

Polymer Blend of Cellulose Acetate Butyrate and Aliphatic Polyestercarbonate

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ABSTRACT: Blends of cellulose acetate butyrate (CAB) and polyestercarbonate (PEC) in the composition range of 0–100 wt % in each component were prepared by thermal compounding. The mechanical, thermal, and rheological properties of the polymer blends were studied. Analysis of the DSC curve showed that CAB was an amorphous polymer and plasticized clearly by PEC as long as its addition was less than 40 wt %. On the other hand, PEC was confirmed to be a crystalline polymer and its crystallinity was affected by the introduction of CAB. The finding that CAB and PEC are at least partially miscible was confirmed by the related dynamic mechanical thermal analysis and DSC data. No evidence of transesterification between CAB and PEC was found from the ^{13}C -NMR and GPC data. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 2908–2914, 2000

Key words: cellulose acetate butyrate; polyestercarbonate; blend; crystallinity; mechanical property; thermal property

INTRODUCTION

Cellulose esters are known as one of the most useful products derived from natural polymers. Even though cellulose esters can be made biodegradable in aerobic, composting, or soil burial environments by controlling their degrees of substitution,^{1–5} the cellulose esters by themselves are unsuitable for common uses as thermoplastics because of their poor processibility (high melt temperatures, viscosities, and relatively low decomposition temperatures). To enhance their plasticities, the addition of low molecular weight plasticizers and/or high molecular weight polymers are usable. Uses of low molecular weight plasticizers have often resulted in mist problems during the molding and the bleeding of the plasticizer from the inside to the outside of the mold-

ings.⁶ For this concern, polymer blendings are considered useful in solving these problems and may also offer opportunities to improve their mechanical properties.

Various studies have been performed on the blends of cellulose esters with synthetic polymers.^{7–10} Recently, Buchanan et al. and others reported that cellulose esters could form partially miscible blends with other biodegradable polyesters.^{11,12}

In our study, we focused on biodegradable polymer blends containing cellulose esters and high molecular weight aliphatic polyestercarbonate (PEC), which has recently been synthesized by the Mitsubishi Gas Chemical Co. as a biodegradable thermoplastic. The specific objective was to blend cellulose acetate butyrate (CAB) and PEC in various ratios through melt-blending techniques to prepare a biodegradable polymer with variable mechanical properties.

Aliphatic polycarbonate has not been evaluated as a useful component in the development of

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a biodegradable polymer until recently because of its inherent disadvantages such as low melting temperature, low yield, and low molecular weight when compared to conventional thermoplastics. However, these drawbacks can be improved by copolymerizing with polyesters.¹³ The PEC used in this study was poly(butylenesuccinate-co-butylenecarbonate), which is a crystallizable thermoplastic with polyester and polycarbonate units. It has attracted some commercial interest because it possesses properties similar to common thermoplastics such as polypropylene and polyethylene. The biodegradability, processibility, and mechanical property of PEC can be controlled by changing the carbonate unit ratio.¹⁴

EXPERIMENTAL

Materials

The CAB used for this experiment was CAB 40425-5000, commercially available from ACROS ORGANICS (New Jersey). The butyryl and acetyl contents were as follows: butyryl, 35–39%, and acetyl, 12–15%. PEC (S50189, $M_w = 116,000$) was kindly supplied by the Mitsubishi Gas Chemical Co. The chemical composition of the PEC was determined by ¹³C-NMR analysis. The ratio of the peak intensities (carbonate carbon at 157 ppm to ester carbonyl carbon at 174 ppm) was used to determine the molar composition of the ester and carbonate units in PEC. This analysis showed that PEC contains a 1/20 molar ratio of carbonate to ester.

Preparation of Blend Materials

CAB and PEC were first mixed in dry solid states followed by melt blending using a Labo Plastomill LPM 18-125 (Toyo Seiki Co. Ltd.). The blending ratios of these polymers were 10/90–90/10 by weight. The temperature, the rotation rate, and the processing period were 200°C, 90 rpm, and 10 min, respectively. The blended materials were hot-pressed into sheets and allowed to age at room temperature for at least 3 weeks. The temperature, the duration period, and the pressure of hot-press molding were 150–200°C, 30 s, and 15.0 MPa, respectively.

Tensile Test

Tensile testing of the prepared sheets was carried out with a Shimadzu Autograph AGS-5kNG. All

sheets were conditioned for 48 h at 20°C and 60% RH. The test was performed at a crosshead speed of 5 mm/min with a span length of 40 mm using 5-mm-wide and 0.4-mm-thick specimens. The Shikibu program (Shimadzu) automatically calculated the tensile strength, Young's modulus, and elongation at break.

Gel Permeation Chromatography (GPC) and Nuclear Magnetic Resonance (NMR) Measurements

Molecular weight measurements were carried out at 40°C with a solvent flow rate of 1.0 mL/min under 7.0 MPa pressure using a GPC (Nippon Bunko GPC-900). The refractive index versus the elution volume relationship was obtained for each sample and correlated to the same relation for the polystyrene standard. NMR spectra were measured in CDCl₃ using (CH₃)₄Si as an internal standard, employing a 300 MHz Bruker AC-300 spectrometer. Spectra of the pure polymers and their blends were recorded separately.

Dynamic Mechanical Thermal Analysis (DMTA)

DMTA was accomplished using an ARES-2kFRT (Rheometric Scientific) operating in the torsion rectangular mode at a heating rate of 10°C/min and a frequency of 6.28 rad/s. The dimension of the specimens used was 40 × 10 × 0.5 mm.

Differential Scanning Calorimeter (DSC)

DSC analysis was performed to study the miscibility and thermal behavior of the blends using a TA Instrument DSC 2920. The apparatus was calibrated with the indium standard and the samples were placed in sealed aluminum cells. The samples were first heated from –100 to 250°C at a heating rate of 10°C/min (first scan). The melting temperature and apparent enthalpy of fusion (ΔH_m) were determined from the DSC endothermic peaks. After the samples were cooled to –100°C at a cooling rate of 20°C/min, the second scan was accomplished also with a heating run at a rate of 10°C/min to 250°C.

Melt-Rheological Properties

The capillary rheological measurements were carried out at 200°C using a capillary rheometer (Toyo Seiki Co. Ltd.) with a die orifice radius of 1 mm and a die length of 10 mm. Crosshead speeds were 10, 20, 50, 100, 200, and 500 mm/min.

Table I Molecular Weights of CAB, PEC, and CAB/PEC Blends Measured by GPC

CAB/PEC	$10^{-4} M_n$	$10^{-5} M_w$	$10^{-5} M_z$	M_w/M_n	M_z/M_n
100/0	5.30	1.41	3.10	2.66	2.19
80/20	3.68	0.99	1.95	2.69	1.97
60/40	3.67	0.87	1.65	2.36	1.91
40/60	3.95	0.91	1.70	2.29	1.87
20/80	4.22	0.96	1.85	2.27	1.93
0/100	5.94	1.16	2.27	1.95	1.95

RESULTS AND DISCUSSION

Since the PEC used did not show thermal decomposition below 220°C in the previous study,¹³ the temperature of thermal compounding was set at 200°C, which is the melting temperature of CAB. At this temperature, the molecular weight of the CAB/PEC blends decreased slightly but the number-average molecular weights were maintained in a range from 3.67×10^4 to 4.22×10^4 (Table I).

Figure 1 shows the mechanical properties of the CAB/PEC blends plotted against the PEC contents. Pure CAB had higher values of tensile strength and the Young's modulus than those of pure PEC, whereas the elongation at break of CAB was lower than that of PEC. Both the tensile strength and the Young's modulus of the blends decreased with an increase in PEC up to 50 wt %, while the elongation at break increased significantly with PEC content up to 80 wt %. The changes in these tensile properties with the PEC content did not follow the composite rule. Furthermore, it is noted that the tensile strength and the Young's modulus of the polymer blends appeared in the lower regions of a line (dotted line in

the figure) directly connecting the tensile strength and the Young's modulus values of CAB to those of PEC, whereas the opposite result (higher region) was obtained for the elongation at break values as shown in Figure 1. It is also interesting to note that a substantial difference existed between the region of PEC content less than 40% and that of more than 60 wt %. In the former region, the changes are more drastic compared with the cases for the latter.

It was found that transparent films could be obtained for a PEC blended ratio of less than 40 wt %. In this region, the crystallinity of PEC was shown to diminish from blending with CAB, indicating that a certain interaction would take place between PEC and CAB. Therefore, the plasticization of CAB by blending with PEC could be considered as the likely cause of the decreases in the tensile strength and the Young's modulus with an accompanying small increase in the elongation at break.

Above 60% of PEC contents, where the crystallization of PEC is no longer suppressed and the corresponding molded films become opaque, the tensile strength and the Young's modulus increased with PEC content for the second time. In this region, the elongation at break increased continuously up to 80% of the PEC content, then decreased. It should be noted that a substantial increase in the elongation value at 80% PEC content (i.e., 500% elongation) as compared to that of 100% PEC content (i.e., 150% elongation) in the result demonstrated the significant effect of blending CAB into the system.

Many symptoms of the occurrence of molecular interaction (i.e., miscibility) between the PEC and CAB are also shown with the measurement of viscoelastic properties. Figure 2 reveals the temperature dependencies of $\tan \delta$ for the neat CAB, PEC, and four blend samples. The neat CAB and PEC showed a single sharp transition (glass-rubber transition) at 143 and -27°C, respectively.

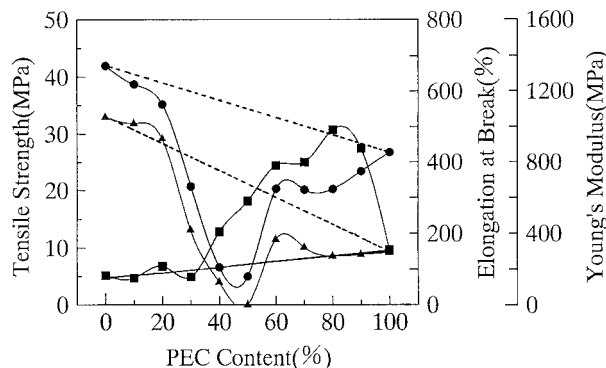


Figure 1 Tensile properties of the CAB/PEC blends containing 0–100 wt % PEC: (●) tensile strength; (■) elongation at break; (▲) Young's modulus.

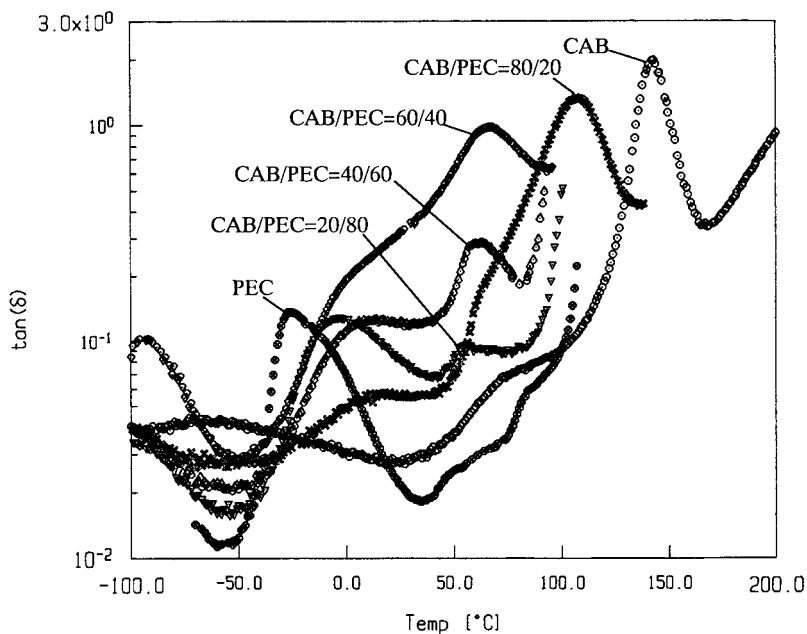


Figure 2 Temperature dependency of mechanical loss tangent ($\tan \delta$) for CAB, PEC, and their several blends.

On blending CAB with 20, 40, 60, and 80 wt % amounts of PEC, the glass-rubber transition temperature (T_g) of CAB decreased to 107, 67, 63, and 56°C, respectively. On the other hand, the T_g of PEC increased from -27°C to -3 and 8°C by compositing 20 and 40 wt % of CAB, respectively. Broadening of these transition peaks was also observable. These facts indicate that these two polymers are at least partially miscible, supporting the above discussion.

The crystallization as well as the miscibility of the blended components can also be studied using DSC analysis. The DSC thermogram was taken as the first and second heating scans. T_g was taken as the midpoint of the inflection (i.e., the intercept of two tangent extrapolation lines) in the DSC second-scan thermogram.

Figure 3 shows the DSC curves of neat CAB and PEC. The former is an amorphous polymer with a high T_g value (135°C), while the latter is a semicrystalline polymer with a low melting temperature (106°C) and a low T_g (-37°C).

As shown in the DSC curves of Figure 4, the T_g of CAB was shifted to lower temperatures regularly with increase in the PEC content. At the same time, the glass transition region of the blends showed a marked broadening to the low-temperature side. This result also confirms the miscibility of CAB and PEC. Furthermore, the blended CAB materials with 20–40 wt % of PEC

did not show a melting endotherm at both the first and the second scans, indicating that these blends are completely amorphous. In Figure 5, the DSC curves for blends having more than a 50 wt % amount of PEC including the neat PEC are shown. In this case, the T_g value of PEC increased with increase in the blending amount of CAB, revealing also the miscibility.

In the case of PEC, a large melting endotherm appeared in the DSC curve, whereas the appear-

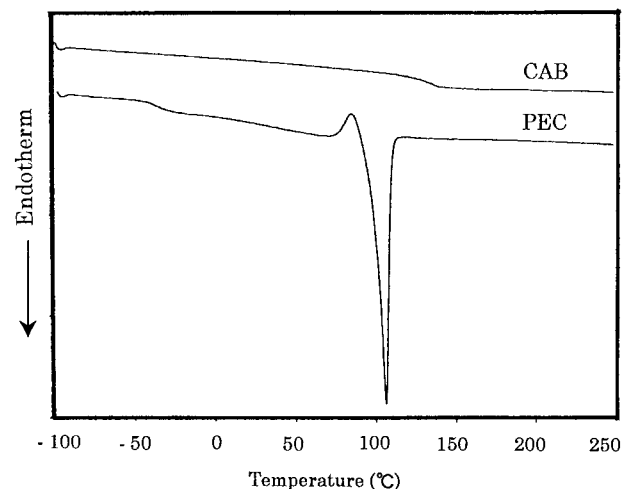


Figure 3 DSC curves (second scan) of neat CAB and PEC.

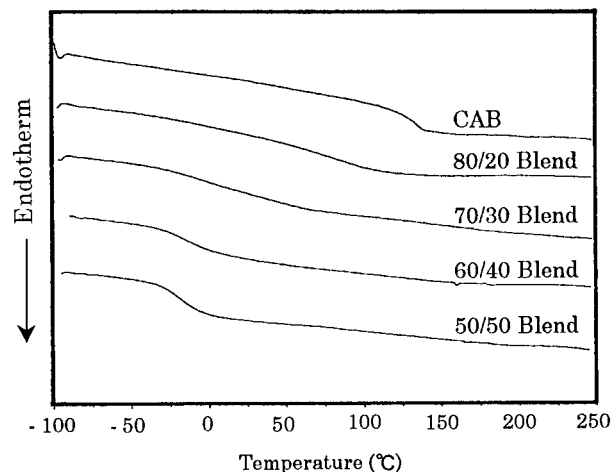


Figure 4 DSC curves (second scan) of CAB/PEC blends containing 0–50 wt % PEC.

ance of the crystallization exotherm was depressed. However, the introduction of 20 wt % of CAB suppressed the occurrence of crystallization during the cooling period just after the first DSC scan and the appearance of the melting endotherm was reduced in the second scan. In other words, there is room to yield a relatively large crystallization exotherm in the second scan, revealing some suppression of crystallization of PEC during the cooling period by the introduction

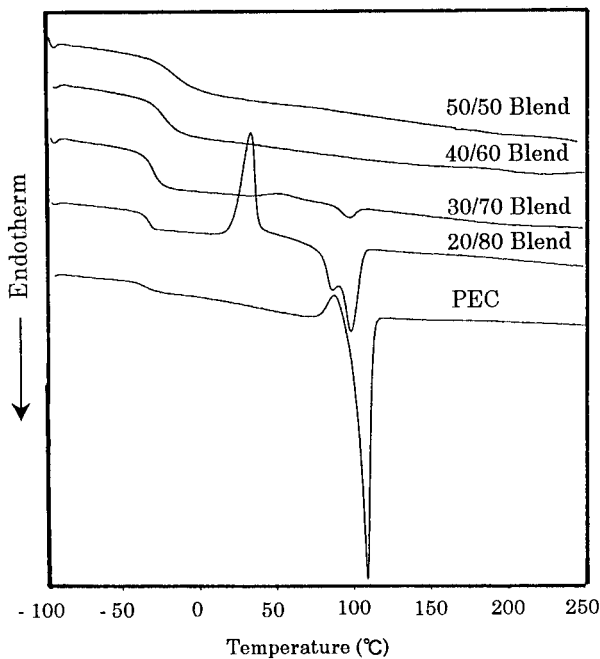


Figure 5 DSC curves (second scan) of CAB/PEC blends containing 50–100 wt % PEC.

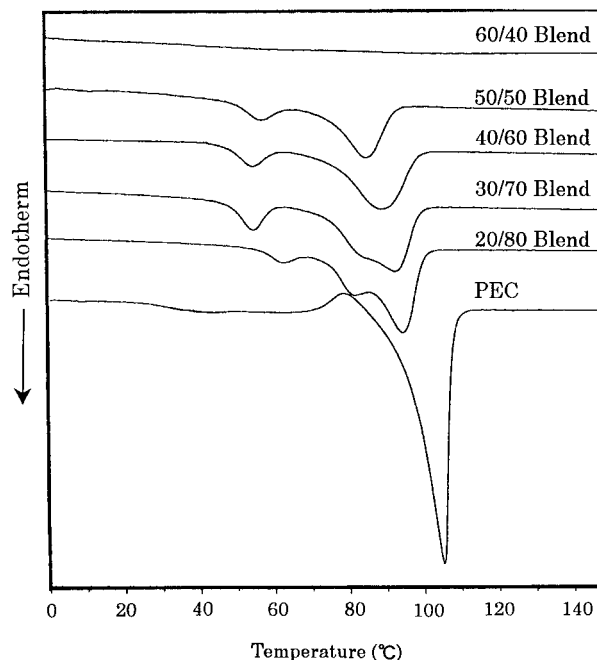


Figure 6 DSC curves (first scan) of CAB/PEC blends containing 40–100 wt % PEC.

of 20 wt % of CAB. This suppression of the crystallization becomes more evident when more than 20% of CAB is blended. Introduction of 30 wt % of CAB into PEC resulted in a trace of the melting endotherm peak, and that of more than 40 wt % prevents completely the formation of this peak.

However, in the first DSC scan (Fig. 6), two melt endotherm peaks occurred even in the blended sample having 50 wt % of CAB, indicating that when these blended samples were allowed to cool slowly the PEC could be partially crystallized even in the copresence of CAB in the molecularly mixed levels. Thus, the formations of a different degree of crystallized PEC caused the two broadened peaks. In this case, the melting temperature (T_m) of PEC was found to be reduced and the heat of fusion (ΔH_m) was decreased with increasing CAB content in the blends. The depression of T_m and ΔH_m in these blends is characteristic of semicrystalline amorphous blends.¹⁵

As described above, in the corresponding second scan previously shown in Figure 5, the 30/70 and 20/80 CAB/PEC blends and pure PEC showed a T_m peak, but the 50/50 and 40/60 blends displayed no T_m peak, that is, the crystalline exotherm starts to appear with the 30/70 blend. These results indicate that crystallization rates of the 50/50 and 40/60 blends are very slow compared with those of the 30/70 and 20/80 blends

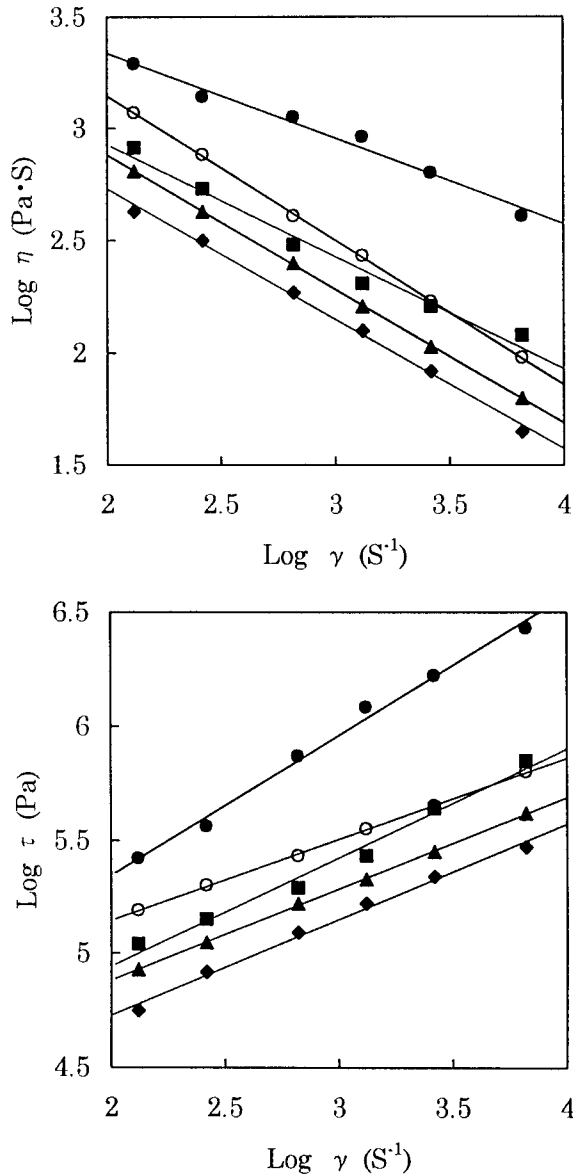


Figure 7 Shear-rate dependencies of melt viscosities and melt stresses for CAB/PEC blends and PP: (●) CAB; CAB/PEC = (■) 90/10, (▲) 80/20, and (◆) 70/30; (○) PP.

and pure PEC. It is obvious that CAB decreases the crystallization rate of PEC in the blended material.

From above discussion, it becomes apparent that CAB and PEC are mutually miscible, indicating that, from the viewpoint of CAB, it can be plasticized by PEC. The melt rheological properties of CAB and its blends with PEC as a plasticizer were evaluated in the study by comparing them with those of injection-grade polypropylene (PP).

The results of these trials are shown in Figure 7. The figure shows the shear-rate dependencies of the logarithmic melt viscosity as well as that of shear stress. From the figure, it is known that the value for both the melt viscosity and the shear stress of CAB were one order higher as compared with those of PP. However, a 10 wt % addition of PEC reduced these values to the levels of the PP values, indicating that PEC can act as the plasticizer for CAB and higher amounts of PEC for additional blending cause higher degrees of plasticization.

During these blendings, there is a possibility that chemical changes might have occurred in the component polymers. For instance, during the thermal compounding, transesterification is considered to take place. To examine these points, the blending was inspected by ^{13}C -NMR spectroscopy. Figure 8 shows ^{13}C -NMR spectra of CAB, PEC, and their 50 : 50 blend. It is known that the resonance of pure CAB remains unchanged even after blending with an equal weight of PEC, indicating that the degree of substitution of CAB did not change during the thermal processing. Furthermore, no other signal attributable to some chemical changes appears in the spectrum. However, it should be noted that the minimum detec-

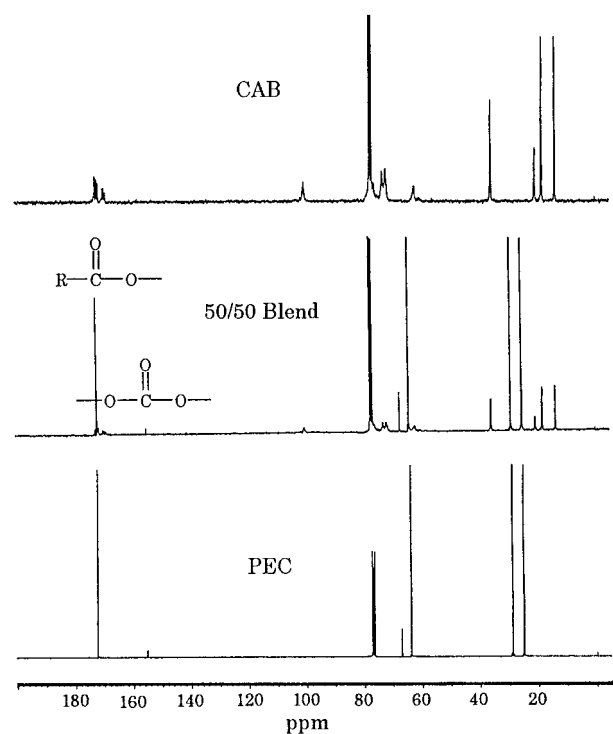


Figure 8 Comparison of ^{13}C -NMR spectra of CAB, PEC, and 50/50 CAB/PEC blends.

tion level of transesterification by the NMR method was not evaluated in the study. Therefore, it was possible that some level of reaction that could have occurred and was not detected in the study. As described previously concerning the data shown in Table I, no characteristic change could be found in the molecular weight aspect.

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