Reinforcing Network Structure: Analysis of the Phase Morphology and Mechanical Properties of Polymer Blends [Poly(methyl methacrylate)/Poly(ε-caprolactone)] with the Addition of a Third Polymer [Poly(vinyl chloride)]

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ABSTRACT: A thin matrix network structure of poly(vinyl chloride), poly(ε-caprolactone), and *in situ* formed poly(methyl methacrylate) (PMMA) was synthesized. The structure was observed with scanning electron microscopy. The dissolution test suggested that a simple method to generate high rates of crosslinking at a lower temperature was obtained. The relationship of the phase morphology and mechanical properties of the blends was studied, and a reinforced material of PMMA was obtained. The obvious increase in the mechanical properties and the reinforcing effect were attributed to the formation of crosslinking and the network structure in the blend. The glass-transition temperatures, obtained by DSC, suggested confined thermal behavior of PMMA chains restricted by a crosslinking system. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1044–1048, 2008

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INTRODUCTION

Poly(ε-caprolactone) (PCL) is a very well known biodegradable aliphatic polyester with interesting properties and applications in biomedicine.[1,2] Poly(methyl methacrylate) (PMMA) is used as a biostable and biocompatible component for orthopedic implants. PMMA/PCL blends are expected to be good candidates for self-curing acrylic-based bone cements according to the theory that a biodegradable phase is dispersed in a continuous biostable acrylic matrix and its biodegradation allows the ingrowth of osseous tissue inside the implanted devices during the healing process.[3] However, the mechanical properties of the blends are at a lower level[4,5] because of the immiscibility of this polymer pair, which results in gross phase separation and poor interfacial adhesion. Therefore, we chose a third polymer, poly(vinyl chloride) (PVC), to modify the physical and chemical interactions between PMMA and PCL.

PVC is an interesting, innocuous polymer with a solubility parameter very close to that of PMMA.[6–9]

The miscibility of this system has been discussed in many reports about PVC/PMMA blends.[10–16] It is a well-known system in which hydrogen bonds involving the carbonyl group of PMMA and the α-hydrogen of PVC are expected. There would be a similar interaction between PVC and PCL.

Moreover, PVC generally undergoes degradation reactions, including dehydrochlorination and oxidative degradation, at a higher temperature. Experientially, the PVC macroradicals produced during degradation reactions would form crosslinked or graft copolymers with PCL, PVC chains, and the monomer methyl methacrylate (MMA) as an initiator of polymerization. However, few studies on these reactions at a lower temperature (i.e., at 80°C or even lower) have been reported. We attempted to make a reinforcing structure and produce a compatibilization effect by adding PVC.

In this study, PMMA/PVC/PCL blends with different proportions (95/5/0, 93/5/2, 90/5/5, 85/5/10, and 95/0/5 weight ratios) were prepared by bulk radical polymerization at 80°C. The mechanical properties and thermal behavior of the blends were examined. The morphology of the blends was also studied with scanning electron microscopy (SEM). The dissolution test implied a high rate of crosslinking
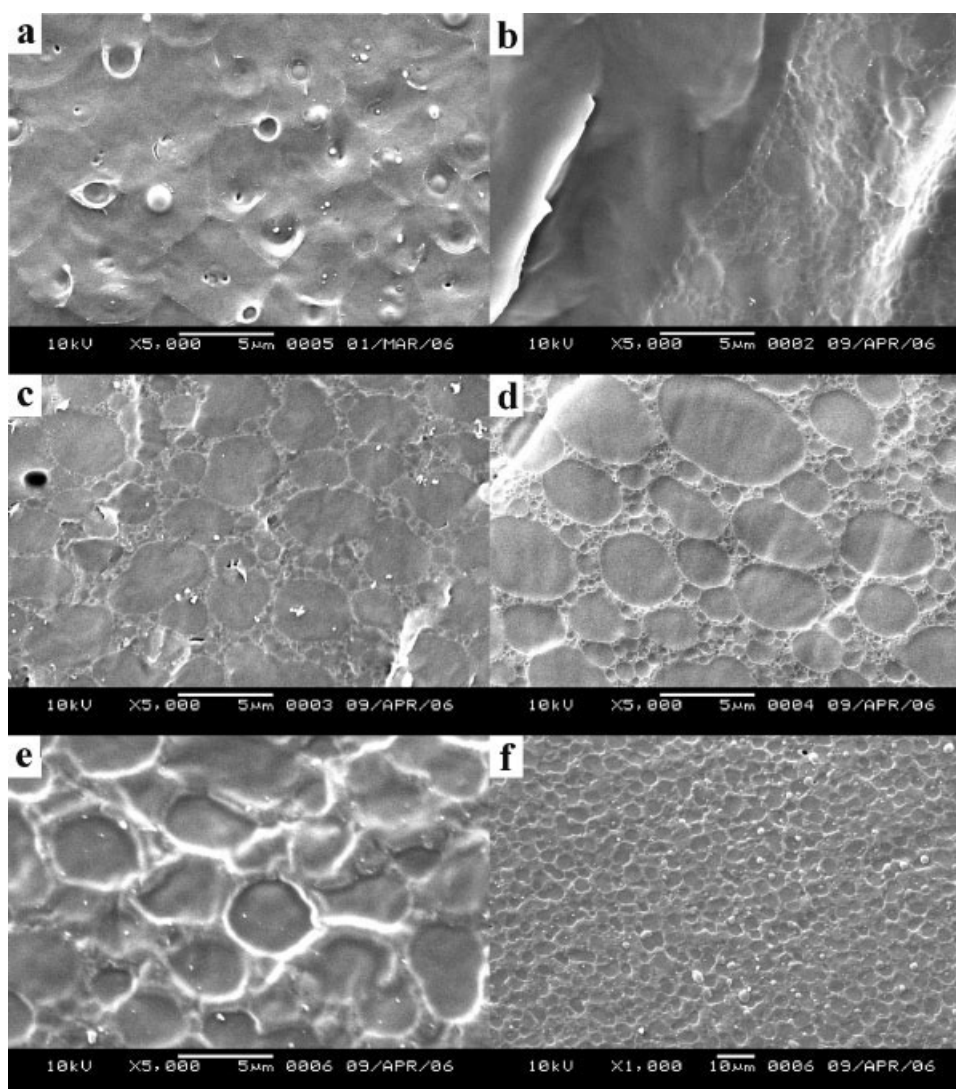
Figure 1 SEM microphotographs of the free-fractured surfaces of (a) PMMA/PCL (95/5), (b) PMMA/PVC/PCL (93/2/5), (c) PMMA/PVC/PCL (90/5/5), (d) PMMA/PVC/PCL (85/10/5), and (e,f) PMMA/PVC/PCL (90/5/5) blends dipped in a mixture of ethanol and acetone (98 mL/2 mL) at 70°C for 4 h.

under the synthesis conditions. A reinforced material of PMMA with an obvious increase in the mechanical properties was obtained.

EXPERIMENTAL

Material

PVC (weight-average molecular weight = 67,000 g/mol) from Shanghai Chlor-Alkali Chemical Co., Ltd. (Shanghai, China), and PCL (weight-average molecular weight = 50,000 g/mol) from Tianshengcheng Co., Ltd. (Wuhan, China), were used as the matrix resins. MMA, purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), was purified by vacuum distillation. 2,2′-Azobisisobutyronitrile (AIBN) was used as an initiator for acrylic polymerization.

Synthesis of the blends

PMMA-based blends were synthesized from a mixture of MMA monomer, PVC, and PCL in different proportions. In a boiling flask equipped with an Allihn-type condenser, PCL and PVC was first dissolved in MMA at 100°C under vigorous stirring and left for 2 h. Afterwards, some AIBN (0.2 wt % with respect to MMA) was added, and the polymerization was carried out with tender mechanical stirring for approximately 30 min at 80°C; this was followed by a curing cycle in a thermostatic oven at 45°C for 16 h. After an annealing program at 100°C for 2 h, blends containing different amounts of PCL and PVC (95/5/0, 93/5/2, 90/5/5, 85/5/10, and 95/0/5 PMMA/PCL/PVC weight ratios) were obtained. The weight-average molecular weights of PMMA were measured by gel permeation chromatography.

They were 57,000, 54,000, 62,000, 56,000, 64,000, and 57,000 g/mol for pure PMMA and 95/5/0, 93/5/2, 90/5/5, 85/5/10, and 95/0/5 PMMA/PCL/PVC, respectively.

Mechanical properties

The tensile and flexural tests were carried out on a universal tensile tester at room temperature according to ASTM D 638 and ASTM D 790, respectively. For all these tests, at least five specimens were used for each measurement.

Gel content

The gel amount (wt %) formed in PMMA/PVC/PCL blends was determined by separation of the insoluble part from the samples dissolved in the solvent, which was tetrahydrofuran. The gel was weighed after drying in a vacuum desiccator. Each estimation was repeated three times, and the average percentage of the gel mass was calculated.

Thermal behavior

Differential thermal analyses were carried out under an atmosphere of N_2 with a Netzsch 200 PC differential scanning calorimeter (Selb Germany) calibrated with indium standards. The following heating program was used: samples were heated at 10°C/min from room temperature to 180°C twice with a quenching step between them.

Morphology

Samples, fractured in liquid N_2, were surface-coated with a thin layer of gold and then observed with an LV-5600 scanning electron microscope (JEOL Co., Tokyo, Japan) at different magnifications.

RESULTS AND DISCUSSION

Morphology

SEM is a direct method for studying the morphology of blends. In this study, the free-fractured surfaces of the blends in liquid nitrogen were observed by SEM to evaluate the compatibility of the composites and the net structure. Figure 1(a–d) shows SEM microphotographs of free-fractured surfaces of blends at a fixed content of PCL with different contents of PVC. As shown in Figure 1(a), the phase separation was significant without PVC as the compatibilizer, and this means that PCL was incompatible with PMMA in this case. With the addition of PVC, small particles disappeared sharply under this magnification, as is apparent from Figure 1(b–d). This was ascribed

TABLE I
Gel Content in the Blends

Sample composition	Gel content (wt %)
PMMA/PCL (95/5)	0
PMMA/PVC/PCL (93/2/5)	13
PMMA/PVC/PCL (90/5/5)	23
PMMA/PVC/PCL (85/15/5)	12
PMMA/PVC (95/5)	22

to the compatibilization effect of PVC through the crosslinking, grafting, and hydrogen bonds involving the carbonyl group of PCL and the α-hydrogen of PVC.

Figure 1(b–d) shows that two types of domains exist at the surfaces of ternary blends: one is discrete and roundest with variant diameters; the other is continuous and fills in gaps of the former. To examine the difference between these two domains, the free-fractured surface of PMMA/PVC/PCL (90/5/5) was dipped in a mixture of ethanol and acetone (98 mL/2 mL) at 70°C for 4 h, and SEM microphotographs are presented in Figure 1(e,f) under two magnifications. It is well known that the velocity and rate of swelling decline with increasing crosslinking. Figure 1(e), compared with Figure 1(c), shows that the discrete domain is rich in crosslinking and the continuous domain encircles the former with less crosslinking or without crosslinking. For the determination of their different mechanical behaviors, they were fractured with different strains; the two types of domains are shown in the SEM microphotographs, and the part rich in crosslinking is more brittle.

Gel content

The gravimetric estimation of the amount of gel is a good, reproducible method of monitoring the crosslinking occurring in polymers. The result of the dissolution test is summarized in Table I. The gel content reached a maximum value at 5 wt % PVC. It is interesting that the amount of gel in the blends was much higher than the PVC content and even the total content of PVC and PCL. This indicates that MMA underwent grafting and participated in crosslinking as a bridge between two macromolecular chains. PCL also underwent intermolecular crosslinking, which never occurs in PCL alone (Scheme 1). Therefore, the crosslinking part contains chains of three polymers: PVC, PCL, and PMMA.

Thermal behavior

The glass-transition temperatures (T_g's) were determined from the values corresponding to the inflection
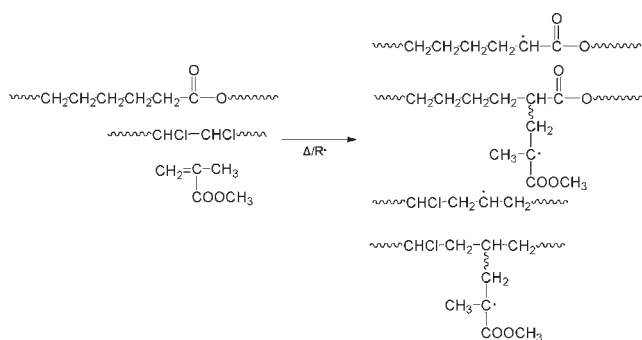
Scheme 1 Main macroradicals participating in crosslinking in the mixture. Δ = heating; R = radicals.

points of DSC curves. T_g of PVC and the melting temperature of PCL were not clearly detectable in the present cases. Figure 2 shows T_g of PMMA in blends with different components. Pure PMMA was synthesized under the same conditions used for the others, and its T_g was 109°C.

As is apparent from Figure 3, the values of T_g in the PMMA/PVC/PCL ternary blends were higher than that of any pure component. This was ascribed to the formation of crosslinking, which resulted in confined thermal behavior of the PMMA chains. The PMMA chains were confined in a crosslinked system and needed more energy to move. It was reported that when impediments were placed in front of thermal fluctuations and larger transversal and longitudinal motions of polymer chains, segments, and shorter fragments in the amorphous phase and the motions were thus restricted, T_g was elevated with respect to that of the same amorphous phase in the bulk under normal conditions.[17] However, if the crosslinked system had good compatibility with PMMA, PMMA would not exhibit confined thermal behavior. Therefore, T_g of PMMA in PMMA/PVC (95/5) was lower than that of pure PMMA, following the Fox equation.

Mechanical properties

The tensile strength and elongation at break of PMMA/PVC/PCL ternary blends with the content of PVC are presented in Figure 3. Both the tensile strength and the elongation of the blends reached a maximum value at 5 wt % PVC and then declined. The tensile strength and elongation of the PMMA/PVC/PCL (90/5/5) ternary blend were higher than those of the PMMA/PVC (95/5) binary blend by approximately 26 and 33%, respectively. Figure 4 shows the effect of the PVC content on the flexural strength and flexural modulus of the blends. The profile is quite similar to Figure 3, with a maximum value at 5 wt %. The profile of the mechanical prop-
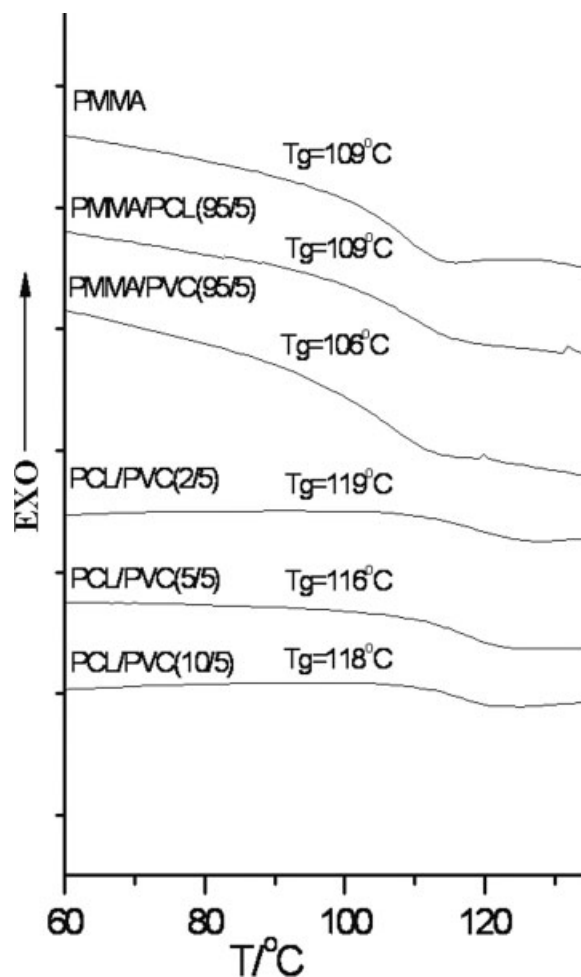

Figure 2 T_g of PMMA in different blends measured by DSC during the second heating at a constant rate of 10°C/min.

erties is clearly similar to the trend of the gel content with the content of PVC. It can be explained by the positive, beneficial effect of the crosslinking on the mechanical properties. However, crosslinking could
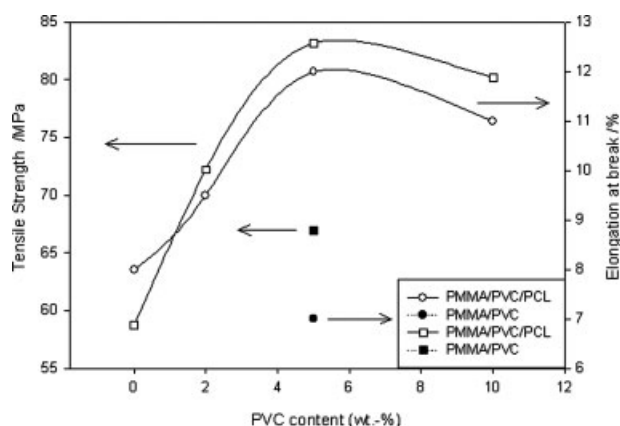
Figure 3 Tensile strength and elongation at break as functions of the PVC content.
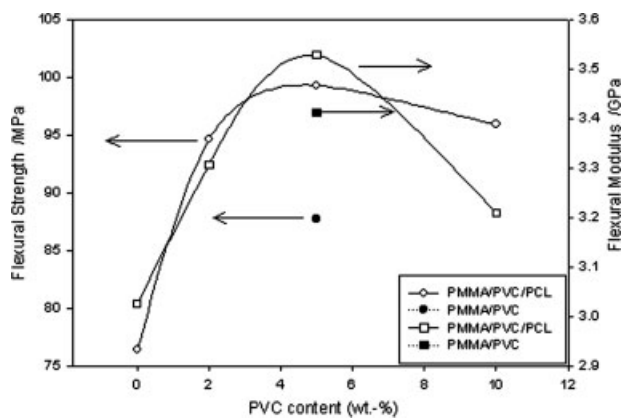
Figure 4 Flexural strength and flexural modulus as functions of the PVC content.

not improve the elongation at break because crosslinking usually makes a material more brittle. However, according to Wu's theory[18] about the brittle–ductile behavior of polymers and blends, when thin matrix ligaments are interconnected to form a pervasive network [e.g., Fig. 1(c,d)], the yielding process can then propagate and pervade over the entire deformation zone and exhibit ductile behavior. For PMMA, which is not a pseudo-ductile polymer, the improvement of the ductile behavior is limited, but it is enough to counteract the loss of toughness caused by crosslinking or even more.

CONCLUSIONS

In this study, a polymer network structure of PVC, PCL, and *in situ* formed PMMA was synthesized with PVC as a compatibilizer. The network structure was observed with SEM. The part rich in crosslinking was discretely dispersed, and the thin matrix ligaments were interconnected and formed a pervasive network. The dissolution test suggested that a simple method to generate high rates of crosslinking at a lower temperature was obtained. The obvious increase in the mechanical properties and the reinforcing effect were attributed to the formation of the crosslinking and the network structure in the blend. T_g, obtained by DSC, suggested confined thermal behavior of PMMA chains restricted by the crosslinking system.

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