Additive Effect of Poly(ethylene oxide) on Polypropylene/Fibrous Cellulose Composite: Effects of Additive Amount of Poly(ethylene oxide) on Young's Modulus and Morphology

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ABSTRACT: In this work, the additive effects of the poly(ethylene oxide) (PEO) on the Young's moduli of two kinds of polypropylene (PP)/fibrous cellulose (FC) composite were studied using the Kerner–Nielsen equation. In the case of the PP/maleated PP (MAPP)/FC + PEO composite, all the values of the moduli with the various PEO contents were in good agreement with the theoretical values obtained from the Kerner–Nielsen equation. Whereas the moduli of the PEO/FC + PP/MAPP composite followed the Kerner–Nielsen equation about 6 vol % of the PEO content and then unexpectedly deviated. In the scanning electron microscopy (SEM) observation, the PP/MAPP/FC + PEO composite was found to have a sea-island morphology corresponding to the PP/MAPP/FC matrix and the PEO phase. This morphology had been unchanged against the increase of the PEO content. Whereas in the case of the PEO/FC + PP/MAPP composite, the SEM micrographs showed that that the interface between the FC and the PP became worse with the increase of the PEO content, indicating that the formation of the PP/MAPP/FC matrix was blocked by the excess PEO. The deviation of the Young's moduli from the Kerner–Nielsen equation was due to the blocking of the PEO. It was found that the adequate combination of the PEO and the MAPP was able to supply the increase of the toughness of the PP/FC composite by investigating the dependence of the PEO/FC + PP/MAPP composite on the MAPP content. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1656–1663, 2009

Key words: composites; fibers; poly(propylene) (PP); polyethers

INTRODUCTION

Cellulose has attracted much attention of many researchers as filler/reinforcement for composite materials.[1–7] In particular, the attention has recently concentrated on its high-modulus and renewability from both viewpoints of mechanical and environmental advantages. Composite based on cellulose has been considered as a useful way to take advantage of the existing features. To satisfy the need for a renewable construction material, a combination of polypropylene (PP) and fibrous cellulose (FC)[1,4–7] has emerged as a new class of structural composites. The PP/FC composite is, however, considerably brittle. Improvement of the mechanical properties has been required.

It is well known that addition of elastomer is effective in improving toughness of brittle polymer.[8–12] The enhanced toughness is to be due to a strain constraint relaxation resulting from void formation in the dispersed elastomer phase. In this relaxation mechanism, the elastomer having a weaker mechanical strength is desirable in the structural viewpoint of the preferential void formation. In our previous work,[13] we reported that PP/poly(ethylene oxide) (PEO) blend sufficiently fulfilled the toughening criterion. PEO is a flexible polymer, and its mechanical strength is considerably lower than that of PP. In addition, although PEO is a crystalline polymer, the elasticity is considerably lower than that of PP. PEO would act as an elastomer in the PP matrix because of its lower elasticity. When tensile stress is applied, the weaker PEO phase is deformed. Many voids are preferentially generated in the PEO phase, leading to the relaxation of strain constraint. PEO and PP are incompatible. The existence of PEO phase hardly impaired ductility of the PP. The improvement method can be similarly applied for the PP/FC composite. In our previous work, we have presented that PEO has been useful to improve both stiffness and toughness of the PP/FC.[13] The

effects of PEO on the tensile and fracture behavior of PP/FC composite depended on the preparation method.[13] The strain and the fracture energy of the PP/FC composite increase with PEO addition. Whereas in the case of the PP added to the FC/PEO composite, the strain and the fracture energy exhibited a great increment when compared with the original PP/FC composite. The difference of both mechanical properties implies that the structure of the PP/FC composite is strongly influenced by the order of the PEO addition.

The purpose of this study is to clarify the effects of additive amount of PEO on the structure of the PP/FC composite. The structure was estimated by the matching of the Young's moduli values against the Kerner–Nielsen equation[14,15] and was studied by wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) measurements, respectively.

EXPERIMENTAL

Materials

PP (meso pentad fraction = 98%) was supplied by Japan Polypropylene Co. The number-average molecular weight (M_n) and the polydispersity (M_w/M_n) were 4.6×10^4 and 5.7, respectively. The density was about 0.90 g/cm^3.

PEO (M_n = 20,000) was purchased from Wako Pure Chemical Industries, Ltd. The density was about 1.13 g/cm^3. According to the company's data, the meting point (T_m) was from 56 to 63°C.

$$\text{PEO:} \quad \text{HO} \left[\text{C}_2\text{H}_4 - \text{O} \right]_n \text{OH}$$
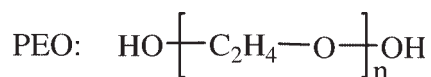
FC (W-100GK) was donated by Nippon Paper Chemicals Co. Ltd. The moisture of the FC was below 0.7 wt %. The dimensions were over 90% pass 100 mesh, and the average length was about 37 µm. The FC was dried in desiccator for 7 days before use. The density was about 1.55 g/cm^3.

Maleated PP (MAPP) was used to modify the FC surface. MAPP (maleic anhydride content ca. 8 wt %) was purchased from Sigma Aldrich. The M_n and M_w/M_n of MAPP were 3.9×10^3 and 2.3, respectively. The density was about 0.90 g/cm^3.
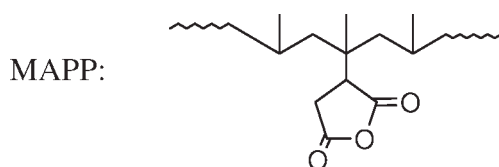
MAPP:

Preparation of composite

PP/FC composite was classified into two types according to the difference in sequence of mixing. In the case of the composite denoted as "PP/MAPP/FC + PEO," this means that PP, MAPP, and FC were first mixed, and then PEO was added. Whereas "PEO/FC + PP/MAPP" means that PEO and FC were first mixed, and then PP and MAPP were done. These PP/FC composites were prepared with a fixed amount (ca. 30 wt %) of the FC using an Imoto Seisakusyo IMC-1884 melting mixer. After a small amount of phenolic antioxidant (Adekastab AO-60, ca. 0.5 wt %) was added, the mixing was performed. The mixing condition was 180°C at 60 rpm. After the addition of all components, the mixing was performed for 5 min. The samples were molded as the films (100 µm) by compression molding at 190°C under 40 MPa for 5 min and were quenched at 20°C. The samples obtained were dried in desiccator over 1 day before measurement and testing.

Tensile testing

Stress-strain behavior was observed using a SHIMADZU EZ-S at a cross-head speed of 5 mm/min. The sample specimens were cut with dimensions 30 mm × 2 mm × 0.1 mm shape in which the gauge length was 10 mm. All of tensile testing was performed at 20°C. The values of Young's modulus were obtained from the slope of the stress-strain curve (until about 1% of the strain value). All tensile data obtained are the average values of five measurements.

WAXD measurement

WAXD diffractograms were recorded in reflection geometry at 2° (2θ/min) under Ni-filtered Cu Ka radiation (λ = 0.154 nm) using a RIGAKUXG-RINT 1200 diffractometer.
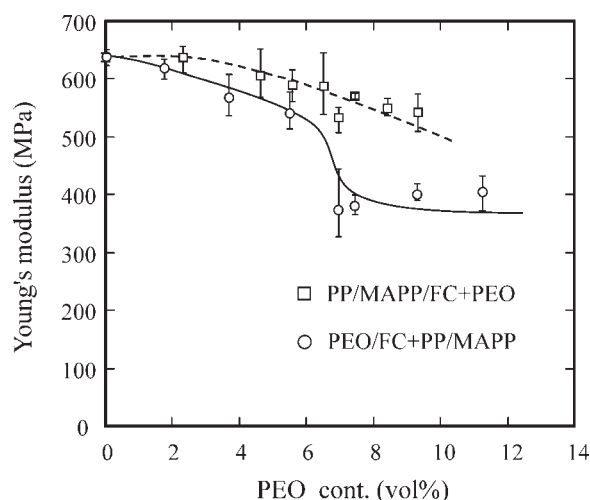

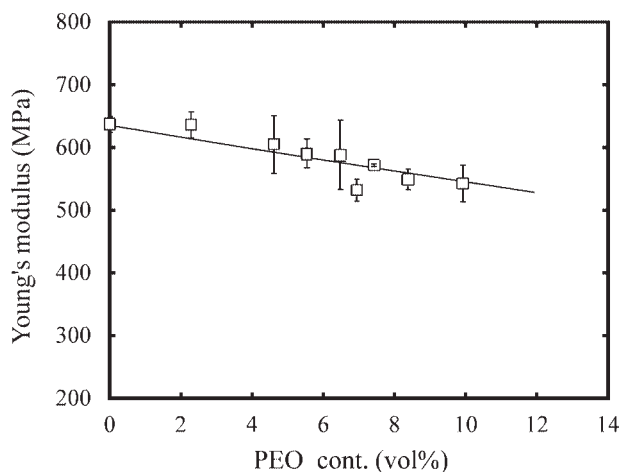**Figure 1** Young's modulus versus PEO content (vol %).

Figure 2 Young's modulus versus PEO content (vol %) for PP/MAPP/FC + PEO: The solid line is a fit, obtained using Kerner–Nielsen equation and the $\Psi(=2)$ is a factor depending on the maximum packing fraction of component.
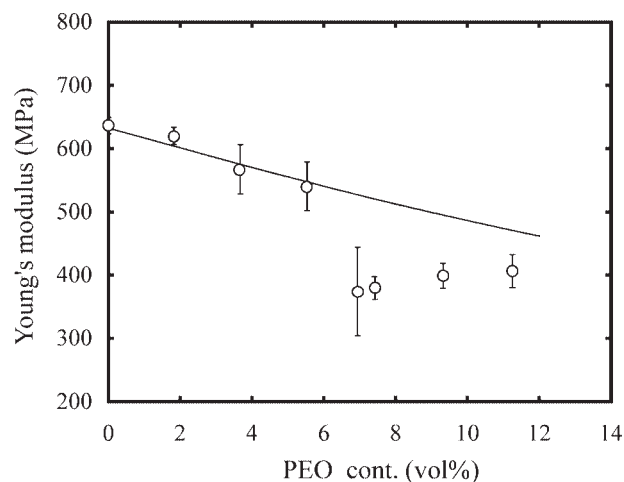

Figure 3 Young's modulus versus PEO content (vol %) for PEO/FC + PP/MAPP: The solid line is a fit, obtained using Kerner–Nielsen equation and the $\Psi(=6)$ is a factor depending on the maximum packing fraction of component.

DSC measurement

DSC measurements were made with a SHIMADZU DSC-60. The samples of about 5 mg weight were sealed in aluminum pans. The measurement of the samples was carried out from 40 to 200°C at a heating rate of 10°C/min under a nitrogen atmosphere.

SEM measurement

The morphology of composite was examined with a JEOL JSM-5800 at 30 kV. The composite films were fractured in liquid nitrogen, and then the fractured surface was sputter-coated with gold.

RESULTS AND DISCUSSION

Figure 1 shows the plot of Young's modulus versus PEO content for the PP/MAPP/FC + PEO and the PEO/FC + PP/MAPP composites. In both cases, the Young's moduli are decreasing with increase in the

PEO. The behavior implies that the existence of PEO disturbs the stress transference from the matrix to the FC. The decreasing tendencies are, however, different in each other. It should be noted here that the moduli of the PEO/FC + PP/MAPP composites rapidly drop at around 7 wt % content of PEO. This behavior implies that a change of the composite structure, for example, FC arrangement, occurs at the PEO content.

Effect of composite structure on Young's modulus can be studied by the Kerner–Nielsen equation.[14,15]

$$M = M_1 \left(\frac{1 + AB\phi}{1 - B\psi\phi} \right) \tag{1}$$
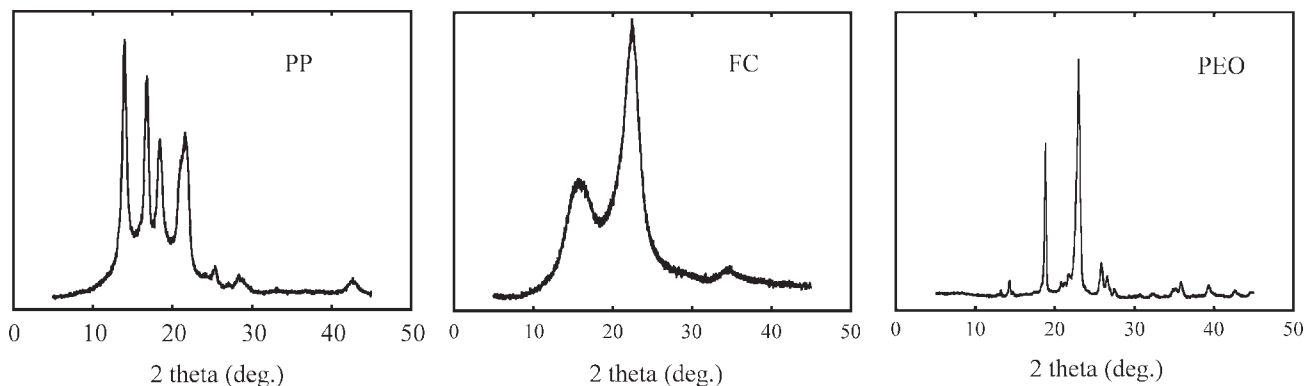
in which

$$A = k_E - 1 \tag{2}$$

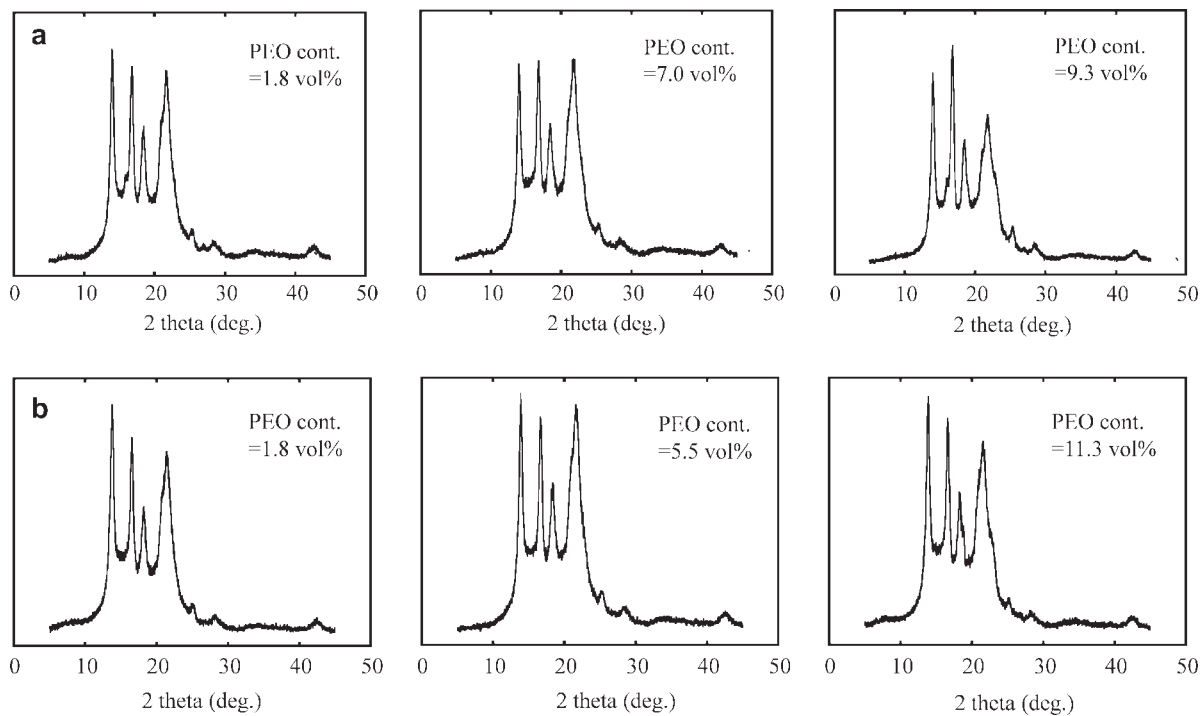**Figure 4** WAXD profiles of PP, FC, and PEO.

Figure 5 (a) WAXD profiles of PP/MAPP/FC + PEO composites with different PEO contents and (b) WAXD profiles of PEO/FC + PP/MAPP composites with different PEO contents.

$$B = \frac{(M_2/M_1) - 1}{(M_2/M_1) + A} \qquad (3)$$

where M, M_1, and M_2 are moduli of the composite, matrix, and additional component, respectively; ϕ is the volume fraction (vol %) of component; k_E is the Einstein coefficient; A is the transference efficiency from the matrix to the fiber; and ψ is a fitting factor that depends on the maximum packing fraction of additional component. The Kerner–Nielsen equation can be applied to ternary composite.[16] The PP/MAPP/FC + PEO and the PEO/FC + PP/MAPP composites can also be regarded as ternary composite due to the low (0.5 wt %) content of MAPP. In the composites, we assume that the matrix and additional component are corresponding to the PP/MAPP/FC and the PEO, respectively. The M_1 (636.8 MPa) and the M_2 (44.1 MPa) were directly obtained from PP (79.5 vol %)/MAPP (0.6 vol %)/FC (19.9 vol %) and from the PEO, respectively. To obtain the k_E, the Poisson's ratio ν is required. The ν value of composite is approximately given by a mixture rule[17]:

$$\nu = \nu_m \phi_m + \nu_f \phi_f \qquad (4)$$

where ν_m and ν_f are the Poisson's ratios of matrix (PP) and filler (FC), respectively; ϕ_m and ϕ_f are the volume fractions of matrix and filler, respectively. The Poisson's ratios used in this approach having the following values: $\nu_m = 0.38$[18] and $\nu_f = 0.30$.[17]
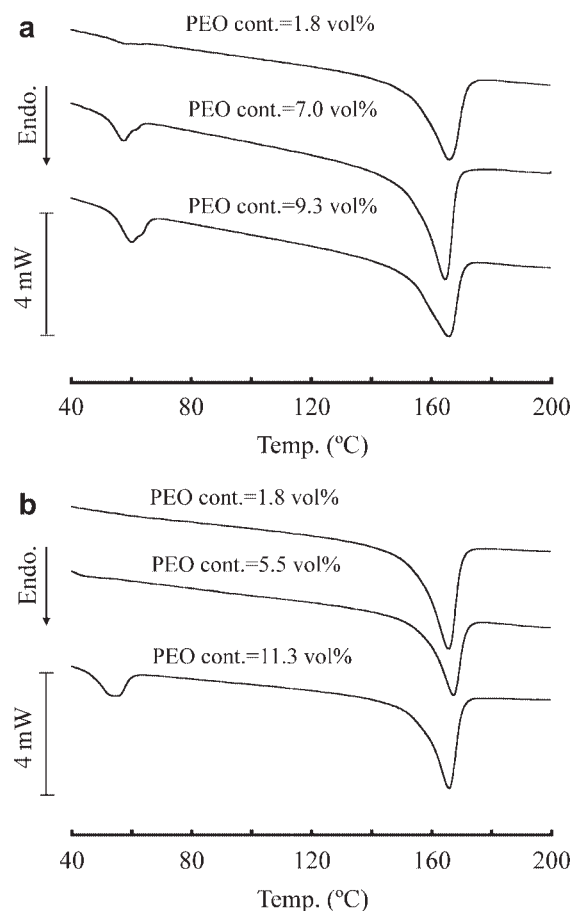

Figure 6 (a) DSC curves of PP/MAPP/FC + PEO composites with different PEO contents and (b) DSC curves of PEO/FC + PP/MAPP composites with different PEO contents.
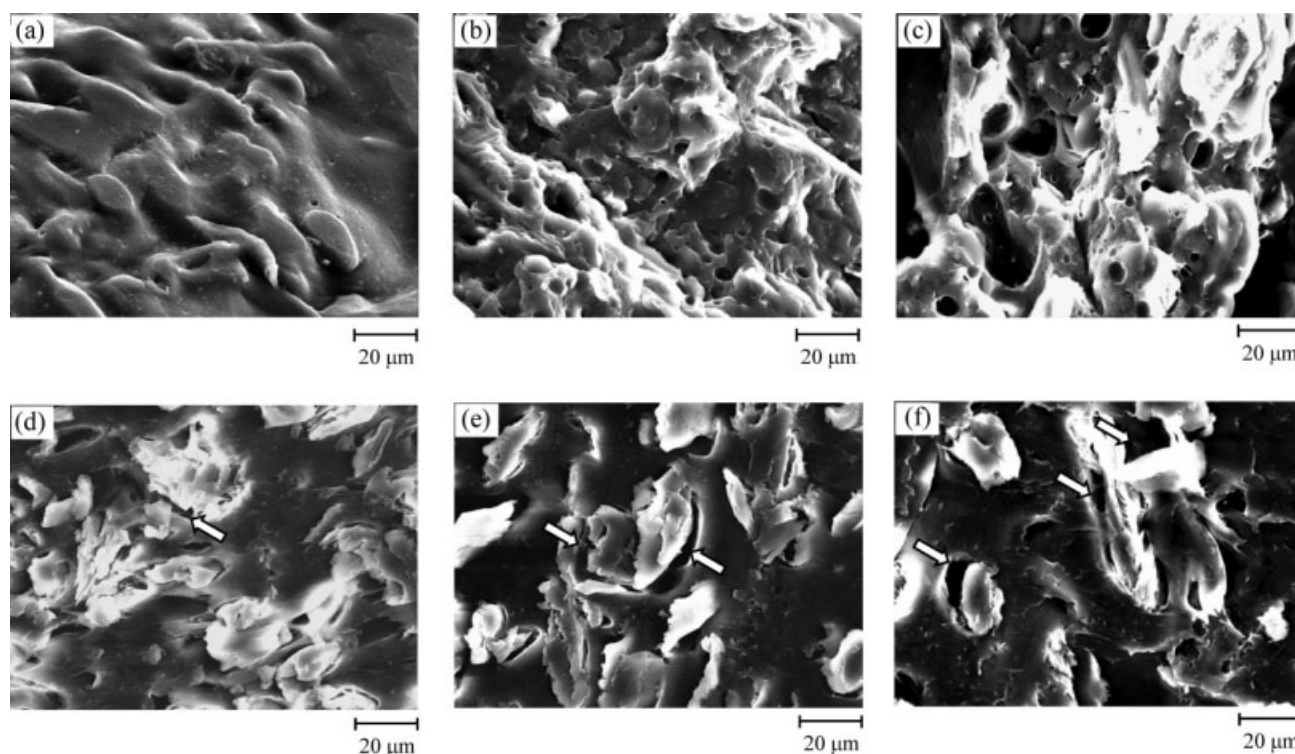
Figure 7 SEM micrographs of fracture surfaces of PP/MAPP/FC + PEO and surfaces of PEO/FC + PP/MAPP. The arrows indicate the PEO interface. a: PP (77.1 vol %)/MAPP (0.6 vol %)/FC (20.0 vol %) + PEO (2.3 vol %); b: PP (72.2 vol %)/MAPP (0.6 vol %)/FC (20.3 vol %) + PEO (6.9 vol %); c: PP (69.7 vol %)/MAPP (0.6 vol %)/FC (20.4 vol %) + PEO (9.3 vol %); d: PEO (1.8 vol %)/FC (20.0 vol %) + PP (77.6 vol %)/MAPP (0.6 vol %); e: PEO (5.5 vol %)/FC (20.2 vol %) + PP (73.7 vol %)/MAPP (0.6 vol %); and f: PEO (11.2 vol %)/FC (20.5 vol %) + PP (67.7 vol %)/MAPP (0.6 vol %).

The ν obtained is 0.36. According to the data of Nielsen,[15] in a rigid matrix having near ν value (0.35), the Einstein coefficient k_E was 3.81. Therefore, in this approach, the ν and the k_E have been regarded as 0.35 and 3.81, respectively, and the values of A and B have been estimated form eqs. (2) and (3).

The Kerner–Nielsen equations obtained are plotted in Figures 2 and 3, respectively. In the case of the PP/MAPP/FC + PEO composite, the values of the Young's modulus are in good agreement with those of the Kerner–Nielsen equation. This behavior suggests that the structure of PP/MAPP/FC matrix is maintained. Whereas in the case of the PEO/FC + PP/MAPP composite, the modulus values follow the Kerner–Nielsen equation about 6 vol % of the PEO content and then suddenly deviate from the equation. This behavior means that the matrix structure is critically changed at around the 6 vol % of PEO content.

Figure 4 shows the WAXD profiles of PP, FC, and PEO. The profile of the PP shows α-form (monoclinic),[19] and that of the FC exhibits crystalline cellulose I pattern.[20] The profile of the PEO also shows two strong reflections at $2\theta = 19.0°$ and $23.5°$,[21]

indicating that the PEO is a crystalline polymer. All the components of the composites used have crystalline parts.

Figure 5(a,b) shows the WAXD profiles of the PP/ MAPP/FC + PEO and PEO/FC + PP/MAPP
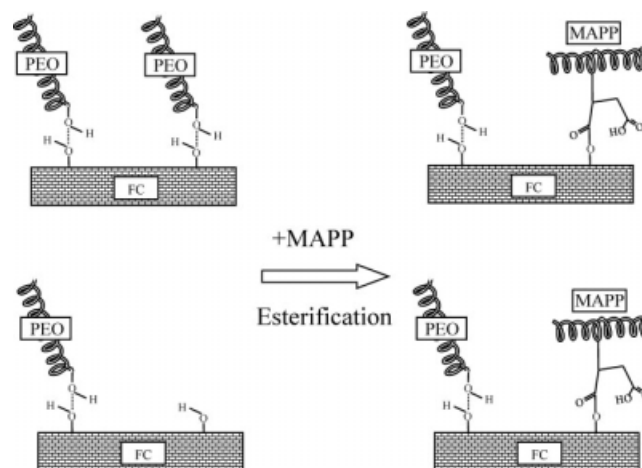

Figure 8 Plausible schematic formation model of the hydrogen and the ester bonds for the FC in the PEO/FC + PP/MAPP composite.
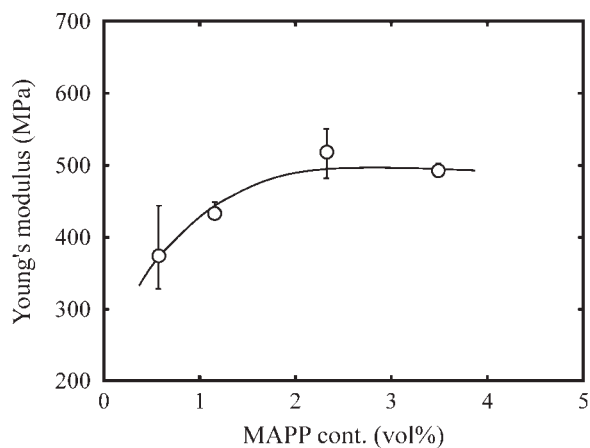
Figure 9 Young's modulus versus MAPP content (vol %) for PEO (7.0 vol %)/FC (20.3 vol %) + PP/MAPP.

composites with various PEO contents. These profiles are generally similar to that of the PP (α-form). It should be, however, noted that the peak around $2\theta = 21.5°$ has a higher intensity and becomes broader with the increase of PEO content. As the peak locations of FC ($2\theta = 22.5°$) and the PEO ($2\theta = 23.5°$) are considerably close, the broader behavior is due to the overlapping peaks of the FC and the PEO. There are no new peaks in the region, and the position of all peaks is in good agreement with that of PP. These results suggest that there are no changes of crystalline forms of each component in both composites.

Figure 6(a,b) shows the DSC curves of the PP/MAPP/FC + PEO and PEO/FC + PP/MAPP composites with various PEO contents. The profiles of both composites are well similar to each other. The T_m corresponding to the α-form of PP can be observed at about 165°C,[22] and the other T_m corresponding to the PEO obviously appears at around 60°C with the increase of the PEO content. Other T_m

is unable to observe. These results support that the changes of the crystalline forms of the PP and PEO components do not occur in both the composites.

In the analysis of the Kerner–Nielsen equation, the deviation is not due to the change of crystalline form but to the change of the PP/MAPP/FC matrix structure. To investigate the structure in both compositions, SEM observation has been carried out. The SEM micrographs of fractured surfaces of the PP/MAPP/FC + PEO composites are shown in Figure 7(a–c). There are many hemispherical holes on the fracture surfaces. These holes are assigned to the PEO phase. The size of the holes obviously depends on the PEO content. The hole exists in the PP phase like an island and does not directly contact the FC part. This phase-separated (sea-island) morphology has been unchanged against the increase of the PEO content. The interface between the PP and the FC has maintained certain unclarity, indicating that the PP/MAPP/FC matrix is maintained. This result is in good agreement with that of the evaluation using the Kerner–Nielsen equation.

Figure 7(d–f) shows the SEM micrographs of fractured surfaces of the PEO/FC + PP/MAPP composites. With the increase of the PEO content, it appears that the interface between the FC and the PP becomes worse (see arrows in the figures). The PP and PEO are typically incompatible blend,[23,24] and hydrogen bond is formed between OH groups in the FC and the PEO.[25] Thus, the defined interface is assigned to the PEO component. In the case of existence of the MAPP component, if the PEO content is too small to cover the FC, the esterification[1] occurs between OH group in the FC and maleic anhydride group in the MAPP, which is compatible with PP. Thus, as shown in Figure 7(d), the boundary becomes blurred between the FC and the PP.

As illustrated in Figure 8, in the case of small amount of PEO, the esterification between the free OH group and the MAPP, and/or an exchange
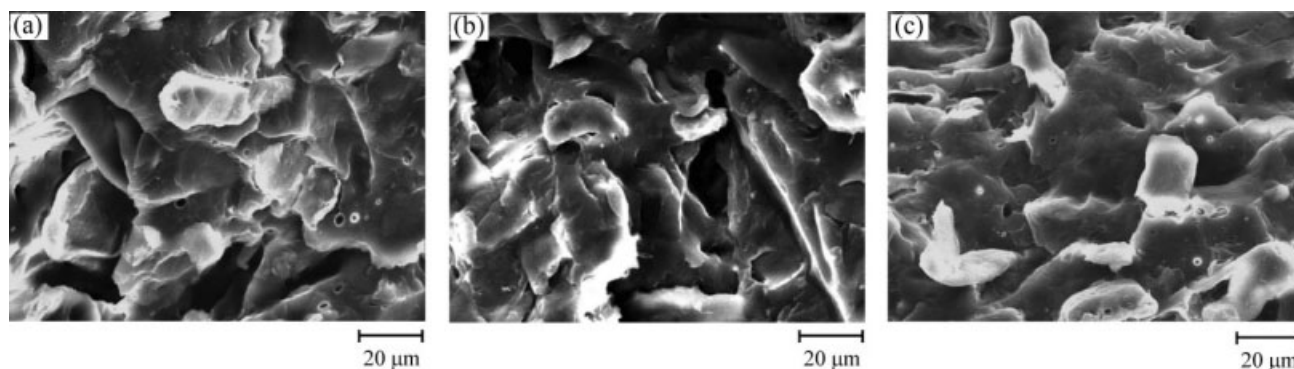

Figure 10 SEM micrographs of fracture surfaces of PEO/FC + PP/MAPP: a: PEO (6.9 vol %)/FC (20.3 vol %) + PP (71.6 vol %)/MAPP (1.2 vol %); b: PEO (6.9 vol %)/FC (20.3 vol %) + PP (70.5 vol %)/MAPP (2.3 vol %); c: PEO (6.9 vol %)/FC (20.3 vol %) + PP (69.3 vol %)/MAPP (3.5 vol %).
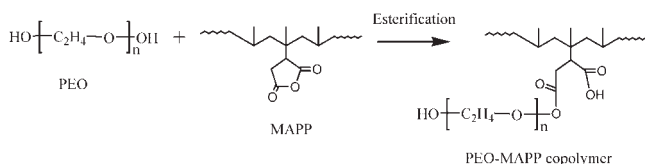
Figure 11 Plausible schematic formation model of PEO-MAPP copolymer in the PEO/FC + PP/MAPP composite.

reaction between the PEO and the MAPP will be allowed on the FC surface. With the increase of the PEO amount, the PEO gradually covers the whole FC surface. The PP/MAPP/FC matrix is unable to be formed above certain PEO content because the ester bond formation between the MAPP and the FC is blocked by the excess PEO. The deviation of the Young's modulus from the Kerner–Nielsen equation is believed to be due to the disappearance of the ester bond.

Figure 9 shows the Young's modulus dependence of the PEO (7.0 vol %)/FC (20.3 vol %) + PP/MAPP composite on the MAPP content. The value of the modulus increases about 2 vol % of the MAPP content and then is almost saturated. As shown in Figure 10, with the increase of the MAPP content, the interface boundary becomes blurred. This suggests that the esterification between the OH group in the FC and the MAPP occurs. The esterification is likely caused by the exchange reaction between the PEO and the excess MAPP. As mentioned earlier, the existence of the grafted MAPP/FC brings about a higher Young's modulus. As the increase of the Young's modulus is saturated around 2 vol % of the MAPP content, the MAPP amount in which the graft reaction is feasible would be about 2 vol % in this composite.

The excess MAPP would react with the PEO having OH group on the end chain and then would yield a copolymer (PEO-MAPP) part (see Fig. 11).
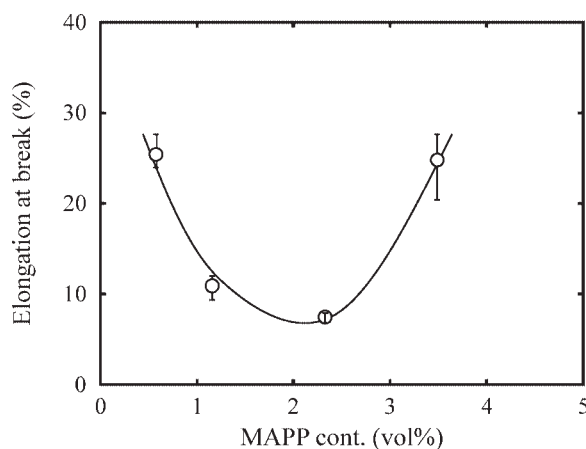

Figure 12 Elongation at break versus MAPP content (vol %) for PEO (7.0 vol %)/FC (20.3 vol %) + PP/MAPP.
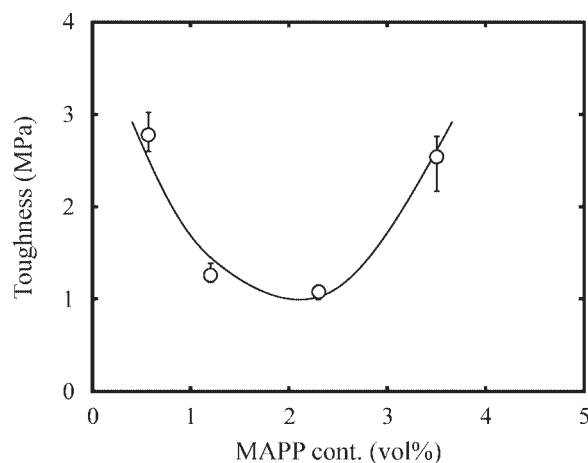

Figure 13 Toughness versus MAPP content (vol %) for PEO (7.0 vol %)/FC (20.3 vol %) + PP/MAPP.

Figure 12 shows the elongation at break versus the MAPP content for the PEO (7.0 vol %)/FC (20.3 vol %) + PP/MAPP composite. The elongation at break has the minimum value at about 2 vol % of the MAPP and then increases with the increase of the MAPP content. This behavior seems to be due to the existence of the PEO-MAPP part, which leads to the improvement of the interface between PP and PEO. It is noted here that the value of the elongation at break is increasing with its higher Young's modulus maintained (see Figs. 9 and 11). Figure 13 shows the value of toughness versus the MAPP content for the PEO (7.0 vol %)/FC (20.3 vol %) + PP/MAPP composite. Here, the toughness was defined as the area under the stress-strain curve. The toughness reaches a minimum value at around 2 vol % of MAPP content and then increases with the increase of the content as well as the value of the elongation at break. These results indicate that the adequate combination of the PEO and the MAPP can provide both of the high Young's modulus and the high elongation at break (i.e., toughness) to the PP/FC composite.

CONCLUSIONS

The effects of the PEO content on the Young's moduli of the two kinds of PP/FC composite were studied using the Kerner–Nielsen equation. In the case of the PP/MAPP/FC + PEO composite, all the values of the moduli with the various PEO contents were in good agreement with the theoretical values obtained from the Kerner–Nielsen equation. Whereas the moduli of the PEO/FC + PP/MAPP composite followed the Kerner–Nielsen equation about 6 vol % of the PEO content and then unexpectedly deviated. In the SEM observation, the PP/MAPP/FC + PEO composite was found to have a sea-island morphology corresponding to the PP/MAPP/FC matrix and

the PEO phase. This morphology had been unchanged against the increase of the PEO content. Whereas in the case of the PEO/FC + PP/MAPP composite, the SEM micrographs showed that the interface between the FC and the PP becomes worse with the increase of the PEO content, indicating that the formation of the PP/MAPP/FC matrix was blocked by the excess PEO. The deviation of the Young's moduli from the Kerner–Nielsen equation was due to the blocking of the PEO. It was found that the adequate combination of the PEO and the MAPP was able to supply the increase of the toughness of the PP/FC composite by investigating the dependence of the PEO/FC + PP/MAPP composite on the MAPP content.

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