In-Situ Polycondensation for Synthesis of Composites of Elastomeric Polymers and Poly(γ-methyl L-glutamate)

Yasukazu AYAKI, Masahiro RIKUKAWA, Masayoshi WATANABE,*
Kohei SANUI, and Naoya OGATA

*Department of Chemistry, Faculty of Science and Technology, Sophia University,
7–1 Kioi-cho, Chiyoda-ku, Tokyo 102, Japan
*Department of Chemistry, Yokohama National University,
156 Tokiwadai, Hodogaya-ku, Yokohama 240, Japan*

ABSTRACT: Composites of elastomeric polymers and poly(γ-methyl L-glutamate) (PMLG) were prepared by the so-called "in-situ polycondensation method" and a solution blend method. Three types of rubbers were used as matrix polymers: styrene-butadiene copolymer and two derivatives. Mechanical properties of these composite polymers were studied by tensile tests and their morphologies were observed by scanning electron microscopy. The tensile strength and modulus of the composite films obtained by the in-situ polycondensation method increased with increasing PMLG content. Although their tensile modulus values increased drastically, their ultimate elongation values were almost the same. The morphologies of the composites and the reinforcing effect of PMLG were dependent on the preparation method, on the contents of PMLG, and on an interaction between matrix polymer and PMLG.

KEY WORDS   In-Situ Polycondensation / Hydrogenated Styrene–Butadiene Copolymer / Poly(γ-methyl L-glutamate) / Mechanical Property / Morphology /

The concept of molecular composite was first proposed by Takayanagi et al.[1] and Helminiak et al.[2] The definition of the concept is that a rigid rod polymer is three-dimensionally dispersed in a flexible matrix polymer on the molecular level. This is an application of the concept of fiber reinforced plastic (FRP). However, the compatibility of rigid rod polymers, which are used as reinforcing materials, with flexible polymers as matrices is usually very poor, so that blending of these two polymers is very difficult either in the melt state or in solution. Therefore, many experiments have been done by using a compatibilizer such as graft copolymer of the two homopolymers, or having some interactions between two polymers such as ion-dipole interaction, hydrogen bonding, charge transfer, or acid-base interaction.

On the other hand, the concept of "in-situ polycondensation" was proposed in previous papers.[3-5] As illustrated in Figure 1, monomers of rigid rod polymers were dissolved in flexible polymer solution and were polymerized to form composites of rigid rod polymers which were dispersed as fine particles within the flexible polymers. The in-situ polycondensation easily provided composite polymers of insoluble and infusible reinforcing polymers to reinforce flexible matrix polymers. Some papers reported on the synthesis of microcomposites of aromatic liquid-crystalline polymers (LCP) in a polyarylate,[3] styrene-butadiene block copolymer (SBR)[4] and the microcomposites of poly(p-phenylene terephthalamide) (PPTA) with poly(acrylonitrile-co-butadiene) (NBR) and SBR.[5] Imai also reported[6,7] the synthesis of polyaramid in

· Monomer
∽ Flexible Chain Polymer (Matrix)
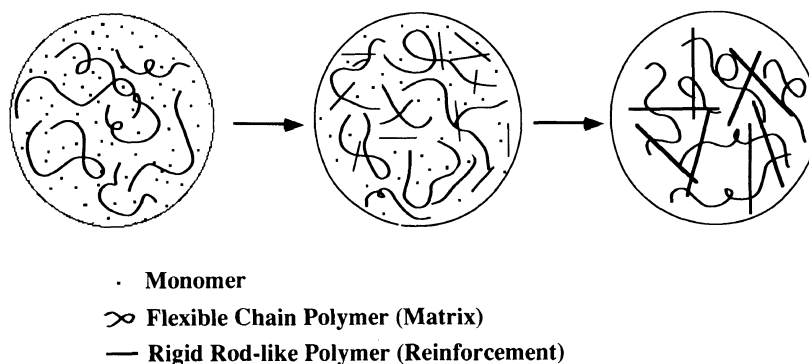— Rigid Rod-like Polymer (Reinforcement)

Figure 1. Concept of the *in-situ* polycondensation.

polyethersulfone solution. These papers described that the *in-situ* polycondensation method was suitable to obtain polymer composites in comparison with the solution blend methods. All of these systems needed reprecipitation to recover composite materials from polymerization solution so as to remove impurities generated in the synthesis of the reinforcing polymer. At that time, some questions arose about whether the morphology of the *in-situ* formed LCP might be changed by aggregations. Therefore, the *in-situ* polycondensation was carried out without reprecipitation procedure by using directly solvent casting. Further, when two polymers have such interactions as hydrogen bonding between flexible polymer and the *in-situ* formed LCP, much improvements of high performance polymer composites would be attained because of the enhanced compatibilities.

This study deals with the *in-situ* formation of poly(γ-methyl L-glutamate) (PMLG) which is used as a reinforcing material. It is known that PMLG forms an α-helix, which is a rigid rod-like state. When γ-methyl L-glutamate NCA (MLGNCA) polymerizes with an initiator, there are no eliminated products except carbon dioxide. Therefore, it is expect that solvent casting can be applied to obtain films directly from the polymerization solution. Composites of SBR or its derivatives and PMLG were prepared both by the *in-situ*

polycondensation and the solution blending methods and their mechanical properties were investigated.

EXPERIMENTAL

Chemicals

Three types of elastomeric polymers were used as matrix polymers: SBR (S40), hydrogenated SBR (HS20), and its derivative (HSM20). S40 ($M_w = 22800$) containing 40 wt% of styrene units and HS20 ($M_w = 50000$) containing 20 wt% of styrene units were commercially available (TR 2000) from the Japan Synthetic Rubber Co., Ltd. HSM20 ($M_w = 50000$), which was a hydrogenated styrene-butadiene block copolymer containing 1 wt% of maleic anhydride and 20/80 (w/w) of styrene/hydrogenated butadiene units, was kindly provided by the Asahi Chemical Industry Co., Ltd., and the preparation had already been reported.[8] All of them were dried under vacuum at room temperature for 7 days before use.

MLGNCA, which was provided by the Mitsubishi Kasei Corp., was used without purification. In an argon-filled dry box, MLGNCA (3.92 g) was dissolved in 400 ml of chloroform. Then 7.0×10^{-2} cm^3 of 10 vol% dichloroethane solution of *n*-hexylamine was added under argon atmosphere and stirring was continued at 30—35°C for 6 h. After

recovery of PMLG by reprecipitation, the intrinsic viscosity (0.01 g, 0.05 g, 0.1 g in 10 ml of dichloroacetic acid) was measured at 25°C.

Syntheses of Composites

In-Situ Polycondensation Method. MLGN-CA was polymerized in 5 wt% of dichloroethane solution of S40, or in 2 wt% of chloroform solution of HS20 and HSM20. The concentrations of the polymerization solutions were limited by solubility of MLGNCA in both solvents. A typical *in-situ* polycondensation was carried out as follows: in an argon-filled dry box, 0.872 g of MLGNCA was dissolved in a chloroform solution of HSM20 (6 g in 200 ml). Then 3.1×10^{-2} cm^3 of 10 vol% dichloroethane solution of *n*-hexylamine was added under argon. The stirring was continued at 30—35°C for 6 h. The polycondensation solution, just as prepared, was cast onto a poly(tetrafluoroethylene) (PTFE) plate, and dried at room temperature for 4 days, then in vacuum for 4 days. Various composites were synthesized in the same way.

Solution Blend Method. 5 wt% dichloroethane solution of S40 was mixed with 5 wt% of dichloroethane solution of PMLG; 2 wt% chloroform solution of HS20 or HSM20 was mixed with 5 wt% of chloroform solution of PMLG. The solution blend was carried out at the same composite concentration as the *in-situ* polycondensation in each matrix polymer. The stirring was continued at 30—35°C for 6 h. Then, the solution was directly used for casting onto PTFE plates to form films. The resulting films were dried at room temperature for 4 days, and in vacuum for 4 days. Several weight ratios of PMLG to the elastomeric polymers were used to prepare composites by this blend method.

Characterization of the Films

Mechanical properties, dynamic mechanical properties, and morphology of the films obtained by the *in-situ* polycondensation solvent casting were investigated.

A small amount of the polycondensation solution was directly spread onto a KBr plate to form the films for FT-IR measurements by drying. FT-IR spectra of the films were measured with Nippon Denshi JIR-RFX 3001.

Dynamic mechanical properties were measured using a Seiko I DMS 100 at 1 Hz, under a nitrogen atmosphere with a heating rate of 2°C min^{-1} for elastomers and its composites.

Morphology of the film surface fractured in liquid nitrogen was observed by scanning electron microscopy (SEM, Hitachi S-430).

Mechanical properties were measured with a Shimadzu AGS-1kNA tensile machine at room temperature at the cross speed of 30 mm min^{-1} for all samples.

RESULTS AND DISCUSSION

PMLG obtained by polymerizing MLGN-CA in chloroform had the molecular weight (M_w) of 23000, which was calculated from the intrinsic viscosity ($[\eta]$) of 0.756 dl g^{-1} according to the following equation[9]:

$$[\eta] = 0.00224 \times M_w^{0.58}$$

The *in-situ* polycondensation of MLGNCA in either HS20 or HSM20 solutions was carried out to measure rates of polymerization of MLGNCA in polymer solutions. Rates were estimated by elemental analysis of the obtained films, as shown in Figure 2 which was measured at 20 wt% content of MLGNCA in polymer solutions of HSM20 and HS20. The rate of polycondensation of MLGNCA in HSM20 solution was slower than that in HS20 solution. MLGNCA didn't react completely in either polymer solutions. After the polymerization for 6 h, the composite films could be obtained directly from the solutions by casting onto a PTFE plate.
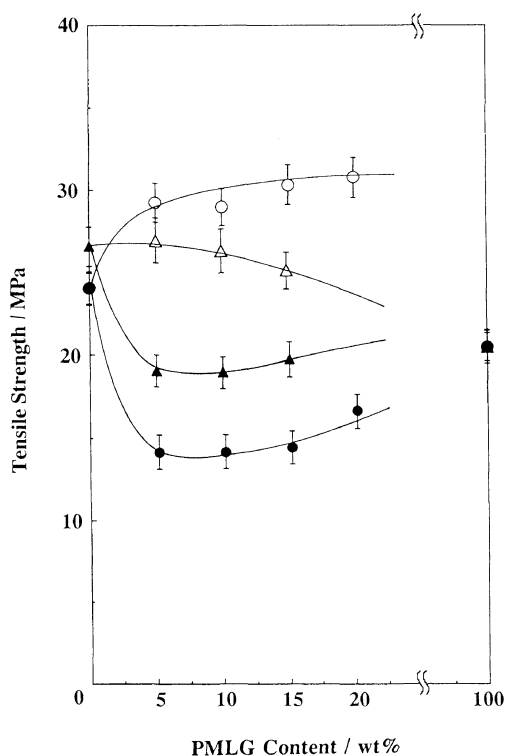
HS20/PMLG composite films were heterogeneous and the film surface was too rough to study their mechanical properties. S40/PMLG and HSM20/PMLG composite systems, however, gave transparent composite films.
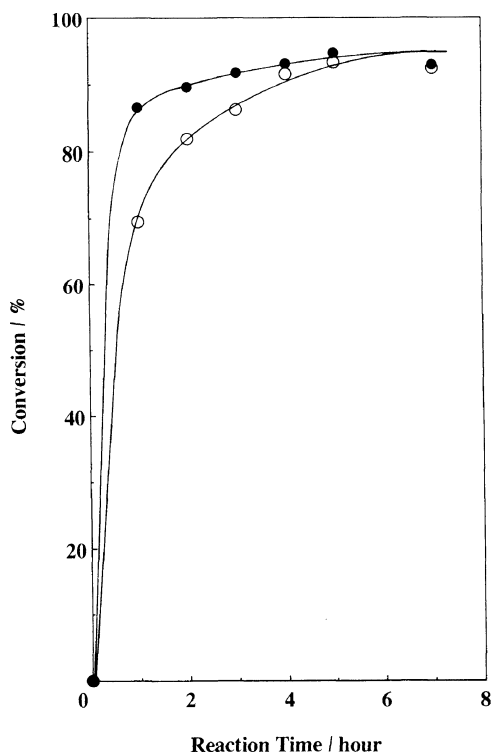
Figure 2. Time conversion curves of polymerizations of MLGNCA in polymer solutions: ○, in HSM20; ●, in HS20.

Figure 3. PMLG content dependence of tensile strength of the composite films: △, obtained by the *in-situ* polycondensation method in S40/PMLG system; ▲, obtained by the solution blend method in S40/PMLG system; ○, obtained by the *in-situ* polycondensation method in HSM20/PMLG system; ●, obtained by the solution blend method in HSM20/PMLG system.

Figure 3 shows tensile strength of the composite films as functions of PMLG contents. The tensile strength of the films prepared by the *in-situ* polycondensation method was higher than that by the solution blend method in both S40/PMLG and HSM20/PMLG composite systems. The HSM20/PMLG composite films obtained by the *in-situ* polycondensation method showed higher tensile strength than that of S40/PMLG composites. The tensile strength of HSM20/PMLG composites increased with increasing PMLG content and was higher than the tensile strength of each corresponding films of HSM20 and PMLG. On the other hand, the composite films of HSM20/PMLG systems obtained by the solution blend method showed the strength of the films lower than that of S40/PMLG system.
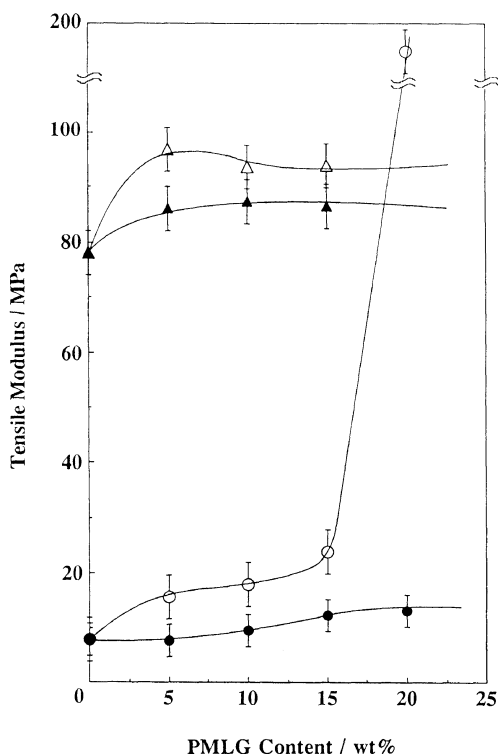
Tensile modulus of the composite films in both systems and both methods, increased with increasing PMLG content, as shown in Figure 4. The modulus of the composite films prepared by the *in-situ* polycondensation method was higher than that by the solution blend method in both systems. When the composite prepared by the *in-situ* polycondensation method containing 20 wt% of PMLG in the HSM20/PMLG composite system, it had very high tensile modulus which was 1/6 its value of PMLG homo-film (tensile modulus of PMLG homo-films is as high as 1160 MPa).

Figure 5 plots the ultimate elongation of the composite films as a function of PMLG content. Normal composite systems indicate that ultimate elongation of polymer composite

328

Figure 4. PMLG content dependence of tensile modulus of the composite films: △, obtained by the *in-situ* polycondensation method in S40/PMLG system; ▲, obtained by the solution blend method in S40/PMLG system; ○, obtained by the *in-situ* polycondensation method in HSM20/PMLG system; ●, obtained by the solution blend method in HSM20/PMLG system.
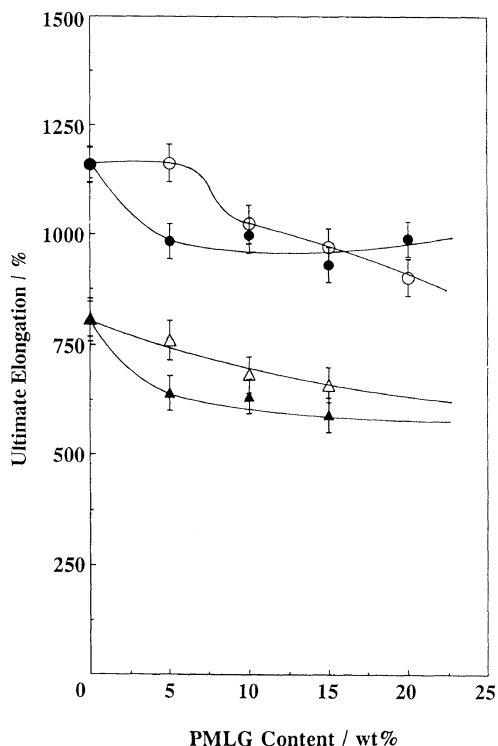
Figure 5. PMLG content dependence of ultimate elongation of the composite films: △, obtained by the *in-situ* polycondensation method in S40/PMLG system; ▲, obtained by the solution blend method in S40/PMLG system; ○, obtained by the *in-situ* polycondensation method in HSM20/PMLG system; ●, obtained by the solution blend method in HSM20/PMLG system.

usually becomes remarkably low with increasing tensile strength or modulus. It is very interesting that this composite system had the ultimate elongation of the composite films enough to maintain the characteristics of elastomers. These mechanical properties might be related to the morphologies of PMLG in the composite films.

Figure 6 shows the fracture surfaces of the composite films. PMLG was dispersed in matrix polymers, not at the molecular level, and aggregated to form particles. The sizes of the particles of PMLG shown in Figure 6-(c), (d) were almost the same. Comparing among Figure 6-(a) and 6-(b), or 6-(c) and 6-(e), the sizes of the particles in the composite films

obtained by the *in-situ* polycondensation method were much smaller than those obtained by the solution blend method in the both S40/PMLG and HSM20/PMLG systems. As shown in Figure 6-(b) and 6-(e), the particle size of PMLG in HSM20/PMLG composite films prepared by the *in-situ* polycondensation method were smaller than those in S40/PMLG composite films. The sizes of the particles of PMLG in the composite films didn't depend on the content of PMLG, but depended on the preparation method and the interaction between matrix polymer and PMLG. At 20 wt% content of PMLG in the HSM20/PMLG composite system synthesized by the *in-situ* polycondensation method (Figure 6-(f)),
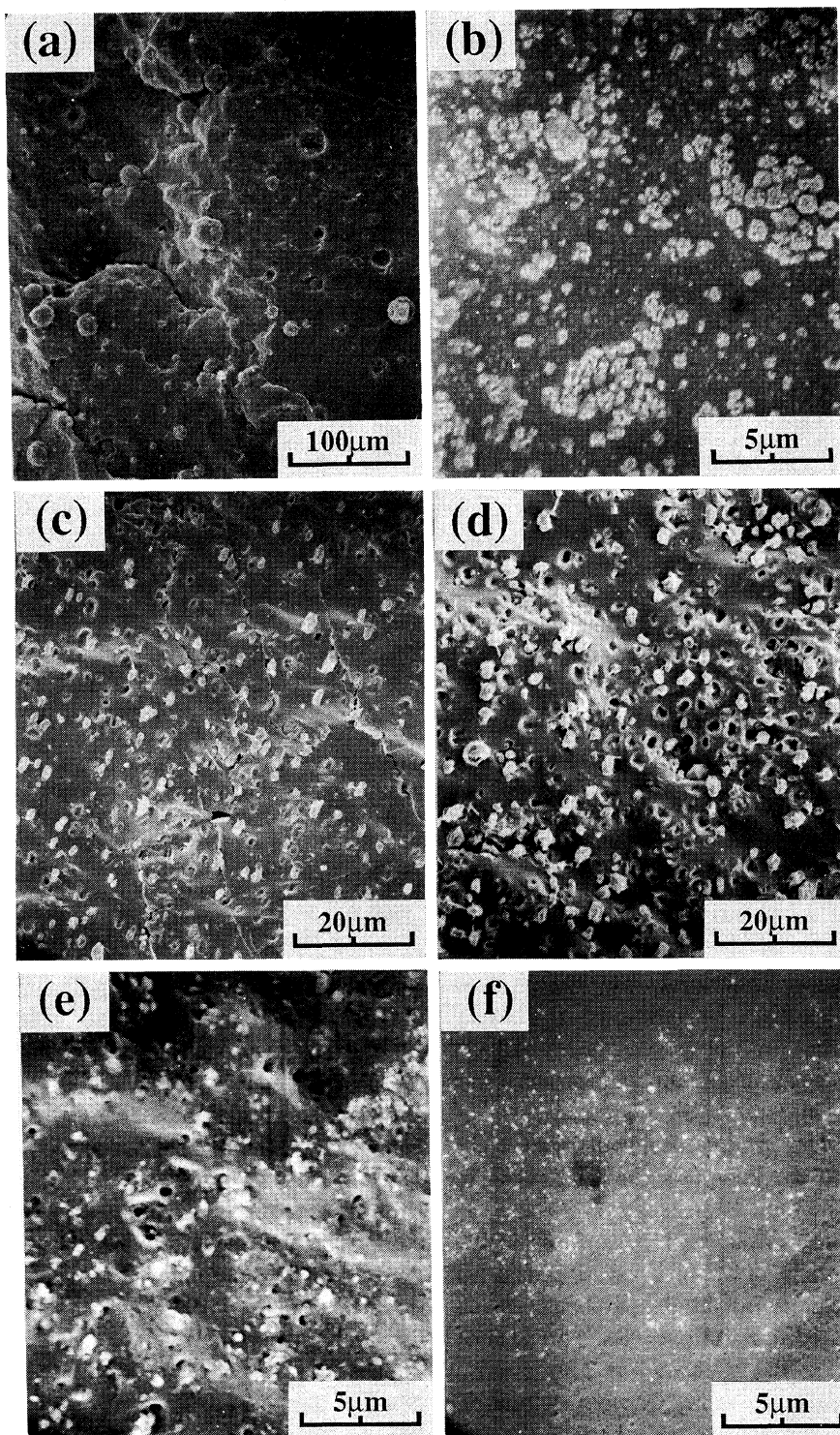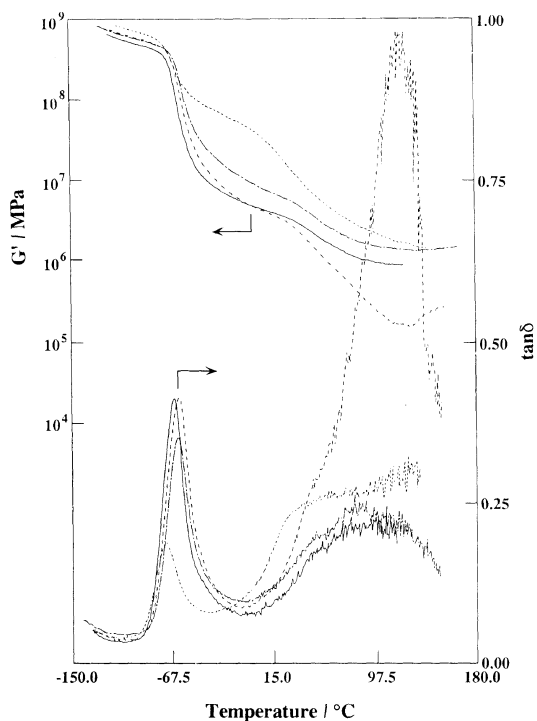
Figure 7. Temperature dependence of G' and $\tan\delta$ of HSM20 and its composite films: ------, containing 20 wt% of PMLG obtained by the *in-situ* polycondensation method; -·--·-, containing 10 wt% of PMLG obtained by the *in-situ* polycondensation method; ---, containing 10 wt% of PMLG obtained by the solution blend method; ——, HSM20 alone.

shown in Figure 7, in which the data of the composite films containing 10 wt% of PMLG prepared by both methods and 20 wt% of PMLG prepared by the *in-situ* polycondensation method are shown. In both cases, G' values of the composites obtained by both methods were higher than that of HSM20 homo-films at low temperature. Modulus values of the composites obtained by the *in-situ* poly-condensation method were also higher than that of HSM20 homo-films in high temperature range. On the contrary, the modulus of the composite obtained by the solution blend method suddenly became low at near room temperature. In the *in-situ* polycondensation system, the intensity of the $\tan\delta$ peak around 50°C corresponding to the glass transition temperature of hydrogenated butadiene unit decreased with increasing PMLG content, while the intensity of the $\tan\delta$ around 60°C corresponding to the T_g of styrene unit increased. This result might suggest that the copolymer from HSM20 and PMLG might have a strong interaction so that the movements of HSM20 chains were restricted because of fine dispersion of PMLG. On the other hand, the film containing 10 wt% of PMLG obtained by the solution blend method showed the same $\tan\delta$ peak corresponding to T_g of hydrogenated butadiene unit as that of HSM20 homo-film and the peak corresponding to styrene unit drastically increased. This might be caused by growth of cracks around the macrodomains of PMLG for concentrated stress.
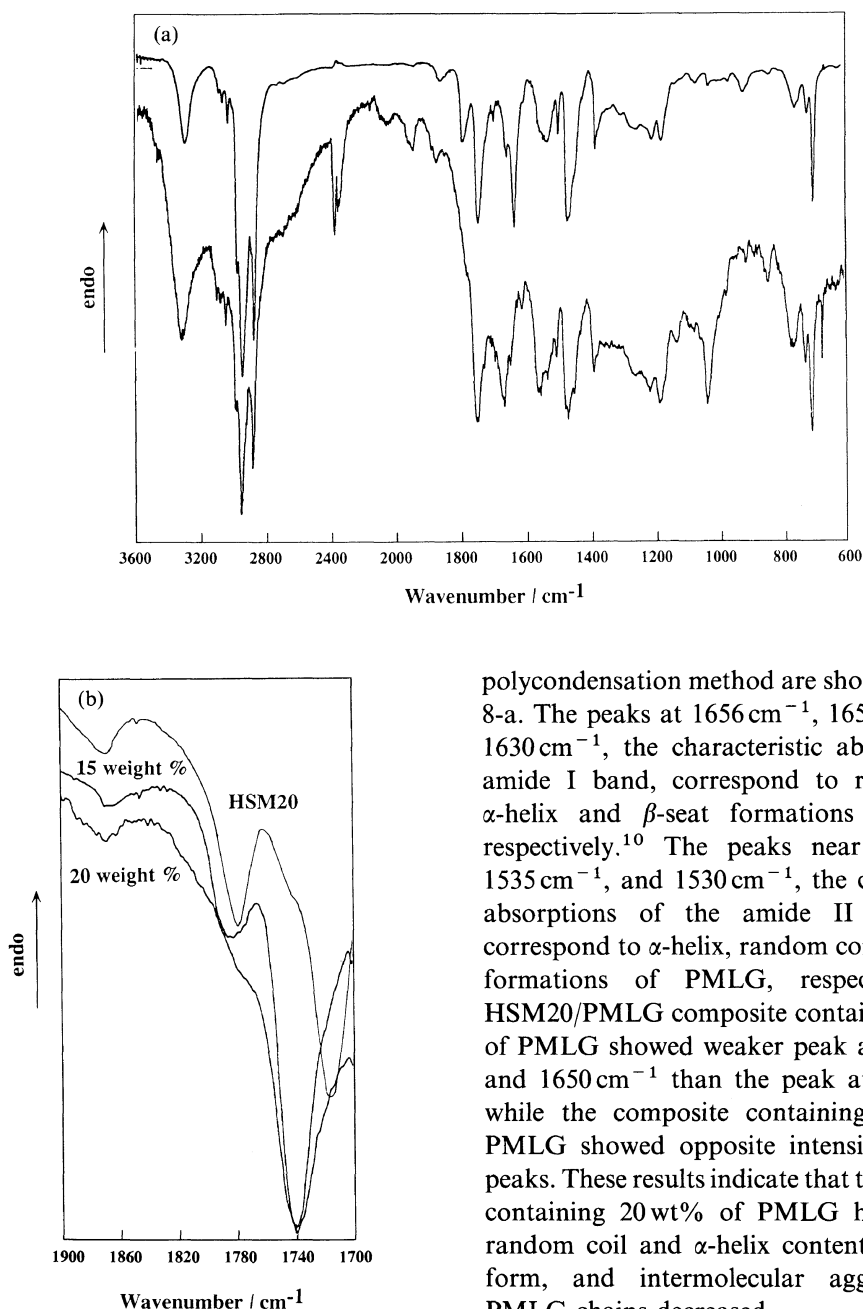
which showed the remarkable improvement of mechanical properties, the fracture surface of the film was extremely smooth in comparison with other photographs. These morphologies were found to be the most important factor for reinforcing PMLG mechanical properties.

Dynamic mechanical measurements, *i.e.*, loss tangent ($\tan\delta$) and storage shear modulus (G') in HSM20/PMLG composite system, are

FT-IR spectra of the composites (15 wt% and 20 wt% content of PMLG in HSM20/ PMLG system) prepared by the *in-situ*

Figure 6. SEM photographs of the fracture surfaces of the composite films: (a) containing 10 wt% of PMLG obtained by the solution blend method in S40/PMLG composite system; (b) containing 10 wt% of PMLG obtained by the *in-situ* polycondensation method in S40/PMLG composite system; (c) containing 10 wt% of PMLG obtained by the solution blend method in HSM20/PMLG composite system; (d) containing 20 wt% of PMLG obtained by the solution blend method in HSM20/PMLG composite system; (e) containing 10 wt% of PMLG obtained by the *in-situ* polycondensation method in HSM20/ PMLG composite system; (f) containing 20 wt% of PMLG obtained by the *in-situ* polycondensation method in HSM20/PMLG composite system.

(a)

endo

3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 600

Wavenumber / cm^{-1}

(b)

15 weight %

HSM20

20 weight %

endo

1900 1860 1820 1780 1740 1700

Wavenumber / cm^{-1}

Figure 8. (a) FT-IR spectra of HSM20/PMLG composites synthesized by the *in-situ* polycondensation method: ——, containing 15 wt% of PMLG, ——, containing 20 wt% of PMLG. (b) FT-IR spectra of HSM20 and its composites obtained by the *in-situ* polycondensation method (15, 20 wt% content of PMLG).

polycondensation method are shown in Figure 8-a. The peaks at 1656 cm^{-1}, 1650 cm^{-1}, and 1630 cm^{-1}, the characteristic absorptions of amide I band, correspond to random coil, α-helix and β-seat formations of PMLG, respectively.[10] The peaks near 1546 cm^{-1}, 1535 cm^{-1}, and 1530 cm^{-1}, the characteristic absorptions of the amide II band, also correspond to α-helix, random coil, and β-seat formations of PMLG, respectively. The HSM20/PMLG composite containing 15 wt% of PMLG showed weaker peak at 1656 cm^{-1} and 1650 cm^{-1} than the peak at 1630 cm^{-1}, while the composite containing 20 wt% of PMLG showed opposite intensities of these peaks. These results indicate that the composite containing 20 wt% of PMLG had a higher random coil and α-helix content than β-seat form, and intermolecular aggregation of PMLG chains decreased.

Figure 8-b shows the FT-IR spectra of HSM20 and its composites synthesized by the *in-situ* polycondensation method. The absorption band at 1780 cm^{-1} due to maleic anhydride units in the composite became broad and decreased with increasing PMLG content,

in comparison with that in HSM20. This indicates that maleic anhydride units in HSM20 might partially react with the end groups of the resulting PMLG during the *in-situ* polycondensation of MLGNCA in HSM20 solution. The graft copolymer produced from HSM20 and PMLG may act as a compatibilizer in the HSM20/PMLG composite system. Therefore, the HSM20/PMLG composite containing 20 wt% of PMLG resulted in a fine dispersion of PMLG in the composite owing to the formation of the graft-copolymer, and such remarkable improvement of mechanical properties was proved by the morphological observation of PMLG in HSM20.

CONCLUSION

S40/PMLG and HSM20/PMLG composites were successfully synthesized by the *in-situ* polycondensation method and the solution blend method. The sizes of the particles of PMLG in the composite films didn't depend on the content of PMLG, but depended on the preparation method and the interaction between matrix polymer and PMLG. The reinforcing effect of PMLG was strongly dependent on the particle size of PMLG in the composite films. The tensile strength of S40/PMLG composite films decreased and its modulus increased with increasing PMLG content. On the other hand, the strength and the modulus of the HSM20/PMLG composites synthesized by the *in-situ* polycondensation method increased with increasing PMLG content. These results were due to a fine dispersion of PMLG in HSM20 by the *in-situ* polycondensation method and also to existing maleic anhydride units to interact with PMLG.

The *in-situ* polycondensation method made possible to prepare composite materials of PMLG and elastomeric polymers which were thermodynamically incompatible. Furthermore, it might be possible to obtain so-called molecular composites by using a more compatible polymer pair which would have much stronger interactions with each other.

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