The enhancing effect of mesogen-jacketed liquid crystalline polymer PBPCS on epoxy resin

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Abstract. The mixtures of mesogen-jacketed liquid crystalline polymers (MJLCP) and epoxy resin (E-51) have been prepared in a certain proportion. The category of the MJLCP is poly{2,5-bis[(4-butoxyphenyl)oxycarbonyl] styrenes} (PBPCS). Methyl tetrahydrophthalic anhydride (MeTHPA) is served as a curing agent, and N, N-dimethylbenzylamine plays the role of catalyst. Then, based on the curing process, the modified materials have been acquired by casting molding. The effect of PBPCS's improvement has been researched through the mechanical properties test, dynamic thermal mechanical test and scanning electron microscope (SEM). The results indicated that PBPCS could apparently improve the mechanical properties of resin E-51. Compared with unmodified materials, the elongation at break and the tensile strength of PBPCS have been improved remarkably through modification. Both mechanical properties of the 4wt% PBPCS/E-51/MeTHPA were enhanced by 48% and 153% separately, and the characteristics of the 3wt% one were raised by 47% and 19% respectively. Also, the ductile fracture morphology of the resins was exhibited in SEM photograph clearly.

1. Introduction

Owing to greater mechanical, chemical resistance, and dielectric properties, epoxy resins are in multiple utility in the fields of aviation, aerospace, chemical engineering, transportation industry and electronic and electric technologies, etc [1, 2]. Nevertheless, as a thermosetting resin, brittleness becomes a major barrier of this kind of material. What’s more, poor thermal stability also restricts further application in advanced industry [3, 4]. Some researches attribute the formation of self-reinforcing structures in epoxy resins to the blending with liquid crystalline polymers, which consist of rigid mesogenic groups and flexible chains. In addition, liquid crystalline polymers, which has been detected and witnessed in epoxy resins in the form of disperse particles or fibers, can also lead to microcracks and shear zones that absorb a large number of the fracture energy in a resin matrix. As a result, they can strikingly improve the toughness and strength of epoxy resins. Compared to epoxy resins toughened by other ordinary methods, incorporating liquid crystalline polymers into epoxy networks exhibits higher thermal stability, toughness and tensile strength.

The genre of MJLCPs [5-8] is a new type of liquid crystalline polymer. In the late 1980s, Zhou, et al. reported the MJLCPs, which are side-on side-chain liquid crystalline polymers, has a short spacer or a single covalent bond that connects the mesogen to the polymer backbone [9]. PBPCS, whose chemical structure is same as that of side-chain liquid crystalline polymer, is a typical kind of
medogen-jacketed liquid crystalline that based on vinly terephthalic. But some properties of PBPCS are similar to those of main-chain liquid crystalline polymer. This means that MJLCPs [10], a special category of SCLCPs, can be easily synthesized and possess stable liquid crystalline phases like main-chain liquid crystalline polymers do. Recently many studies on the morphology of liquid crystal phase transition and its applications to advanced functional materials have become of great importance. However, there has been no report on the method of resin’s modification with MJLCP up to date.

In this work, stoichiometric amounts of PBPCS were dissolved in epoxy resins (E-51). By casting and molding, all samples were cured in accordance with curing process that was determined by curing kinetics. Static and dynamic mechanical properties of the epoxy resins modified by PBPCS would be studied in detail.

2. Experimental procedure

2.1. Materials

Epoxy resin E-51 (the content of epoxy was about 0.051mol•kg⁻¹) was supplied by Sinopec Group(Baling, China) and used without further purification; Methyl tetrahydro phthalic anhydride (MeTHPA), N, N-dimethylbenzylamine and dichloromethane with the purity of analytical level were provided by Aladdin corporation. The PBPCS (Mn=77000, Mw/Mn=1.7) was synthesized according to literature [11]. Its structure stated as figure 1.

![Figure 1. The structure of PBPCS.](image)

2.2. Characterization

Tensile and flexural properties were menstruated on the basis of Chinese National Standard GB/T 2567-2008 on a universal testing machine of type Instron26022(Shimazu, Kyoto, Japan). And Impact strengths were tested by a TCJ LCD type pendulum impact testing machine (Jilin, China), also according to Chinese National Standard GB/T 2567-2008. Morphology and structure of the fracture surfaces was observed with a SEM(S-4800, Hitachi Construction Machinery Co., Ltd. Japan) at the acceleration voltage of 20kV. Dynamic mechanical analysis was carried out with the assistance of METTLER TOLEDO DMA(USA) by using three-point bending mode at a frequency of 1Hz with the temperature limits from 50°C to 200°C at the heating rate of 3°C per minute. Ultrasonic cleaner, the type of which was SB 5200DTDN, was provided by Xinzhi Biological Technology Co., Ltd. Ningbo (China).

2.3. Preparation of PBPCS/E-51/MeTHPA materials

Five samples were prepared according to corresponding mass fraction of PBPCS in epoxy resin: 1%, 2%, 3%, 4% and 5%. The PBPCS and epoxy resin E-51 were mixed homogeneously in dichloromethane, and the solvent was removed at 90°C. After the temperature of mixture cooling down to the normal temperature (25°C), the stoichiometric amounts of MeTHPA and N, N-dimethylbenzylamine were added to the mixture under continuous stirring. The blends were then poured into a preheated mold coated with silicone resin. After degassing in the vacuum for about half an hour, all the samples were cured at 90°C and 120°C for 2 hours respectively and at 140°C for 1.5
3. Results and discussion

3.1. Mechanical properties of PBPCS/E-51/MeTHPA materials

3.1.1. Tensile properties. Variations of elongation at break and tensile strength of E-51/MeTHPA with varied mass ratio of additive PBPCS are illustrated in the table 1.

| Materials         | Properties | Tensile strength/MPa | Elongation at break/% |
|-------------------|------------|----------------------|-----------------------|
| E-51/MeTHPA       | 51.09±1.36 | 3.60±0.91            |
| 1%PBPCS/E-51/MeTHPA | 66.31±2.21 | 5.22±1.35            |
| 2%PBPCS/E-51/MeTHPA | 66.92±1.88 | 6.61±1.27            |
| 3%PBPCS/E-51/MeTHPA | 68.83±1.72 | 7.08±1.22            |
| 4%PBPCS/E-51/MeTHPA | 75.48±2.79 | 9.10±1.73            |
| 5%PBPCS/E-51/MeTHPA | 73.46±1.35 | 8.79±0.94            |

Obviously, the additive PBPCS has improved the tensile strength and elongation at break of pure E-51/MeTHPA. The statistics in the table 1 showed the trend of increasing of tensile strength and elongation at break from the mass ratio of additive PBPCS of 1wt% to that of 4wt%, followed by a tendency of decreasing, with the growth of 1wt% of the content of additive PBPCS, at that of 5%. The maximum tensile strength and elongation at break both corresponded at the point of 4wt% of the amount of additive PBPCS added into E-51/MeTHPA (4wt% PBPCS/E-51/MeTHPA) materials, where both were respectively 48% and 153% higher than value of those of pure E-51/MeTHPA materials. As a result of the alignment of the rigid mesogenic groups of PBPCS during the solidity and the enclosure of orientation in epoxy networks, the materials were to be reinforced. Simultaneously, flexible chains of PBPCS and epoxy resin matrix, interpenetrating to form micro rubber phase that can absorb part of the energy, accumulated inside the materials. So elongation at break of the modified materials has been greatly improved. When the mass ratio of the additive PBPCS reached 5wt%, the tensile strength and elongation at break of modified materials appeared to have a slight decrease, but were still higher than those of the pure E-51/MeTHPA, which possibly attributed to the uneven dispersion of excessive PBPCS in epoxy resin matrix.

3.1.2. Impact properties. The result of impact measurement of PBPCS/E-51/MeTHPA materials is illustrated in figure 2.

![Figure 2](image2.png)

Figure 2. Impact properties of PBPCS/E-51/MeTHPA materials.

![Figure 3](image3.png)

Figure 3. Bending strength of of PBPCS/E-51/MeTHPA materials.
The curve indicated that the impact strength value of PBPCS/E-51/MeTHPA materials was higher than that of pure E-51/MeTHPA materials. In particular, the impact strength value of 3wt% PBPCS/E-51/MeTHPA was 1.47 times as high as that value of pure E-51/MeTHPA. Since the statistics of impact strength showed the energy absorption before fracture, the results in figure 1 could be considered as that in the existence of additive PBPCS, the epoxy resin E-51 could result in impacting crack deformation of the surrounding matrix networks. However, the impact strength of the materials was to decrease when exceeding the certain mass ratio of the additive PBPCS because the compatibility between the epoxy resin matrix and the PBPCS became less effective. So the results of impact measurement indicated that PBPCS was able to toughen epoxy resin E-51 effectively.

3.1.3. Flexural properties. The result of flexural strength measurement derived from the static three-point winding tests was shown in figure 3. Apparently, the trend of variation of varied mass ratio of the additive PBPCS in the materials of E-51/MeTHPA resembled tensile and impact strength. The flexural strength initially exalted with the mass ratio of the additive PBPCS up to 3 wt %. It reached the maximum when the content was about 3 wt %. After that, it suffered a slight decline with the increase of the mass ratio of the additive PBPCS. The maximum flexural strength value of PBPCS/E-51/MeTHPA was 19% more than that of the pure E-51/MeTHPA. When the mass ratio of PBPCS that added into E-51 was less than 3 wt %, PBPCS presented island structure and had a uniform dispersion in epoxy resin matrix. While the mass ratio of PBPCS was greater, phase separation was observed in the modified epoxy resins.

3.1.4. SEM. To provide a direct comparison, the morphology of the tensile fracture surfaces of all the materials were investigated by SEM, as shown in figure 4(a). It showed the smooth fracture surface of pure epoxy resin E-51. These fissures were formed initially as river pattern and spread swiftly by the method of parallel lines. It was a sign of brittle rupture. But with the incorporation of PBPCS to epoxy resin E-51, as shown in figures 4(b)-4(f), a wide range of ductile sunken areas were shown at the fracture surfaces, indicating a typical tough feature [13]. It proved that PBPCS has played a part in toughening and reinforcing the materials.

Figure 4. SEM graphs of PBPCS/E-51/MeTHPA materials (a:0wt% PBPCS; b:1wt% PBPCS; c:2wt% PBPCS; d:3wt% PBPCS; e:4wt% PBPCS; f:5wt% PBPCS).
3.2. Dynamic mechanical behaviors (DMA)

DMA is an efficient tool to acquire the information about the microstructure of thermoset networks and the mechanical damping of materials as the function of thermometer [14, 15]. The temperature dependence of dynamic storage modulus (E’) and loss angle (tan delta) were displayed in figures 5 and 6.

![Figure 5. Storage modulus versus temperature of PBPCS/E-51/MeTHPA materials.](image1)

![Figure 6. Tan delta versus temperature of PBPCS/E-51/MeTHPA materials.](image2)

Table 2 summarized the value of E’ and the value of glass transition temperature (Tg) at 60℃. The value of storage modulus of all PBPCS/E-51/MeTHPA materials was higher than the value of that of pure E-51/MeTHPA at 60℃, suggesting that the former was more rigid than the latter. What’s more, PBPCS/E-51/MeTHPA materials with greater mass ratios of PBPCS tended to possess greater E’ values, proving the dominated role of the semi-rigid structure of the MJLCP.

| Materials              | Properties | E’/GPa | Tg /℃ |
|------------------------|------------|--------|-------|
| E-51/MeTHPA            |            | 1.763  | 151.4 |
| 1%PBPCS/E-51/MeTHPA    |            | 2.126  | 156.2 |
| 2%PBPCS/E-51/MeTHPA    |            | 2.166  | 155.5 |
| 3%PBPCS/E-51/MeTHPA    |            | 2.222  | 156.3 |
| 4%PBPCS/E-51/MeTHPA    |            | 2.293  | 156.1 |
| 5%PBPCS/E-51/MeTHPA    |            | 2.235  | 157.2 |

From the curves of tan delta versus temperature (figure 6), there was no existence of other α-transition peak in the high-temperature range, potentially owing to the dispersion of PBPCS in epoxy resin E-51. On the tanδ-temperature chart, the temperature that corresponded to the maximum tan δ was delimited as Tg, indicating rotational freedom in the segments between crosslinks [16]. In table 2, the Tg of the modified epoxy resins was slightly higher than pure epoxy resin E-51, hence the rigid chains of PBPCS were aligned during the process of curing and the enclosure of location in epoxy networks. In order to keep orientation in the networks, rigid units needed more energy, so Tg of PBPCS/E-51/MeTHPA materials went higher than that of pure E-51/MeTHPA.

4. Conclusions

Based on the analysis above, the introduction of PBPCS into epoxy resin E-51 could increase both toughness and strength of the epoxy resin matrix. Compared to unmodified materials, the results showed that PBPCS could distinctly harden the epoxy resin E-51. The 4wt% of mass ratio of modifier enhanced the elongation at break and tensile strength by 153% and 48% separately. The bending and impact strength were raised by 19% and 47% apart with 3wt% of mass ratio PBPCS added. In
addition, the value of $T_g$ was increased by 4-6 ℃, and the SEM image showed obvious ductile fracture morphology. Consequently, the MJLCP PBPCS could act as an effective and successful reinforcing and toughening modifier of epoxy resin.

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