LCP/PC composite with the number of recycling stages seems to be very similar to that of the recycled LCP/virgin PC, as in Figs. 4, 5, 11 and 12.

8.2. Morphology development in recycled LCP/PC

In the recycling of the LCP/PC binary composite, the results of the morphology study are well associated with the mechanical properties. Fig. 13(a)–(d) shows that the fracture surface tends to be smooth and the transition between the skin layer and the core region becomes smaller after recycling. The smaller the transition region, lesser the amount of highly oriented fibers resulting in the tensile bar and hence lower the strength. Fig. 14(a)–(d) shows that the LCP phases have been dispersed more evenly with the increase of the recycling cycles. Particularly, after three stages of recycling, the diameter of the LCP droplet in the core area is less than 1 μm. It is difficult to prove that the aspect ratio of the LCP fiber has been changed by the recycling processes. However, as in the case of glass fiber reinforced plastics, it is reasonable to assume that the average length of the LCP fiber or fibrils becomes shorter after each recycle process. This, together with the decrease in molecular weight of the PC during the recycling process, contributes to the decrease in Young's modulus. On the basis of results of the two recycling routes and the extent of the decrease in the mechanical properties and the MFR, it is obvious that the degradation of PC in the LCP/PC binary composite during the recycling process is more detrimental than that of the LCP in the degradation of the properties of the composites after recycling.

9. Conclusions

1. Comparison of the virgin LCP/virgin PC binary composite with the recycled LCP/virgin PC binary composite

shows that there is only a slight decrease in Young's modulus, but a significant decrease in the tensile strength and the tensile strain for the latter one.
2. In contrast to the effect of virgin LCP resin, the addition of multi-stage recycled LCP, regardless of the number of recycling stage of the LCP, did not alter the viscosity of the composites of recycled LCP/virgin PC.
3. A significant decrease in Young's modulus occurs when the LCP/PC binary composite is recycled. The trend in the decrease of tensile strength and tensile strain of the recycled LCP/PC composite with the number of recycling stages seems to be very similar to that of the recycled LCP/virgin PC.
4. The dispersion of the LCP fibrils becomes more even in the recycled LCP/PC composites. The fracture surface tends to be smooth and the transition between the skin layer and the core region becomes smaller with the increase of the recycling cycles.

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