Crosslinking of Poly (propylene carbonate) by Peroxide Crosslinking Agent Dicumyl Peroxide (DCP)

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Abstract: The gel content, glass transition temperature (Tg), tensile strength, and elastic modulus of crossliked Poly (propylene carbonate) (PPC) were investigated using modulated differential scanning calorimetry (MDSC) and tensile tester respectively. PPC can be crosslinked by peroxide crosslinking agent Dicumyl peroxide (DCP) and in a solution casting and heating process. The concentration of DCP showed a great influence on the crosslinking of PPC. The crosslinking of PPC resulted in the increase in gel content, mechanical strength, elastic modulus and Tg. The optimum of mechanical properties may be attained at 1% DCP.

Key words: Polycarbonate; Crosslink; Dicumyl peroxide; Triallyl isocyanurate
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1 Introduction

Poly (propylene carbonate) (PPC) synthesized from carbon dioxide and propylene oxide has been proved to be biodegradable polymer owing to the ester bonds on its backbone. In this regard, it has attracted considerable attention recently[1-4]. The PPC exhibited good biodegradability in both soil-burial and buffer solution. Moreover, the PPC exhibited superior thermal and mechanical properties. However, the alternating PPC also showed poor mechanical properties and relatively lower glass transition temperature (Tg). Crosslinking is an important method for improving polymer properties, in particular, high-temperature properties.

In the present study, the crosslinking of PPC is investigated. The crosslinked PPC was prepared using peroxide crosslinking technique by solution casting. The aim of this paper is to show some effects of crosslinking agent content on properties of crosslinked PPC.

2 Experimental

2.1 Materials

The PPC used in this work was prepared in our pilot-scale experimental apparatus. The polymerization product was dried directly without further treatment. Trichloromethane, AR, was obtained from Tianjin Fuyu Chemical Inc. of China. Dicumyl peroxide (DCP) was supplied by Shanghai Gaoqiao Chemical Co. Ltd. of China.

2.2 Preparation of Crosslinked PPC

PPC and the crosslink agent were dissolved in trichloromethane at 60℃ for more than 3 h. Most solvent was allowed to evaporate at 80℃. To further remove residual solvent, all the blends were dried under vacuum at 60℃ for more than 48 h until constant weight. The resulting blends were compression molded into plates. The mold was heated to 160℃ and kept for 5 minutes prior to the introduction of blend. The molding temperature is 160℃. The crosslinking time is 30 minutes. The samples for analysis and mechanical testing were cut out from the compression molded plates.

2.3 Molecular Weight Determination

The number average molecular weight (M_n) value of the PPC was determined with a gel permeation chro-

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matography (GPC) system

2.4 Thermal Analysis

DSC trace of the crosslinked PPC was determined in a modulated thermal analysis DSC instrument (model 200 PC) under a nitrogen flow of 20 mL/min.

2.5 Mechanical Property

The static tensile properties were measured at 23℃ using a SANS CMT tensile tester. The crosshead speed was set at 50 mm/min. The samples were standard dogbone tensile bars (ASTM D638) with dimensions of 25 mm×4 mm×1 mm, cut from the compression molded plates.

2.6 Determination of Gel Content

The gel content was determined according to ASTM 2765. Weighed samples in small pieces and in a copper net were put into boiling dimethyl sulfoxide for 24 h. The extracted samples were dried to a constant weight in a vacuum oven. The gel content is expressed in terms of the percentage of the weight remaining. The values of gel fraction deviated from the average by less than 2%. The gel content was calculated using the following equation:

$$\text{gel content} = \frac{\text{final weight of sample}}{\text{initial weight of sample}} \times 100\% \quad (1)$$

3 Results and discussion

3.1 Gel content

Fig. 1 shows the evolution of gel for PPC crosslinked with different amounts of DCP when the TAIC content was constant (4%). Gel was formed at low levels of peroxide. The gel content increased with increasing peroxide concentration. This is as expected since the higher the level of peroxide used, the higher the concentration of polymer radicals generated. The gel content did not change when DCP content was higher than 1%. The maximum gel content obtained from this technique is about 60%.

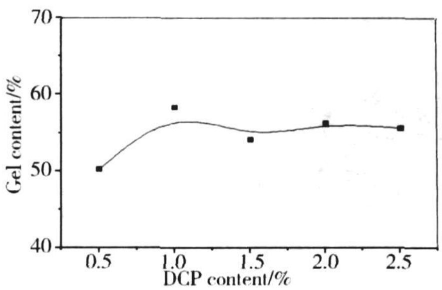

Fig. 1 Variations of gel for crosslinked PPC with various DCP contents

3.2 Glass transition temperature

The viscoelastic properties of polymers are markedly dependent on the type of crosslink and on the degree of crosslinking. Crosslinking raises the glass transition temperature, Tg, of a polymer by introducing restrictions on the molecular motions of the chain. Low degrees of crosslinking such as those found in normal vulcanized rubbers act in a similar way to entanglements and raise Tg only slightly above that of the uncrosslinked polymer[5]. However, in thermosets such as epoxy resins, Tg is markedly increased by crosslinking[5]. Fig. 2 shows the variations of Tg for crosslinked PPC with various DCP contents when the TAIC content was constant (4%). The Tg increased slightly with increasing peroxide concentration. However, the Tg did not change when DCP content was higher than 1%.

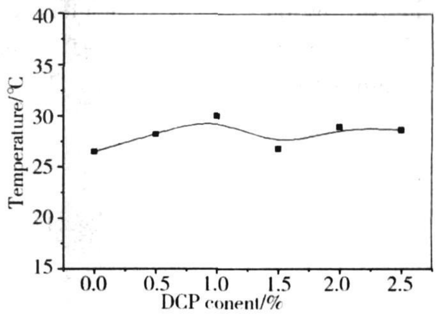

Fig. 2 Variations of Tg for crosslinked PPC with various DCP contents

3.3 Tensile properties

Fig. 3 shows the variations of mechanical properties for crosslinked PPC with various DCP contents when the TAIC content was constant (4%). In the presence of peroxide, crosslinking occurred, leading to significant changes in the mechanical properties. A transition point of mechanical properties is clearly seen at 1% DCP. Before this point, the mechanical properties increased rapidly with increasing peroxide concentration. Beyond this point, the mechanical properties did not increase almost with increasing peroxide concentration. The tensile strength increased from 13.5 MPa (0% DCP) to 26.4 MPa (1% DCP). The elastic modulus changed from 320 MPa (0% DCP) to 670 MPa (1% DCP). This demonstrated that the effect of the crosslink network on the mechanical properties is significant. This can be explained by the restriction of chain movement brought about by the crosslink network.

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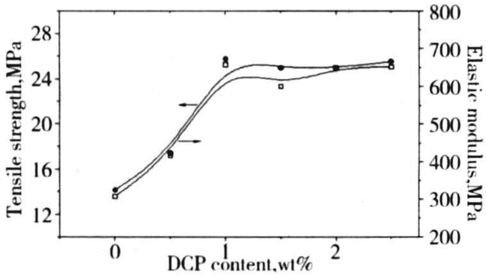

Fig. 3 Variations of mechanical properties for crosslinked PPC with various DCP contents

4 Conclusions

PPC can be crosslinked by peroxide crosslinking agent DCP in a solution casting and heating process. The concentration of DCP and TAIC showed a great influence on the crosslinking of PPC. The crosslinking of PPC resulted in the increase in gel content, mechanical strength, elastic modulus and Tg. The optimum of mechanical properties may be attained at 1% DCP.

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聚甲基乙撑碳酸酯的交联

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摘 要: 利用过氧化物过氧化二异丙苯 (DCP) 和多官能团化合物三烯丙基异氰尿酸酯 (TAIC), 对聚甲基乙撑碳酸酯 (PPC) 进行了交联研究。研究发现, DCP和 TAIC的用量对 PPC的交联均有较大影响, PPC交联后, 其凝胶含量、机械性能、弹性模量、玻璃化转变温度均有所增加, 1% 的 DCP和 4% 的 TAIC用量可得到较理想的交联 PPC材料。

关键词: 聚碳酸酯; 交联; 过氧化二异丙苯; 三烯丙基异氰尿酸酯

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