

Estimation of the Biobased Carbon Content of Polypropylene Resin in Composites on the Basis of the Carbon 14 Concentration

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ABSTRACT: The aim of this study was to estimate a procedure for the biobased carbon content of polypropylene (PP) resin isolated from composites containing additives or fillers on the basis of the carbon 14 concentration ratio, as measured by accelerated mass spectrometry (AMS). To reliably estimate the biobased carbon content of plastics, additives and fillers in the composites had to be removed because they often contain significant amounts of biobased carbon. To obtain specimens with purity suitable for estimation, an isolation procedure for PP from the composites was devised. The dissolution of the composites in 1,2,3,4-tetrahydronaphthalene at 150°C, followed by immediate centrifugation of the hot solution, yielded PP as semicrystalline precipitates by allowing the hot solution to cool during centrifugation. The recovery of the resin through the scooping off of the precipitates was typically 90%. This simple procedure provided a suitable specimen for the estimation of biobased carbon content by AMS on the basis of ASTM D 6866.

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INTRODUCTION

Biobased plastics, such as poly(lactic acid) and poly(hydroxyl alkanolic acid), are already produced commercially and are steadily gaining in popularity with public awareness of the environment. Furthermore, the production of polyethylene and polypropylene (PP), which are major thermoplastic resins, is now achieved from biomass resources.^{1–3} To be certain that one is purchasing biobased plastics, it should be confirmed and certified that they are actually produced from biomass, and, if they are, how much biobased plastic is contained in the plastics. Products of biomass origin and products of petroleum origin are indistinguishable because they have the same physical and chemical properties when they have same molecular structure. Therefore, in an attempt to increase general consumer knowledge and promote biobased plastics, the Japan Bioplastics Association⁴ is managing the BiomassPla mark certification system as an identification system for products of biomass origin. Under this system, products that meet the stipulated standards are certified as BiomassPla and are permitted to use the BiomassPla logo shown in Figure 1. The amount of biobased synthetic polymer in these products has to be 25.0 wt % or more in one of the authentication conditions in the aforementioned system. The amount of biobased synthetic polymer is the ratio of the biomass origin constituent of the biobased plastics chemical composition.

The biobased carbon ratios of plastics can be estimated by the ratio of ¹⁴C to ¹²C, as measured by accelerator mass spectrometry and conforming to ASTM D 6866 (“Standard Test Methods for Determining the Biobased Content of Natural Range Materials Using Radiocarbon and Isotope Ratio Mass Spectrometry Analysis”). The principle of this method using ¹⁴C is based on a dating measurement for historical materials in archeology.^{5,6} ¹⁴C is a radioisotope of carbon atoms with a half-life of 5730 years. ¹⁴C atoms are continuously generated from ¹⁴N atoms because of their interaction with cosmic radiation in the modern atmosphere. The ratio of ¹⁴C to ¹²C in modern air is constant at approximately 1×10^{-12} despite the period. Plants absorb carbon dioxide in the atmosphere and incorporate it into their structure by photosynthesis. The ratio of ¹⁴C to ¹²C in a plant is 1×10^{-12} immediately after photosynthesis. The ¹⁴C in plant materials gradually decays into ¹⁴N. The number of ¹⁴C atoms continuously decreases and halves after 5730 years. Therefore, the age of materials, including carbon atoms, can be estimated with the ratio of the number of ¹⁴C atoms to that of ¹²C atoms and the half-life of ¹⁴C. The ratio of ¹⁴C to ¹²C can be measured by accelerated mass spectrometry (AMS), although this ratio is as low as 1×10^{-12} . The standard year is defined as 1950 according to the formulas for radiometric dating in ASTM D 6866-08. In ASTM D 6866-08, formulas for radiometric dating are applied to the determination of the biobased

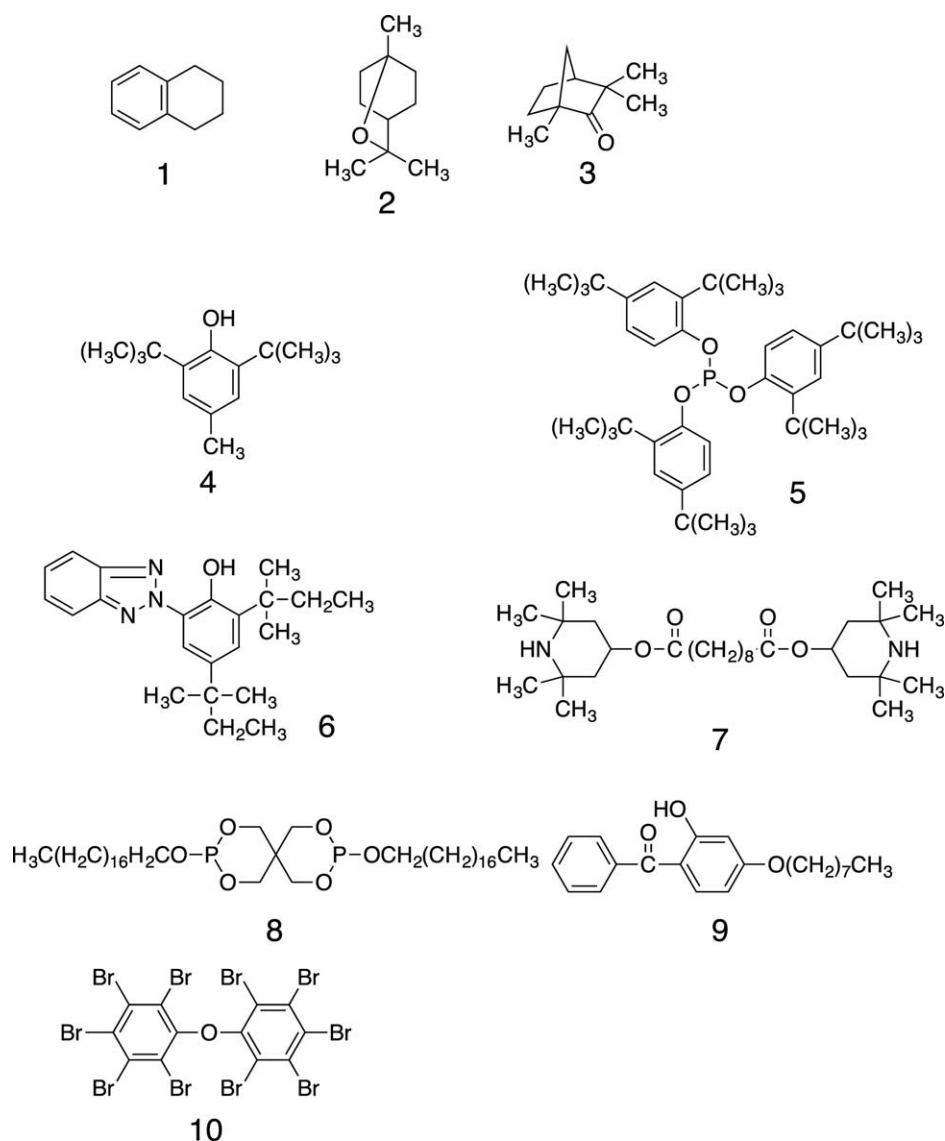


Figure 1. Symbolic mark of the biomass certification system.

carbon content. The percentage of modern carbon (pMC) value can be estimated by a comparison of the ratio of measured ^{14}C to ^{12}C and the standard ratio of ^{14}C to ^{12}C determined from the appropriate primary reference (oxalic acid) of Standard Reference Material 4990c supplied by the National Institute of Standards and Technology (NIST).⁷ Theoretically, the biobased carbon ratio for petroleum-based materials is estimated at 0%, and that for biobased materials is estimated at 100%. Our previous reports^{8–10} described the estimation of biobased carbon ratios for full biopolymers [(poly(lactic acid), poly(3-hydroxy-

butyrate), and cellulose], partial biopolymers [poly(trimethylene terephthalate) and cellulose acetate butyrate], petroleum-based polymers [PP, polycaprolactone, and poly(butylene succinate)], and also various polymeric composites with additives and fillers and discussed the repeatability and accuracy of this evaluation method. For reliable estimation of the ratios, we devised pretreatments for AMS samples, such as lower temperature oxidation and reaction by phosphoric acid.¹⁰

In this article, we report a generally applied pretreatment for an AMS specimen of PP composites with various additives and fillers. The PP isolation procedure used in this study was based on several simple principles related to the density and solubility of each component of the PP composites.^{11–13} That is, the density of PP (0.90–0.92 g/cm³) was lower than those of near-insoluble additives (fillers, e.g., 2.71 g/cm³ calcium carbonate, and 2.1–2.2 g/cm³ graphite).¹⁴ PP is soluble in hydrophobic solvents, such as hydrocarbons and chlorinated hydrocarbons, at elevated temperatures and is nearly insoluble at room temperature. Fillers,



Scheme 1. Typical additives for PP.

such as cellulose, starch, and calcium carbonate, are essentially insoluble in hydrophobic solvents, and the density of these is greater than those of organic solvents. As shown in Scheme 1, organic additives, which are mostly low-molecular-weight substances, have reasonable solubility in organic solvents, even at room temperature. Various hydrophobic compounds, including hydrocarbons such as xylene and dodecane and chlorinated hydrocarbons such as 1,2-dichlorobenzene and 1,2,4-trichlorobenzene, are known to be good solvents for PP at elevated temperatures. Considering the density, boiling point, solvency, and commercial availability of the solvents, we chose three chemicals, 1,2,3,4-tetrahydronaphthalene (tetralin or **1**; 0.97 g/cm³, bp = 207°C), 1,8-cineole (**2**; 0.92 g/cm³, bp = 176°C), and (-)-fenchone (**3**; 0.95 g/cm³, bp = 193°C). These were slightly more dense than PP and smaller than the fillers and had high enough boiling points for handling at elevated temperatures above 150°C. Terpenoid compounds **2** and **3** are not commonly used as solvents for the polymers. However, they might show different solvencies for resins and organic additives with rather polar groups because of their chemical structures with ether or carbonyl functions.

Our experimental scheme for PP isolation from the composites was as follows: during centrifugation of a hot solution of the composite, high-density insoluble fillers precipitated to the bottom of a centrifugation test tube, and when the solution was cooled to room temperature, PP precipitated and collected near the surface of the solution, whereas hydrophobic organic additives remained in the solution. The scooping up (or filtering) of the floating PP precipitates and rinsing with a volatile solvent (ethanol) yielded a specimen with favorable purity suitable for the reliable AMS results.

Various kinds of additives, antioxidants, UV absorbers, nucleation agents, flame retardants, and fibers were applied to PP products, usually in combination with them.¹¹ The extensive testing of composites covering many additives is actually impossible. Therefore, as solvent-insoluble fillers, we chose some notable additives, calcium carbonate (powdered oyster shell), starch, and cellulose, which may often be applied in quantity in propylene composites and may drastically alter the evaluation of the biobased carbon content upward because of their bio-origin, carbon. Soluble additives used in commercial PP products are too numerous to count. However, a limited number of compounds should be sufficient to test the scheme because almost all of them have a common characteristic property because of the hydrophobic functional groups, which are sufficient to hold compatibility with the resin.^{13,15} For example, phenol antioxidant [3,5-di-*tert*-butyl-4-hydroxytoluene (**4**)], phosphite antioxidant [tris(2,4-di-*tert*-butylphenyl)phosphite (**5**)], triazole UV absorber [2-(3,5-di-*tert*-amyl-2-hydroxyphenyl)benzotriazole (**6**)], and hindered amine photostabilizer [bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate (**7**)] have multiple methyl, tertiary butyl, and amyl groups, and further, phosphite antioxidant [3,9-bis(octadecyloxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane (**8**)] and benzophenone UV absorber [2-hydroxy-4-*n*-octyloxybenzophenone (**9**)] have alkyl or methylene chains. Despite the differences in their chemical skeletons and functions, they could be classified together from the standpoint of solubil-

ity in hydrophobic solvents. Therefore, we concluded that the testing of some typical additives was sufficient.

In this study, our intent was to confirm whether this isolation procedure of PP was good enough to be adapted as part of a standard method for the estimation of the biobased carbon content in PP industrial products with petroleum-based PP supplied as a reagent. To confirm whether a hot solution of the composite provided PP precipitates that could be readily separated from solutions by scooping or filtration, the precipitates were studied by scanning electron microscopy (SEM) and X-ray diffraction, and we also assessed whether the removal of additives from the composites was suitable for estimation. The precipitates were analyzed by Fourier transform infrared (FTIR) spectroscopy and ultraviolet-visible (UV-vis) measurements.

EXPERIMENTAL

Materials

The materials in this study were purchased from the following companies: isotactic PP [number-average molecular weight = 67,000, 12 g/10 min (230°C/2.16 kg), melting temperature = 160–165°C], graphite (grain size < 20 μm), and **8** (Sigma-Aldrich Co.); **1** and corn starch (Wako Pure Chemical Industries); **2**, **3**, **4**, **5**, **6**, **7**, **9**, and decabromodiphenyl ether (**10**; Tokyo Chemical Co.); microcrystalline cellulose powder (Avicel PH-M25, mean size = 25 μm; Asahi Chemical Industry Co., Japan); and calcium carbonate from oyster shell (Gofun, Nakagawa Gofun Seizou Co). Other chemicals were reagent grade and were used without further purification.

Preparation of the PP Composites

Each PP composite sheet with a thickness of 0.50 mm was prepared according to a previous report.¹⁰ PP fine powder with a particle size of less than 125 μm and an additive were mixed with a mortar and a pestle. The resulting mixture was heated to 200°C at 20 MPa for 5 min in a stainless steel mold and was gradually cooled by standing at room temperature.

Isolation of Propylene from Composites

The typical procedure for recovering PP as fine precipitates from the composites was as follows: 400 mg of a specimen and 40 mL of a solvent in a glass centrifuge tube (50 mL) were stirred with a magnetic bar and heated under a nitrogen atmosphere in an aluminum dry bath at 150°C for 15 min. While the solution was hot, the tube was immediately spun for 15 min at 3500 rpm (2000 G) in a conventional centrifugal separator (Kubota Co., 2420). PP precipitates, which formed when the solution was cool and flocked near the surface of the solution, were scooped up with a stainless steel mesh or a spatula and transferred to another centrifuge tube. The precipitates were dispersed in 40 mL of ethanol (0.79 g/cm³) with a spatula and an ultrasonic bath and were collected on the tube bottom by centrifugation at 3500 rpm for 5 min followed by decantation of the solvent. After it was rinsed three or four times with ethanol, the high-boiling solvent was thoroughly removed. The removal of the solvent could be easily checked by the loss of the characteristic odor of the solvents. The precipitates for the X-ray diffraction study were dried *in vacuo* for 24 h without heating to prevent alteration of the crystallinity of the PP. For other

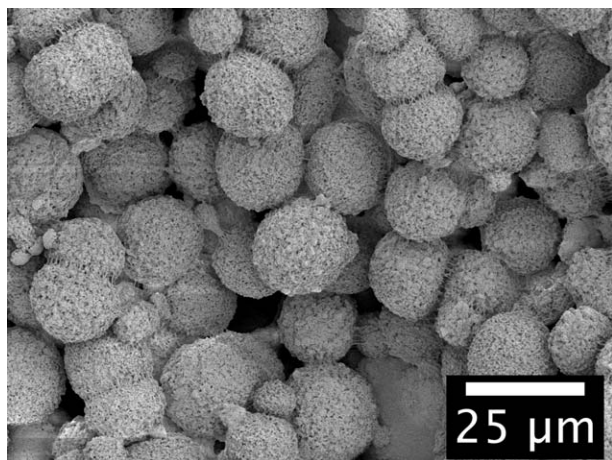


Figure 2. SEM observation of the recovered precipitates prepared from a 2 solution of PP.

purposes (weighing of the recovered resin, UV-vis spectroscopy, IR spectroscopy, and AMS measurements), rinsing was performed twice, and drying was conducted at 60°C to shorten the procedure.

Observation of the PP Precipitate with SEM

The PP precipitates were carefully fixed to an adhesive tape on a platform for SEM observation to prevent deformation of the specimens. Platinum deposition (4 nm thick) on the surface of the precipitates was conducted before observation with a field emission scanning electron microscope (Hitachi High-Technologies Co., S-4300).

Preparation of the Films for the Measurement of the UV-Vis Spectra

PP films for the measurement of the transmission UV-vis spectra were prepared from the PP composites and their recovered precipitates. The samples were placed between a pair of glass plates and heated under a nitrogen atmosphere at 200°C for 15 min with a pair of stainless steel thickness gauges to prepare films with a thickness of 0.1 mm. UV-vis spectra of the films were recorded at a scanning rate of 120 nm/min and a slit width of 2 nm on a spectrophotometer (Shimadzu Co. U-3000).

Measurement of the Biobased Carbon Content

The measurement of the ratios of the three carbon isotopes (^{14}C , ^{13}C , and ^{12}C) by AMS was conducted at the Institute of Accelerator Analysis, Ltd. (Japan), according to a procedure reported in our previous studies.⁸⁻¹⁰ The biobased carbon ratio was calculated with the following three equations:

$$\Delta^{14}\text{C} = \left[\frac{{}^{14}\text{A}_s - {}^{14}\text{A}_r}{{}^{14}\text{A}_r} \right] \times 1000 (\%)$$

$$\text{pMC} = \Delta^{14}\text{C} / 10 + 100 (\%)$$

$$\text{Biobased Carbon Ratio} = \text{pMC} \times 0.93 (\%)$$

where ${}^{14}\text{A}_s$ and ${}^{14}\text{A}_r$ are the ratios of ^{14}C to ^{12}C for a sample and a reference, respectively. Modern carbon-based oxalic acid was a reference supplied as Standard Reference Material 4990c by NIST. ${}^{14}\text{A}_s$ was corrected with the ratio of ^{13}C to ^{12}C by the

method regulated by ASTM D 6866-08. The biobased carbon ratio was also corrected by a factor of 0.93.

X-Ray Diffraction

Wide-angle X-ray scattering (WAXS) of the PP specimens was recorded on a Rigaku Miniflex II diffractometer with Cu K α Ni-filtered radiation. Plates of pure PP 24 mm in diameter and 2 mm in thickness were prepared on aluminum pans for WAXS investigation by heating at 200°C for 15 min and the pressing of the resin surfaces with a glass plate. After it was heated at 200°C, the resin plate was quenched in an ice-water bath, and another plate was annealed at 155°C for 24 h after it was molded at 200°C. Precipitate samples for the WAXS experiments were obtained by the normal method with centrifugation and by the slow cooling of the hot solution in an aluminum block bath for 1 h. The scanning rate was 2°/min. WAXS patterns of the PP precipitates were obtained in the same way by the filling of the sample in the aluminum panes.

RESULTS AND DISCUSSION

PP pellets or composite sheets were dissolved in 100 volumes of solvents by heating to 150°C, with the ramp usually over 10 min. When the hot solution was cooled to room temperature during centrifugation, the solubility of the PP decreased, and this resulted in white precipitates of the resin. The precipitates, which collected near the surface of the solution, could be recovered by scooping with a spatula or a stainless steel mesh or by filtration with a porous polytetrafluoroethylene membrane (Millipore Co., pore size = 0.45 μm). The average recovery rate from the reagent PP was 95% on the basis of the amount of precipitates collected by filtration of the entire solution. SEM observation showed that the precipitates were coarse-surfaced particles with diameter of 5–20 μm , as shown in Figure 2. The precipitates were bulky in appearance. However, they were not a swelling gel, and they were always solid enough to be readily scooped or filtered with the membrane filter.

Graphite powder, which is often used in large quantities as a fire retarder, was a suitable additive to confirm the availability of this PP isolation procedure from the staining of the recovered PP resin and visible observation. The composite of PP/graphite (75/25) gave a black sediment on the bottom of the test tube and white precipitates near the surface [Figure 3(b)];

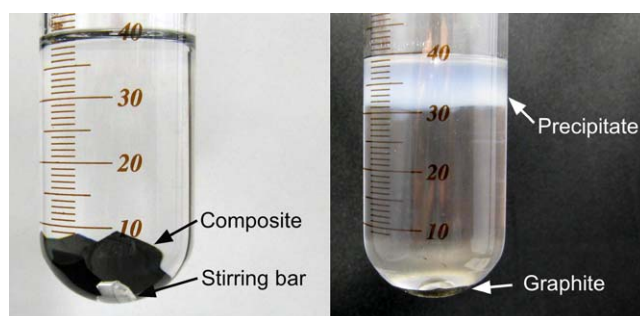


Figure 3. Photographs of the composite of PP/graphite (75/25) in 1 (a) before heating and (b) after centrifugation of the hot solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

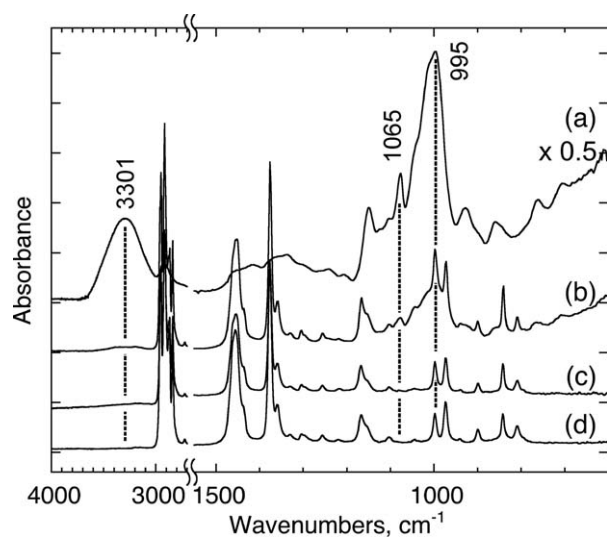


Figure 4. IR spectra of (a) starch, (b) composite PP/starch (50/50), (c) precipitates, and (d) PP reagent.

this indicated that this procedure met a fundamental requirement for the isolation of PP from the composites.

To quantitatively assess the removal of additives from composites, PP composites containing starch and cellulose, which could be added in large amounts by virtue of the apparent increase in the biobased component of plastic products, were tested by FTIR analysis. The composites formed fairly loose precipitates in the test tubes after centrifugation. Figure 4 shows FTIR the spectra for the starch, PP/starch (50/50) composite, recovered PP, and reagent PP. The loss of absorbance derived from starch¹⁶ around 1050 cm^{-1} in the recovery PP indicated the effectiveness of this operation {the rejection ratio was calculated as follows: $[1 - (A_1/P_1)/(A_0/P_0)] \times 100$ (%), where A_0 and P_0 are the amounts of additive and resin, respectively, in the composite and A_1 and P_1 are amounts of the additive and resin, respectively, in the precipitates} as calculated from a decrease in the absorbance (>98%). The composite of the PP/cellulose powder (50/50) showed the same clear isolation as that of the PP/starch composite. The PP isolation from the composites containing starch or cellulose was confirmed on the basis of content of the remaining additive-derived biobased carbon

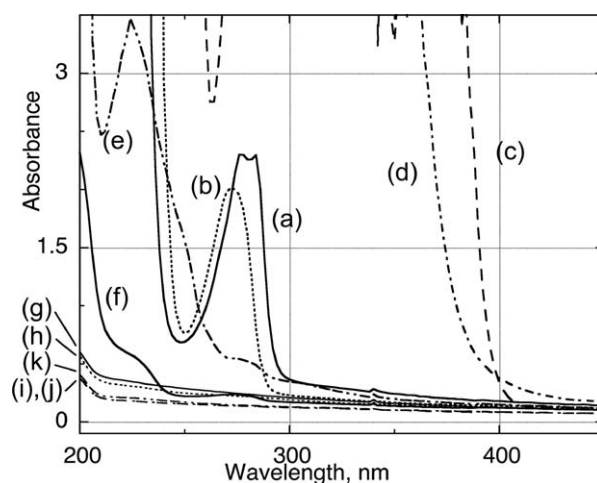


Figure 5. UV-vis spectra of films of the PP/additive composites (95/5) and corresponding recovered precipitates: (a) PP/4, (b) PP/5, (c) PP/6, (d) PP/9, (e) PP/10, (f) PP (reagent), (g) precipitate from PP/4, (h) PP/5, (i) PP/6, (j) precipitate from PP/9, and (k) precipitate from PP/10.

measured by AMS. The biobased carbon contents of the recovered precipitates (Table I, entries 1 and 2) were below the limit of AMS measurement (<0.12%); this indicated satisfactory rejection for the fillers as compared with the original composites (34.17%). This result also indicated that the biobased solvent (2) did not remain in the precipitates. In the case of the PP/calcium carbonate composite, the isolation procedure was also effective, but the rejection ratio of the additive was moderate (entry 3, 88%). The poor separation of the resin precipitate was probably due to the smaller grain size of calcium carbonate (Gofun). The rejection rate of biobased carbon in the precipitates was improved with other solvents (entry 4 or 5) or heating at 180°C (the rejection rate for entry 6 was 95%), probably because of the higher density of the solvents and the longer centrifugal separation until the formation of a precipitate. The formation of precipitates was observed at a solution temperature range of 80–90°C in a separate experiment without centrifugation. The recovery of PP for the composites of PP/cellulose (50/50) and PP/graphite (75/25) were 90.9 ± 0.3 and $91.3 \pm 1.9\%$, respectively, on the basis of the amount of resin in the composites (number of repetitions = 3). The recovery by scooping of

Table I. Biobased Carbon Ratios of the Recovered PP Precipitates and Composites

Entry	Material	Isolation conditions	pMC (%)	Measured for precipitate (%) [rejection rate (%)]	Calculated for original composite (%)
1	PP/starch (50/50)	2 , 150°C	<0.13	<0.12 (>99)	34.17
2	PP/cellulose fiber (50/50)	2 , 150°C	<0.13	<0.12 (>99)	34.17
3	PP/calcium carbonate (75/25)	2 , 150°C	0.58	0.54 (88)	4.46
4	PP/calcium carbonate (75/25)	3 , 150°C	0.53	0.49 (89)	4.46
5	PP/calcium carbonate (75/25)	1 , 150°	0.33	0.31 (93)	4.46
6	PP/calcium carbonate (75/25)	1 , 180°C	0.26	0.24 (95)	4.46

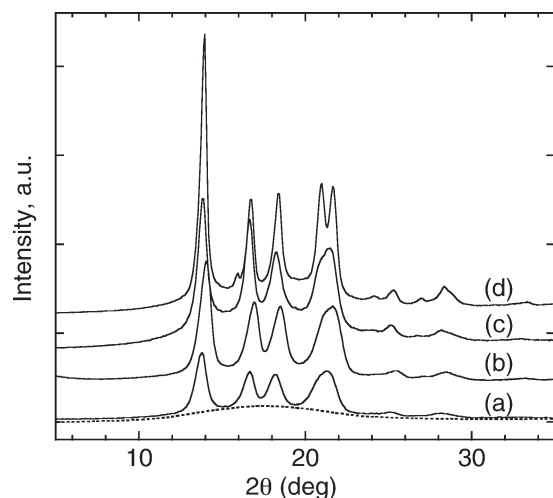


Figure 6. Wide-angle X-ray diffraction patterns for precipitates by (a) normal cooling and (b) slow cooling of hot solutions in an aluminum dry bath, (c) for a resin plate prepared by rapid cooling in an ice–water bath, and (d) by annealing at 155°C for 24 h.

the precipitates in solutions of the composites tended to be lower than that by filtration of the entire solution from the pure resin ($94.5 \pm 2.4\%$) because of loss during the handling of the precipitates.

Figure 5 shows the UV spectra of the PP films containing organic additives (**4**, **5**, **6**, **9**, and **10**; 95/5) and the films prepared from the corresponding precipitates. Each original film [Figure 5(a–e)] had strong absorption in the ultraviolet region because of the aromatic skeletons of the additives. Alternatively, the films from precipitates showed no substantial absorption band except for background by light scattering and were rather more transparent than the film prepared from the PP reagent, which may have contained a small amount of unknown constituents. The loss of the absorption bands for the composites with a variety of organic additives indicated the efficiency of this isolation process.

At room temperature, 10 mg of each of the organic additives (**4**–**10**, Scheme 1) readily resolved in 10 mL of solvent, **1**, **2**, or **3**, in a few minutes, and more rapidly at 150°C, and even after the solutions were cooled to room temperature, almost all of the organic additives were still soluble except for in **8**. Hot **1** or **2** solutions of **8** formed a small amount of precipitate by standing at room temperature. However, diluted solutions did not (1 mg/10 mL). The solvency had to satisfy the demands of the isolation process for PP because additives in composites are generally minimal and usually less than 1%. X-ray diffraction of the precipitates obtained from the PP reagent showed an overlap between the crystalline and amorphous patterns; this indicated that the precipitate was a semicrystalline PP, as shown in Figure 6(a). The crystalline diffraction of the precipitates corresponded to an α -form pattern.^{17,18} The peaks were broader than that of a resin plate prepared by annealing at 155°C [Figure 6(d)]. However, they were comparable with those of precipitates prepared by the slow cooling of the hot solution in

the aluminum block [Figure 6(b)] and a resin plate prepared by the quenching of melt resin with an ice–water bath [Figure 6(c)]. When the test tube was rapidly cooled with running water, the hot solution did not form a swelling gel but dense precipitates. Therefore, strict cooling conditions for the hot solution during centrifugation were not required for the recovery of the PP precipitates from hot solutions. The hot solutions of the composites with additives also formed dense precipitates; these could be readily separated and showed the same diffraction pattern as that from the pure propylene reagent. These findings suggest that the formation of pure precipitates without the inclusion of an additive may depend on the prompt crystallization of the polymer from the solutions and a high degree of crystallinity of the polymer.¹¹

CONCLUSIONS

Considering the solubility and density of each component in PP composites, we examined the isolation procedure of PP for AMS analysis by the centrifugal separation of the hot solutions of the composites. Soluble additives and fillers in the various model composites were effectively removed to isolate pure PP specimens suitable for AMS analysis. The recovery rates of PP from hot solutions of composites (typically 90%) and rejection rates for the additives and fillers (>99%, in the case of calcium carbonate, 95%) indicated that this procedure was an effective pretreatment of the PP products before AMS measurement. This procedure was applicable for isotactic and syndiotactic PP but not atactic PP because of the low recovery rate of the resin.

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