Polyblend CPP and Bionolle with PP-*g*-MAH as Compatibilizer: I. Compatibility

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ABSTRACT: Melt-blending polypropylene-*co*-ethylene (CPP) and Bionolle with polypropylene-grafted maleic anhydride (Modic) as a compatibilizer was done. The effect of variational Modic concentration on the compatibility was evaluated using ultimate strength data and SEM micrographs, while the true molecular compatibility over all blend composition ranges was examined by calculating and comparing the theoretical value of glass transition temperature with the experimental value. The results suggest that 15 wt % Modic appears to be an optimum concentration, as indicated by a relatively high ultimate strength over all blend composition ranges and formation of the so-called cocontinuous phase in the blend morphology. Additionally, the value of glass transition temperature calculated theoretically agrees quite well with the experimental value, indicating that at a certain blend composition, the blend sample was found almost compatible. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1277–1282, 1999

Key words: polyblend; CPP; bionolle; Modic; compatibility

INTRODUCTION

Since the first commercial polymer blend or "polyblend" was introduced by Dow Chemical in 1948,[1] research and development of new polyblends have been of a great and rapidly growing interest all over the world. This is because polyblends have shown superior properties over the pure component, either stronger, more flexible, resistant to environmental influences, or have other desirable properties. There are several hundred polyblends that can be found in the review articles of Krause,[2] Plochocki,[3] and Teyssie,[4] and hundreds of other articles are available every year in the leading journals. Through blending, one can compensate for the deficiency of one polymer with the advantage properties of other polymers, and vise versa.

Unfortunately, most of the existing polyblends are not degradable under natural environmental conditions, so that once polyblends have reached the end of useful or service life, they are mainly discarded by open dumping, sanitary landfill, incineration, or simply litter. Obviously, this will create other problems in waste management. To maintain the quality of our life and preserve the environment, it would be highly desirable if the synthesized polyblends are biodegradable. To achieved this goal, one of the convenient ways is to blend nonbiodegradable polymer with biodegradable polymer. This idea is quite logical, because the biodegradable polymer has a structure that is vulnerable to microbial attack or hydrolytic process.

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However, it is well known that both nonbiodegradable and biodegradable polymers are incompatible; consequently, if these two polymers are blended, the commonly observed phenomenon is a heterogeneous product with relatively weak interfacial adhesion, and accordingly, results in relatively poor mechanical performance. To make these two polymers become compatible, a block or graft copolymer is usually introduced.[5–9] This third component acts as a compatibilizer in which part of the copolymer chains link physically or chemically with one polymer and partly with the other.

In accordance with this idea, the present work is aimed at preparing a compatible biodegradable polyblend by melt blending CPP and Bionolle with Modic as a compatibilizer. In this respect, the evaluation of the blend compatibility over a wide composition range will be the subject of discussion in the current article, although the evaluation of the biodegradability of polyblend will be presented in the next article.[20]

EXPERIMENTAL

Materials

Powdered polypropylene-*co*-ethylene (trade mark CPP) with 2.5 mol % ethylene units, MFR 10 was supplied by Chiso Corporation, Japan. Peletized polybutylene succinate (Bionolle) with number-average molecular weight, M_n = 90,000 (grade 1010) was received from Showa High Polymer Co. Ltd., Japan. Peletized polypropylene-grafted maleic anhydride (Modic) was purchased from Mitsubishi Chemical Co. Ltd., Japan. All materials were used as commercial grade without further characterization and purification.

Polyblend Preparation

Blending of a 50-g sample was performed using Laboplastomill (Toyoseiki Co. Ltd., Japan). The blending condition was ca. 200°C, with a roller blade speed of 30 rpm; time for mixing was 8 min. After the mixing was completed, the melt-blended sample was taken out quickly. The blend sample was made sheets using 0.5-mm thickness of a spacer under pressure of ca. 150 kg/cm^2 at ca. 200°C for 3 min, with a preheating time of 3 min; thereafter, it was cooled under pressure of ca. 100 kg/cm^2 with circulating water (ca. 20 °C) for 5 min. The blend composition was varied as CPP/Bionolle: 100/0, 95/5, 75/25, 65/35, 50/50, 25/75, 10/90, and 0/100 with a compatibilizer (Modic) concentration of 0, 5, 10, 15, 20, and 30 wt %.

Mechanical Properties Measurement

The sheet of blend sample was cut into a dumbbell shape according to ASTMD 1822-L. Elongation at break as well as tensile strength of the samples were measured using a tensiometer Strograph-R1 (Toyoseiki Co. Ltd., Japan) at a crosshead speed of 100 mm/min at ambient temperature (ca. 20°C).

Scanning Electron Microscopy

The sample was fractured after dipping in liquid nitrogen. Prior to electron microscopy the fractured surface was coated with gold. A micrograph was taken by a JEOL model Super Probe 733 scanning electron microscope (SEM).

Differential Scanning Calorimetry

About 10–20 mg of the sample was put into a DSC pan and crimped. The specific heat transition was measured by using a Perkin-Elmer DSC7 under a nitrogen atmosphere at a scanning rate of 20°C/min, from −50°C through the glass transition temperature (T_g) and the melting point to 170 °C. The instrument was calibrated with high purity standard. The glass transition temperature was evaluated in the chosen temperature range of 0 to 70°C. The determination of the glass transition temperature was carried out at the midpoint of a transition-specific heat increment.

RESULTS AND DISCUSSION

Because most polymers are immiscible, polyblends usually have to be compatibilized to improve the mechanical properties. As shown in Figure 1(a) and (b), it is evident that the uncompatibilized CPP/Bionolle blend displays poor tensile strength and elongation at break. On the other hand, the compatibilized blends show significant improvement on the tensile strength and elongation at break. This mechanical performance more or less can be correlated with the morphologies of the blends (see SEM in Fig. 2). In the absence of a compatibilizer, all three blend systems [Fig. 2(a)–(c)] exhibited two distinct phases, i.e., a dispersed and a continuous phase. This heterogeneous phase will certainly bring about poor me-

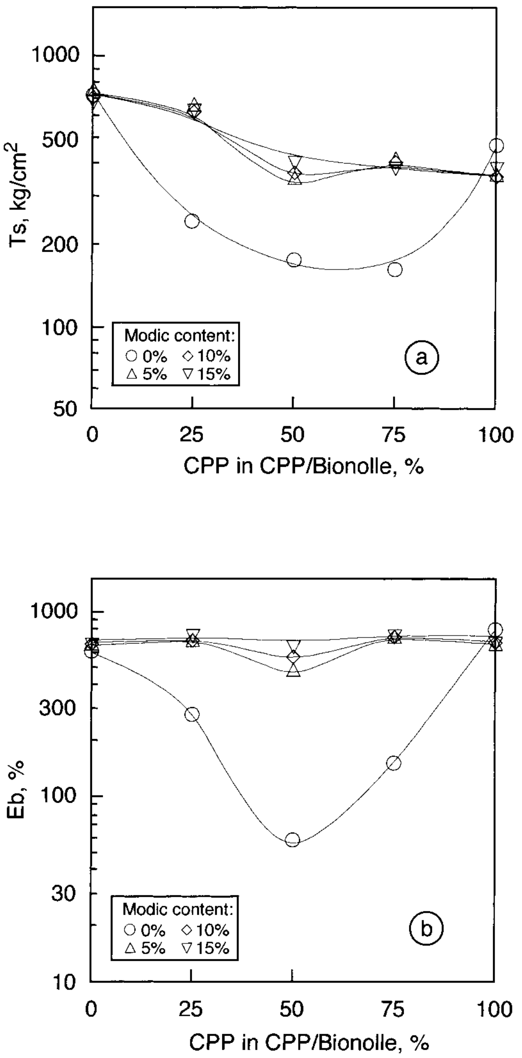
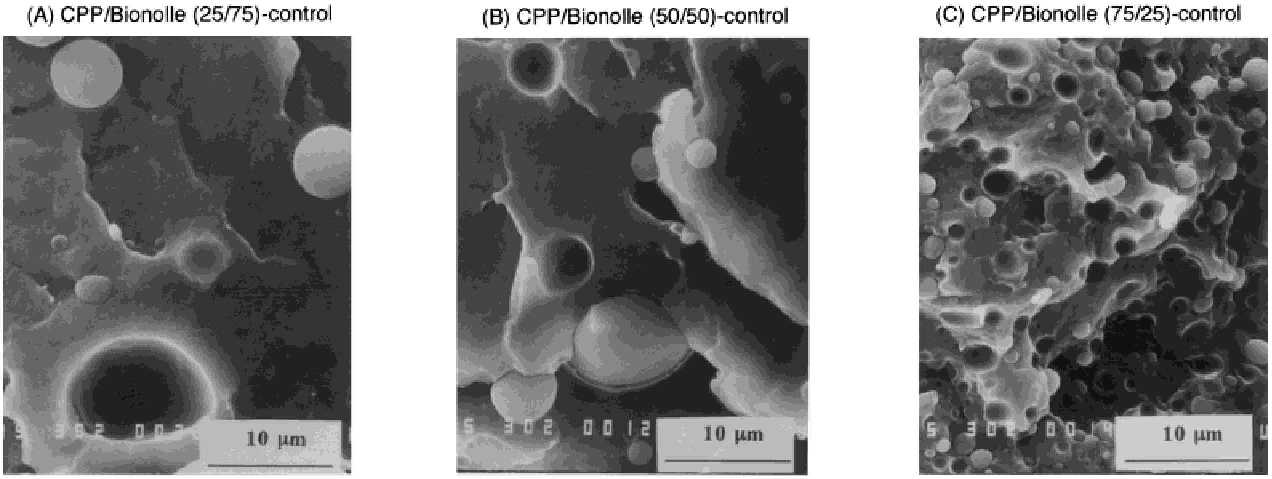


Figure 1 Tensile strength (T_s) and elongation at break (E_b) vs. blend composition at different concentration of Modic.

chanical properties. Upon compatibilization of the blends, however, the shape of the dispersed phase becomes more irregular and attaches well or gradually embeds into the continuous phase. As a result, although large deviations existed, the morphology of compatibilized blends was more homogenous [Fig. 2(d)–(f)]. The latter morphology was referred to as the cocontinuous phase.[10] As reported by Gorelik,[11] the continuous phase in the polyblend improved the physicomechanical properties so that the cocontinuous phase may be treated as having a similar effect. As seen in Figure1(a) and (b), this is a fact, even though the compatibilization mechanisms based on an interfacial reaction and *in situ* formation of the compatibilizer should here be envisaged. Indeed, because CPP contains very few ethylene units (2.5 mol %), it can be assumed to be miscible with propylene-grafted maleic anhydride (PP-*g*-MAH). As a rule, the latter is expected to be uniformly distributed in its host CPP phase, rather than being localized at the interface. Nevertheless, during processing, it is possible that part of the PP-*g*-MAH migrates to the interface, where the maleic anhydride groups attached to it react with end groups (or ester groups of backbone) of poly(butylene succinate). Thus, a PP-*co*-PBS block structure could be generated *in situ*, leading to compatibilization. To predict the optimum concentration of the compatibilizer required for obtaining a relatively high ultimate strength over all composition ranges, the mechanical properties of the polyblend with the composition of CPP/Bionolle (50/50) was measured. The blend composition of (50/50) was chosen based on the fact that this composition shows the lowest ultimate strength among other blend compositions. As demonstrated in Figure 3, the optimum concentration (C_{opt}) of the Modic compatibilizer was found to be 15 wt %. Although for the polyblend containing CPP-rich (CPP/Bionolle > 75/25) and the CPP-minor (CPP/Bionolle < 25/75) shown in Figure 1(a) and (b), addition of 5 wt % Modic was enough to attain relatively high mechanical properties. At a reasonably high compatibilizer concentration the excess molecular chains are likely concentrated at the interface, as reported by Fayt,[12] Favis,[13] and Eklind.[14] Furthermore, if the excess molecules present in the interface is sufficiently high, then it may lead to deterioration of mechanical properties owing to coalescence and softness of the compatibilizer. The latter effect was clearly observed in Figure 3, where the tensile strength and elongation at break, after reaching the maximum, tended to level off and then decreased with further increases of the compatibilizer concentration.

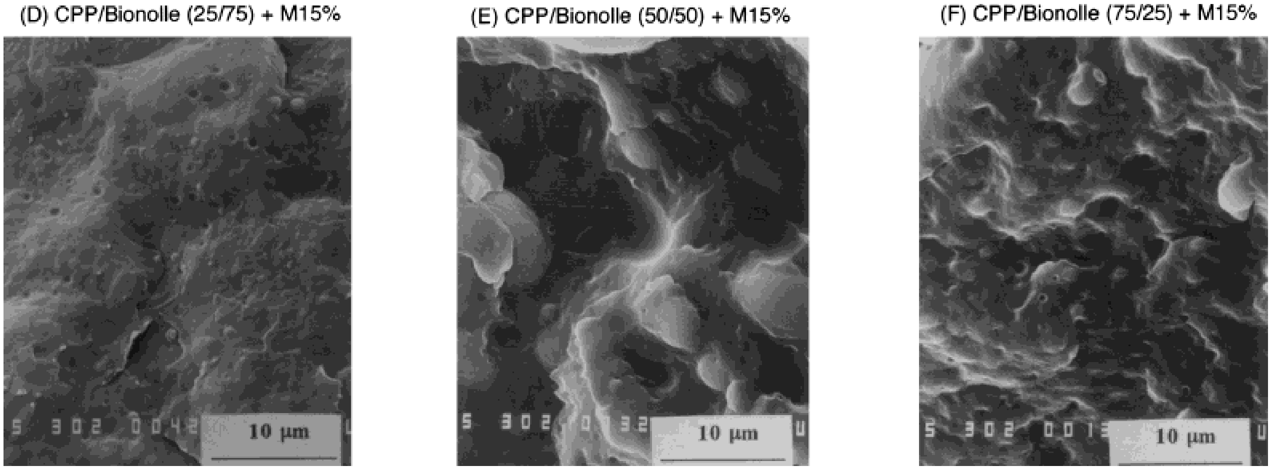
From Figure 2(d) one can also observe that the reactive compatibilizer dispersed the minor phase to significantly finer droplets and homogenized the droplet size, leading to a more stabilized morphology. According to Heikens,[6] Favis,[13] and Matos[15] the reduction of the spherical dispersed phase is due to the balance of surface tension keeping the spherical in one piece, and the viscous force tending to disrupt it. For the blends with a composition of CPP/Bionolle (50/50) and (75/25), the size of the dispersed phase found al-



(A) CPP/Bionolle (25/75)-control

(B) CPP/Bionolle (50/50)-control

(C) CPP/Bionolle (75/25)-control



(D) CPP/Bionolle (25/75) + M15%

(E) CPP/Bionolle (50/50) + M15%

(F) CPP/Bionolle (75/25) + M15%

Figure 2 SEM micrographs of the cross section of CPP/Bionolle blends. Control: without Modic and M15%: with Modic 15 wt %.

most no changes, but mostly it was embedded in the matrix [Fig. 2(e) and (f)].

To examine and elucidate more about the compatibility of compatibilized CPP/Bionolle blends, the glass transition temperature (T_g) was measured. It is generally accepted that a miscible polymer blend is homogeneous, and usually displays a single T_g, between T_gs of pure components, while the compatible blend still shows both T_gs, but eventually shifted one to another. As expected, from Figure 4 it was found that the T_gs of the compatibilized CPP/Bionolle blends with a composition of CPP/Bionolle $\leq$ 50/50 are generally 1, while for the blend samples containing CPP-rich (CPP/Bionolle $>$ 50/50) the T_g appeared not to be a single transition. A similar behavior that is not a sharp single transition or two transitions have also been reported by Kwei,[16] when the content of PVF_2 was 80% in the PVF_2/PMMA/PHEMA blend. In other words, the blended CPP/Bionolle with 15 wt % Modic are almost compatible blends. To correlate glass transition temperature with a variation of blend composition, the classical thermodynamic theory derived by Gordon[17] and Couchman[18,19] for binary polymer mixtures was used. For closely mixed polymers, the glass transition temperatures are largely not affected by the excess mixing entropies. Hence, the model derived by Couchman,[19] in general, may be rewritten as follows:

$$\sum_{i=1,2,\ldots} M_i \int_{T_{g_i}}^{T_g} \Delta Cp_i \, d \ln T = 0 \qquad (1)$$

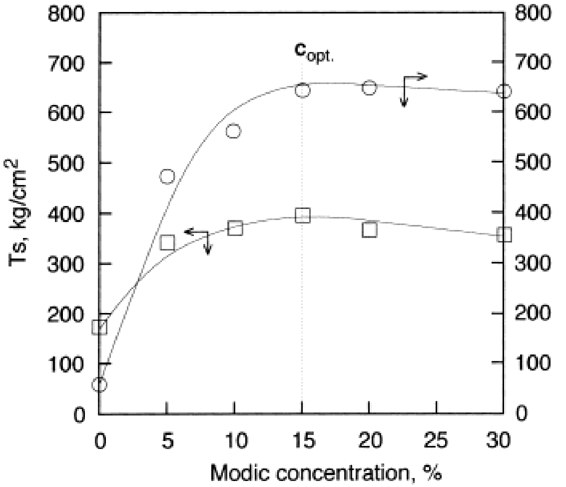


Figure 3 Optimum concentration of Modic for obtaining relatively high mechanical properties of polyblend. CPP/Bionolle: 50/50.

where M_i is the mass fraction of each component; ΔCp_i is the specific heat increment of each component, J/g°C; Tg_i is the glass transition temperature of each component, °C; and T_g is the glass transition temperature of the polyblend, °C. In the case of Tg_i being negative (minus degree Celsius), the Tg_i must be converted into Kelvin (K) for the calculation of Tg polyblend (also in K).

For ternary polymer mixtures, integration of eq. (1) result:

$$M_1\Delta C_{p_1}\ln(T_g/T_{g_1}) + M_2\Delta C_{p_2}\ln(T_g/T_{g_2}) + M_3\Delta C_{p_3}\ln(T_g/T_{g_3}) = 0 \quad (2)$$

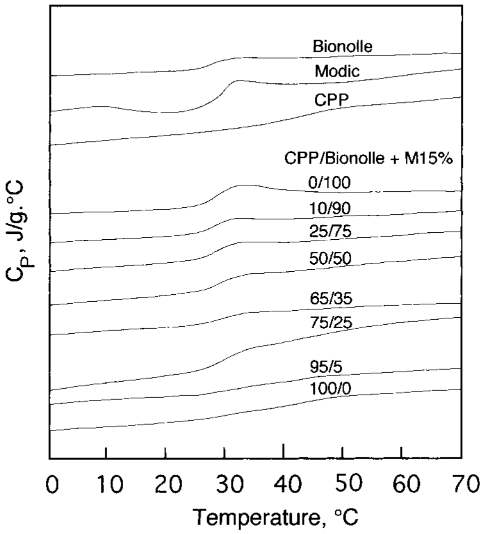


Figure 4 T_gs of polymers and polyblends measured by DSC using specific heat program with scanning rate of 20°C/min.

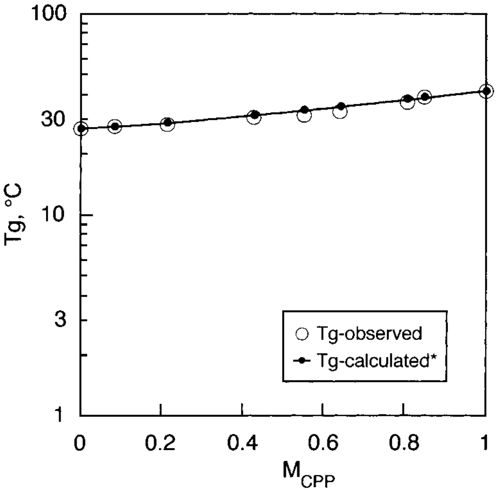


Figure 5 Observed (open circle) and calculated (solid line-circle) T_gs of polymers and polyblends. M_{CPP} is the weight fraction of CPP in ternary mixtures of CPP–Bionolle–Modic, and * using eq. (3).

or for convenience, eq. (2) can be rearranged to:

$$T_g = \exp\left(\frac{M_1\Delta C_{p_1}\ln T_{g_1} + M_2\Delta C_{p_2}\ln T_{g_2} + M_3\Delta C_{p_3}\ln T_{g_3}}{M_1\Delta C_{p_1} + M_2\Delta C_{p_2} + M_3\Delta C_{p_3}}\right) \quad (3)$$

Index 1, 2, and 3 denote CPP, Bionolle, and Modic, respectively. The values of ΔC_p and T_g of each component (determined the same way as the polyblends) were ΔC_{p1} = 0.2038 J/g°C, T_{g1} = 41°C, ΔC_{p2} = 0.2366 J/g°C, T_{g2} = 27°C, and ΔC_{p3} = 0.1407 J/g°C, Tg_3 = 28°C. Using eq. (3) and these data, the glass transition temperature of polyblends have been calculated and presented in the same figure with the experimental one (Fig. 5). It is apparent that theoretically calculated T_g values are in good agreement with experimental values, even though it should be noted here that there exists a little discrepancy between observed and calculated values for the blend sample containing CPP-rich (CPP/Bionolle ≥ 50/50). In general, the result suggests that CPP/Bionolle blends with 15 wt % Modic are almost compatible over all composition ranges.

CONCLUSION

It has been shown that two incompatible polymers (CPP and Bionolle) become almost compatible at a certain blend composition when they are blended in the presence of a compatibilizer

(Modic). The extent of compatibility depends on the Modic concentration and composition of the blends. It was pointed out that the optimum Modic concentration to obtain relatively high ultimate strength over a wide composition range was 15 wt %. Comparing the ultimate strength data, SEM micrographs, and glass transition temperatures, the results are generally in good agreement. Additionally, the correlation between glass transition temperature and blend composition was quite satisfactorily described by a classical thermodynamic theory derived by Couchman,[19] which means that almost a true molecular compatibility was formed in the ternary blend.

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