Enhancement of flame retardancy and mechanical strength of environmentally friendly plastics for use in electronics

Makoto Soyama

March 2017

Enhancement of flame retardancy and mechanical strength of environmentally friendly plastics for use in electronics

Makoto Soyama
Nano-Science and Nano-Technology

Submitted to the Graduate School of
Pure and Applied Sciences
in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy in
Engineering

at the University of Tsukuba

Table of Contents

Chapter 1.

General background

1-1. Environmental issues with plastic composites used in electronics

Electronics consist of various materials. In particular, plastic composites are largely used in housings and electronic components because of their good electronic, mechanical, and molding properties. In most electronics, thermoplastics, such as polycarbonate and polystyrene, are used in housings, and thermosetting plastics, mainly epoxy resin compounds, are used as insulating materials in electronic components. These plastics composites are required for high flame retardancy to prevent fire from originating in electronics.

However, there are two major environmental issues caused with these plastic composites with regard to electronics. The first is the inclusion of organic halogen compounds as a flame-retarding additive (flame retardant) [1, 2]. These compounds generate harmful substances, such as dioxin, when burned. This problem has limited thermal treatment of plastic composite wastes and their reuse for other purposes. The second is the use of petroleum resource as a raw material to produce plastics, which consumes a large amount of energy, causing petroleum-resource depletion and generation of a large amount of carbon dioxide that contributes to global warming.

Hence, attempts have been made to replace these halogen compounds with other safer flame retardants. However, current flame-retardant replacements are not suitable with regard to maintaining important practical properties of plastic composites, such as impact strength, bending strength and flame retardancy, for use in electronics. Bioplastics produced from plant sources have been studied with keen interest as environmentally friendly material that contributes to conserving petroleum and reducing the generation of carbon dioxide [3-5]. Mass-produced bioplastics, such as poly(lactic acid) and poly(hydroxyalkanoic) acid, have been used in textiles and tableware. However, these bioplastics have insufficient mechanical strength, heat resistance, and flame retardancy for use in electronics. Moreover, since most bioplastics are made using starch produced from edible plants, the fear of food shortages in the future has increased interest in producing bioplastics from inedible plants or the inedible parts of edible plants.

1-1-1. Flame-retardant technologies of plastic composites for electronics

To prevent fire from originating in electronics, the main plastics in their parts contain flame retardants. Their flame-retarding mechanisms are generally trapping of combustion radicals, forming flame-retardant layers on resin surfaces, and decreasing temperature during ignition.

The most common forms of halogen compounds, such as organic bromine compounds, have been used in most electronics. These compounds decompose along with plastics during burning then retard combustion by trapping radicals generated from the plastics, as well as by forming gas-phase-barriers against oxygen. There is a serious problem with such halogen compounds, however. During burning, the compounds generate toxic substances, such as dioxin and halogen derivatives, which can injure people and contaminate the environment.

Therefore, most are classified as specific hazardous substances in the European Union (RoHS Directive). Furthermore, antimony oxide is usually used together with halogen compounds to increase their flame-retarding effectiveness, but the oxide is toxic. In addition to fire-related dangers, the treatment of plastic waste that includes halogen compounds and their reuse for other purposes are therefore extremely difficult.

Attempts have been made to replace halogen compounds with other safer flame retardants such as phosphorus compounds, e.g., red phosphorus and phosphoric ester, or metal hydroxides, e.g., aluminum hydroxide and magnesium hydroxide [6-10]. Phosphorus compounds form flame-retardant layers on resin surfaces and generate non-flammable gases during combustion to achieve high flame retardancy. However, the generation of harmful phosphine from red phosphorus and the chronic toxicity of some phosphate esters have become problematic. In recent years, chemical safety of phosphate esters has been improved, and some meet the requirements of eco labels such as Blue Angel of the European Environmental Evaluation Standards. Moreover, metal hydroxides, such as aluminum hydroxide and magnesium hydroxide, were developed as endothermic agents during ignition. To increase the flame retardancy of plastics, however, large amounts of metal hydroxides must be added, which decreases the fluidity during molding and strength of the plastics. This makes such plastics composites with the hydroxides unsuitable for the housings of electronics.

1-1-2. Bioplastics using plant resources for measures against global warming and petroleum-resource depletion for electronics

Since plants are produced through photosynthesis of carbon dioxide and water, bioplastics derived from plant resources are expected as new environmentally friendly material to help in preventing global warming and petroleum-resource depletion. Starch is annually produced at 1.4 billion tons, and cellulose, the largest amount of plant resource on Earth, is annually produced at 80-150 billion tons. Current bioplastics including poly(lactic) acid and poly(hydroxyalkanoic) acid, which are mainly produced from edible plants such as starch, have already been expanding on a scale of 1 million tons for general products, such as textiles and tableware, and some durable products such as electronics and automobiles.

Fears of future food shortages, however, are driving efforts to use inedible plant sources such as cellulose. Cellulose is a polysaccharide consisting of D-glucose units linked together by 1-4 glycosidic bonds into linear chains. It has an extensive hydrogen-bonded and partially crystallized structure that makes it very stiff and non-melt processable. Esterification is commonly used to produce thermoplastics from cellulose, mainly by using various acids such as acetic acid, propionic acid, and nitric acid. Because of these cellulose derivatives' narrow process windows between their melting and degradation temperatures, large amounts of external plasticizers, such as glycerin, polyethylene glycol, and triethyl citrate (TEC), generally must be added. However, adding external plasticizers can reduce the bending strength and heat resistance of cellulose ester composites. Furthermore, these cellulose derivatives absorb a large amount of water when dipped in water. These issues have limited their use in durable products such as electronics.

To overcome these problems, a number of studies have been conducted on modifying cellulose and its derivatives by bonding them with long chain units such as alkyl compounds. The long alkyl chains investigated were carboxylic acids and their derivatives, such as carboxylic anhydrides and carboxylic acid chlorides [11, 12], and alkyl halides with alkalis [13], which were bonded with hydroxyl groups on the glucose units of cellulose [14-16]. A cardanol-bonded cellulose diacetate (CDA) by bonding CDA and cardanol, which is a principal organic ingredient in cashew nut shells, was developed for a previous study [7]. However, this cardanol-bonded CDA was unsuitable with regard to its impact strength and flame retardancy for use in electronics.

1-2. Outline and scope of this study

To solve current environmental issues of plastic composites used in electronics, as mentioned in section 1-1, the author developed safer flame-retardant technologies for petroleum-derived plastics, i.e., polycarbonate used in housings and epoxy resin compounds used in electronic parts. The author also improved cellulose-based bioplastics derived from inedible plants with regard to the impact strength and flame retardancy for use in electronics.

In chapter 2, the author describes safer flame-retardant technologies of petroleum-derived plastics conventionally used in electronics.

In section 2-1, the author introduces a flame-retardant polycarbonate resin composite whose flame retardancy is greatly enhanced by adding fly ash (a by-product from thermal power plants). Fly ash with comparatively small average particle sizes (<10 μm) increases the flame retardancy of polycarbonate because of the hydrogen bond that forms between the polycarbonate and hydroxyl group on the fly-ash surface. This bond primarily improves the heat resistance of the polycarbonate and isomerizes it to promote carbonization. The polycarbonate composites with fly ash exhibits other important properties, such as mechanical properties and moldability, which are comparable to those of a flame-retardant polycarbonate reinforced with glass fiber, used for electronics. Applying fly ash eliminates the need to use current flame retardants such as organic halogen compounds; thus, promoting the perceived environmental safety of flame-retardant polycarbonate. Being able to use less raw resin by adding fly ash also means that less energy is required to manufacture flame-retardant polycarbonate.

In section 2-2, the author describes the improvement in the flame retardancy and heat resistance of the phenol-aralkyl-type epoxy resin for use in the internal components of electronics by using synthesized triazine containing phenol aralkyl resin (benzoguanamine-modified phenol biphenylene resin) as a new non-flammable substance -generating agent. This resin contains a benzoguanamine unit to release non-flammable nitrogen substances during ignition and increase the resin's reactivity toward epoxy resins and biphenylene units to maintain the thermal-degradation and water resistance of the resin. The addition of benzoguanamine-modified phenol biphenylene resin in the epoxy resin compound improves the compound's flame retardancy and heat resistance and increases its glass-transition temperature while maintaining its water resistance and mechanical properties.

In chapter 3, the author discusses the improvement in the mechanical properties and flame retardancy of a cardanol-bonded CDA, a bioplastic derived from non-edible plant resources.

In section 3-3-1, the author argues that olefin-based resins work as impact modifiers for a modified cardanol (3–pentadecylphenoxy acetic acid: PAA) bonded CDA (PAA-bonded CDA) while maintaining other properties, including bending strength, heat resistance, water resistance, and thermoplasticity. Improvement in the impact strength of PAA-bonded CDA while satisfying its good bending strength and breaking strain was achieved by using hydrophobic olefin resins such as polyethylene and polypropylene, which were due to high affinities of the olefin resins to hydrophobic cardanol side chains of PAA-bonded CDA.

In section 3-3-2, the author demonstrates that adding polyether silicones to PAA-bonded CDA improves its impact strength. The polyester silicones with relatively high polarity become highly dispersed in PAA-bonded CDA composites. The polyether silicones that are optimized in terms of their amount, polarity, and viscosity enhance the impact strength of PAA-bonded CDA composites. The results of an experiment the author conducted for this study indicate that adding the polyether silicone with moderate polarity relative to PAA-bonded CDA results in shearing deformation; thus, greatly enhancing its impact strength.

In section 3-3-3, the author argues that the combination of other bioplastics, glass fiber, and safe flame retardants with PAA-bonded CDA, improves mechanical properties including impact strength as well as flame retardancy. Adding a specific polyester resin, glass fiber, and complex flame retardants including aluminum hydroxide and a phosphoric compound to PAA-bonded CDA greatly increases both its impact strength and flame retardancy while maintaining bending strength, water resistance, and thermoplastisity. The addition of polybutylene succinate adipate (PBSA) as the polyester, which has flexibility and high compatibility to PAA-bonded CDA, greatly enhances the impact strength. Including glass fiber in composites consisting of PAA-bonded CDA and PBSA increases the composites' bending strength while maintaining high impact strength. Adding aluminum hydroxide and phosphate phosphate, i.e., cresyl diphenyl phosphate, as complex flame retardants to the composite with PBSA and glass fiber also exhibit sufficiently high flame retardancy and maintain such practical properties required for housings in electronics.

References

[1] Camino G, Costa L. *Polym. Deg. Stab.* **1988**, 20, 271.

[2] Cullis CF. *J. Analyt. Pyroly.* **1987**, 11, 451.

[3] Yu L, Dean K and Li L, *Prog Polym. Sci.* **2006**, 31, 6, 576.

[4] Willams C. K., Hillmyer M. A., *Polym. Rev.* **2008**, 48, 1

[5] Gupta A. P., Kumar V., Eur. *Polym. J.* **2007**, 43, 4053

[6] Iji M., Toyama K. and Tanaka S., *Cellulose* **2013**, 20, 559-569

[7] Iji M., Moon S. and Tanaka S., *Polymer Journal*, **2011**, 43,738-741.

[8] Termine EJ, Taylor KG. *Reinforced Plastics* **1990 ,** 34, 12,28.

[9] Termine EJ, Taylor KG. *SPI Compos. Inst. Annu. Conf. Expo. Proc.* **1990**, 45: 17C1.

[10] Huggard MT. *Soc. Plast. Eng. Annu. Tech. Conf.* **1993**, 51(2): 1753.

[11] Sealey J. E., Samaranayake G., Todd J. G. and Glasser, W. G., *J. Polym. Sci., Part B: Polym. Phys.* **1996**, 34, 1613-1620.

[12] Edgar K. J., Pecorini T. J. and Glasser W. G., *ACS symposium series,* **1998**, 688, 38-60.

[13] Isogai A., Ishizu A. and Nakano J., *J. Appl. Polym. Sci.*, **1986**, 31, 341-352.

[14] Roy D., Semsarilar M., Guthrie J. T. and Perrier S., *Chem. Soc. Rev.,* **2009**, 38, 2046-2064.

[15] Teramoto Y. and Nishio Y., *Polymer,* **2003**, 44, 2701-2709.

[16] Enomoto-Rogers Y., Kamitakahara H., Takano T. and Nakatsubo F., *Biomacromolecules*, **2009**, 10, 2110-2117.

Chapter 2.

Safe flame retardant technologies of petroleum-derived plastics

In chapter 2, the author describes to develop safe flame-retarding technologies for petroleum-derived plastic composites which are conventionally used in electronics.

Thermoplastics such as polycarbonate are used in housings, and thermosetting plastics, mainly epoxy resin compounds are used as insulating materials in electronic parts. They are required high flame retardancy and then, included toxic halogen compounds as flame retardants.

In section 2-1, the author demonstrated the use of fly ash as a new flame retardant for polycarbonate. Adding fly ash which is by-produced from thermal power plants enhanced the flame retardancy of polycarbonate which is used for the exteriors of electronics, and further the author revealed its flame-retarding mechanism. Applying the fly ash eliminates the need to use the halogen compounds as flame retardants and thus promotes the perceived environmental safety of flame-retardant polycarbonate. In addition, being able to use less raw resin by adding the fly ash means that less energy is required to manufacture flame-retardant polycarbonate.

In section 2-2, the author described the improvement in the flame retardancy and heat resistance of phenol aralkyl type epoxy resin compounds used as an insulating materials in electronic parts by using a benzoguanamine-modified phenol biphenylene resin as a new non-flammable substance-generating agent.

Section 2-1.

Flame retardancy of polycarbonate enhanced by adding fly ash

2-1-1. Introduction

Flame retardancy is an essential property for preventing the plastics used in the housing of electronics, such as polycarbonate and polystyrene, from accidental burning. Hence, organic halogen compounds have been added to these plastics as flame retardants. Incinerating plastics containing such organic halogen compounds, however, generates halogen gases, creating a major environmental safety hazard. Therefore, phosphorus compounds, sulfonates and silicone compounds, which are safer but less effective as flame-retardants than the halogen compounds, are now being used as flame retardants for polycarbonate, which has comparatively high flame retardancy compared with other plastics such as polystyrene and its derivatives used in housing [1]. The manufacture of polycarbonate, however, consumes more energy and is more expensive than the manufacture of other applicable plastics. The energy required and the cost must be reduced to expand the use of polycarbonate.

Combining plastics and inorganic fillers requiring a little energy to produce them is an effective way to reduce the energy required for manufacturing the plastics. The inorganic compounds typically used as fillers (such as silica, calcium carbonate, and talc) also make plastics slightly less flammable [2-7]. To significantly increase the flame retardancy of plastics, though, large amounts of these fillers must be added and such large amounts lower the fluidity and strength of the plastics. This makes such plastics unsuitable for the housing of electronic equipment. In addition, the overall energy consumption is not greatly reduced since energy is used in the manufacture of the inorganic compounds.

In response to this problem, the use of fly ash: a by-product from thermal power plants as a new flame retardant for polycarbonate was examined. Fly ash, composed of mainly silica and alumina, is a by-product obtained when ground coal is fed into burners to generate power and shows dark color because of unburned carbon content. As a result, little energy is needed to produce it, and in Japan this corresponds to designating a by-product as a renewable resource. A huge amount of fly ash is generated worldwide; in Japan alone, the annual production was about seven million tons in 2000 [8].

Some fly ash is used in the construction industry, mainly in cement and concrete manufacturing, while the remainder is disposed of in landfill sites. Using fly ash in a beneficial way would be preferable to dumping it, so many researchers have been looking for useful applications. One example is to mix fly ash with plastics to lower production costs; this has been done in the commercial production of commodity plastics such as polypropylenes [9]. This research has shown that adding fly ash to plastics leads to decreased moldability as well as lower manufacturing costs, but the particular properties of fly ash as a flame retardant have not been much examined.

Thus, the flame-retarding property of polycarbonate with added fly ash was investigated. In this paper, the flame-retarding property and its underlying mechanism as well as other main properties such as mechanical properties and moldability of this resin compound were described.

2-1-2. Experimental

(1) Materials

As a thermoplastic, polycarbonate (Sumitomo Dow Co., Ltd., Caliber 301-22) was used. The fly ash (Yonden Business Industry Co., Yonden fly ash and Fynash FA20) had the consistency of a very fine powder with primarily spherical particles as shown in Figure 2-1-1 with average particle sizes of about 5 and 20 µm. The fly ash primarily consisted of inorganic materials such as silica, alumina, and calcium oxide. Table 2-1-1 shows the chemical characterization of typical fly ash. Three other inorganic materials were used in this study (Table 2-1-2): spherical silica (Denki Kagaku Kogyo K. K., FB 5604, FB 24, FB 3 SDC, SFP 30 M), spherical alumina (Admatechs Co., Ltd., AO-509 and Showa Denko K. K., CB-A05S), and spherical calcium carbonate (Komesho Sekkai Kogyo Co., Ltd., ED-SIII). Trioctyl trimellitate (Daihachi Chemical Industry Co., Ltd., TOTM) was used as a plasticizer. The author also added 0.5 wt% of polytetrafluoroethylene (Daicel Chemical Industries, Ltd., Polyflon MPA FA 500) to prevent dripping during heating.

(2) Methods

Sample compounds were prepared by mechanically kneading the polycarbonate with inorganic fillers and the other additives using an extruder (KCK Co., Ltd., KCK80×2-35VE×5) at 280 °C. Test pieces of the compounds for evaluating the flame retardancy and the flexural property were molded with an injection molding machine (Toshiba Machine Co., Ltd., EC20P-0.4A), at a cylinder temperature of 280 °C and a mold temperature of 80 °C.

The flame retardancy of the molded compounds by the oxygen index method (JIS-K-7201) and the UL94V method of Underwriters Laboratories (UL) Inc. were evaluated. The oxygen index indicates the oxygen concentration required for the material to continue burning. In the UL94V method, a vertically clamped sample of the molded compound is ignited by a gas burner flame applied twice for 10 s to the bottom of the sample. For a material to be classified as V-0 requires that burning stops within 10 s after two ignitions. The V-1 and V-2 classifications require that burning stops within 60 s after two ignitions, but V-2 allows a flaming drip. In all tests, the samples cannot be allowed to burn out.

The flexural strength of the compounds and their modulus were evaluated with a versatile examination machine (Instron Co., Ltd., 5567), under the conditions of a distance of 50 mm between the supporting points and a crosshead speed of 1.6 mm/min. Their Izod impact strength with a notch in the resin was measured with a universal impact tester (Orient Precision Machine Ltd., C1).

The moldability of the compounds was evaluated according to the melt flow property, which was evaluated along the flow length (spiral flow) of the compounds in a metal molding. The plasticization conditions were set so that an injection temperature of 280 °C was achieved. The mold temperature was maintained at 80 °C. The injection rate was 100 mm/s, and the thickness of the product was 1 mm.

The thermal stability of the compounds was measured in air (200 ml/min) at a heating rate of 10 °C/min by thermogravimetric analysis (EXTAR6000 TG/DTA, Seiko Instruments Co.).

The pyrolysis gas of the compound (0.5 mg - 1 mg) was identified by mass spectrometry. In addition, the amount of generated gas as compared with the peak area of a GC-MASS (QP-5050A [GC-17A], Shimadzu Co.) chart was calculated. The heating temperature was set to 800 °C for the thermal decomposition division, a helium gas atmosphere was used in the heating treatment, and the interface temperature was measured at 300 °C.

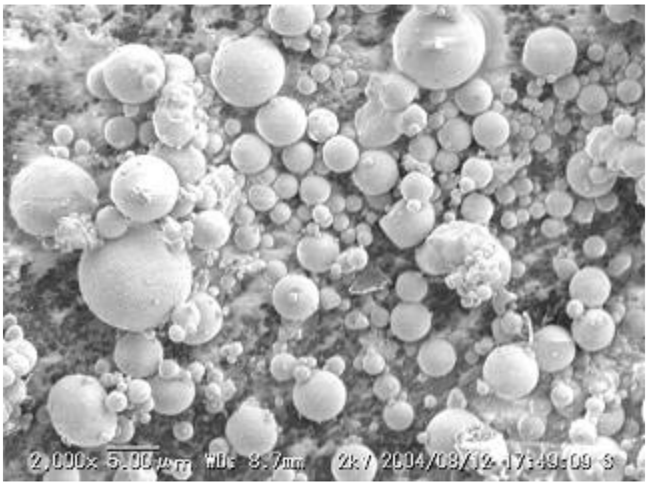
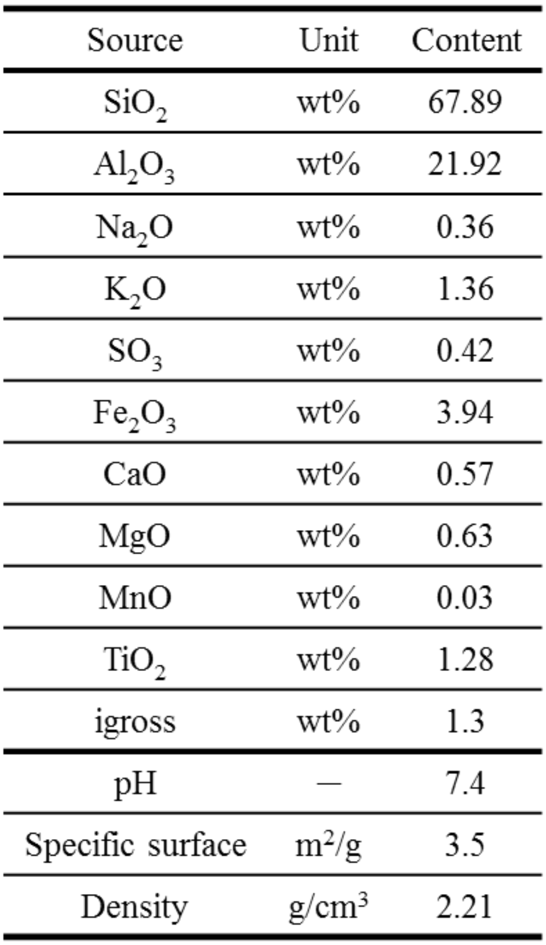


FIGURE 2-1-1 Scanning electron microscopy image of fly ash.

TABLE 2-1-1. Chemical characterization of typical fly ash



Source	Unit	Content
SiO_2	wt%	67.89
Al_2O_3	wt%	21.92
Na_2O	wt%	0.36
K_2O	wt%	1.36
SO_3	wt%	0.42
Fe_2O_3	wt%	3.94
CaO	wt%	0.57
MgO	wt%	0.63
MnO	wt%	0.03
TiO_2	wt%	1.28
igross	wt%	1.3
pH	—	7.4
Specific surface	m^2/g	3.5
Density	g/cm^3	2.21

TABLE 2-1-2. Characteristics of the inorganic compounds used in this study

Inorganic compound	Source	Content (%)	Specific surface (m^2/g)	Average particle diameter (μm)
Fly ash	SiO_2 Al_2O_3	Table1	3.5	20
			5.5	5
Spherical silica	SiO_2	100	2	32
			2.5	18
			2.4	11
			3.7	3
			5	0.6
Spherical alumina	Al_2O_3	>99.8	0.6	10
			1.4	2.8
Spherical calcium carbonate	$CaCO_3$	93.0	7	3

2-1-3. Results and discussion

(1) Flame-retarding effect of inorganic filler for polycarbonate

The effects of the kind and particle size of the inorganic fillers on the flame retardancy of polycarbonate were compared as shown in Figure 2-1-2. The results confirmed that silica, alumina, and fly ash, which all have hydroxyl groups on their surface, made the polycarbonate more flame retardant. Fly ash with small particle sizes and wide specific surfaces tended to make the polycarbonate highly flame retardant. In particular, fly ash with an average particle size of 10 μm or less greatly improved the flame retardancy of the polycarbonate compared to the effect of the other fillers. On the other hand, calcium carbonate, with few hydroxyl groups on its surface, did not make the polycarbonate more flame retardant [10]. In addition, Figure 2-1-3 showed that increasing the quantity of fly ash with an average particle size of about 5 μm improved the flame retardancy of the polycarbonate.

(2) Flame-retarding mechanism for polycarbonate with fly ash

The flame-retarding mechanism for polycarbonate with fly ash by evaluating the progress of carbonization, through quantitative analysis of thermal decomposition products, and from the change in the thermal degradation was clarified. A similar evaluation using added silica as a reference, because silica is the main component of the fly ash was conducted.

(3) Progress of carbonization

The fly ash promoted carbonization of the polycarbonate, since both the fly ash and the silica reference was found to increase the ratio of carbon to hydrogen in the compounds containing them after ignition as shown in Table 2-1-3. The progress of the carbonization by observing the material around the ignition area and measuring the fixed quantities of carbon and hydrogen were evaluated. Ballistreri A. et al. showed the change in the chemical structure of the polycarbonate as it carbonizes; through this change, the proportion of carbon increases relative to that of hydrogen [11].

(4) Quantitative analysis of thermal decomposition products

The thermal decomposition products of the polycarbonate with added fly ash or silica were quantitatively analyzed. Table 2-1-4 lists the thermal decomposition gases, and Figure 2-1-4 shows the results of gas chromatography mass spectrometric analysis (GC-MASS). The gas components and generation rates showed that the total quantity of thermal decomposition gas decreased by about 60% because of the presence of fly ash or silica, which reduced the generation of phenols and bisphenol A in the middle-molecular-weight portion in the thermal decompositions of the polycarbonate from the comparison of phenol derivatives and benzene derivatives in Table 2-1-5. This suggests that fly ash or silica changes the thermal decomposition mechanism of the polycarbonate, and that the decomposition products do not gasify but rather are fixed as a char through the dehydration condensation reaction, indicating that the polycarbonate is made more flame retardancy.

The fragmentation mechanism of the polycarbonate with added fly ash from the thermal decomposition analysis was deduced. The polycarbonate decomposes thermally through reduction of the isopropylidene group or the carbonate group, as proposed by some authors [12-16]. The division mechanism shows how the generation of phenols reduces the carbonate group. The fact that fly ash or silica reduced the phenols in the thermal decomposition gas of the polycarbonate shows that these additives inhibited reduction of the carbonate group and promoted reduction of the isopropylidene group.

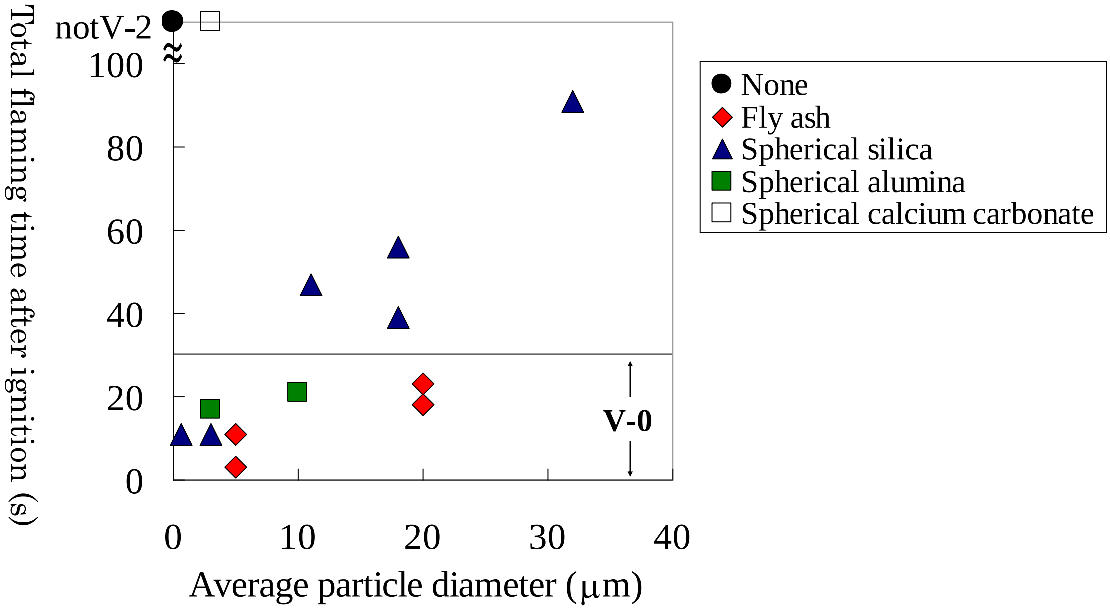


FIGURE 2-1-2 Flame-retarding effect of polycarbonate with 30 wt% of inorganic compounds.

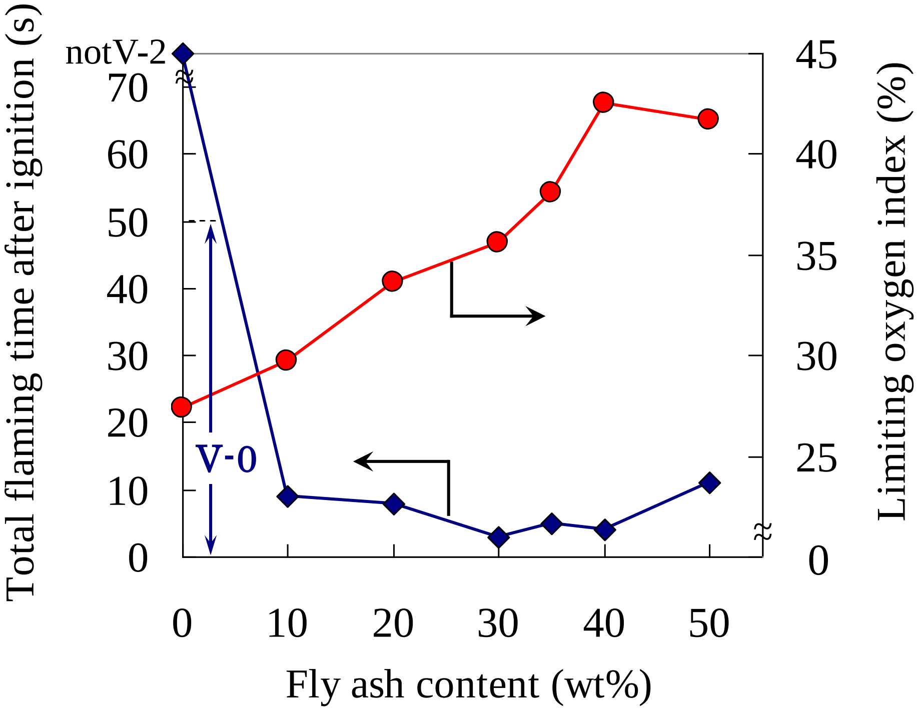


FIGURE 2-1-3 Flame- retarding effect of fly ash (particle size 5 μm) added to polycarbonate.

TABLE 2-1-3. Changes in the C/H ratio caused by ignition for polycarbonate with fly ash

Sample	Ignition	C/atm%	H/atm%	C/H
Polycarbonate	before	48.0	43.1	1.11
Polycarbonate	after	48.6	42.6	1.14
Polycarbonate with 30 wt% fly ash	after	49.1	40.1	1.22
Polycarbonate with 30 wt% spherical silica	after	48.3	37.1	1.30

TABLE 2-1-4. Thermal decomposition products assigned by mass spectroscopy

Peak No.	Structure
1	Benzene
2	Toluene
3	Phenol
4	*p*-Cresol
5	*o*-Cresol
6	*p*-Ethyl phenol
7	Isopropyl phenol
8	Ally phenol
9	Diphenyl carbonate
10	Carbonize acid 4-methyl ester
11	4,4'-Methylenebis-phenol

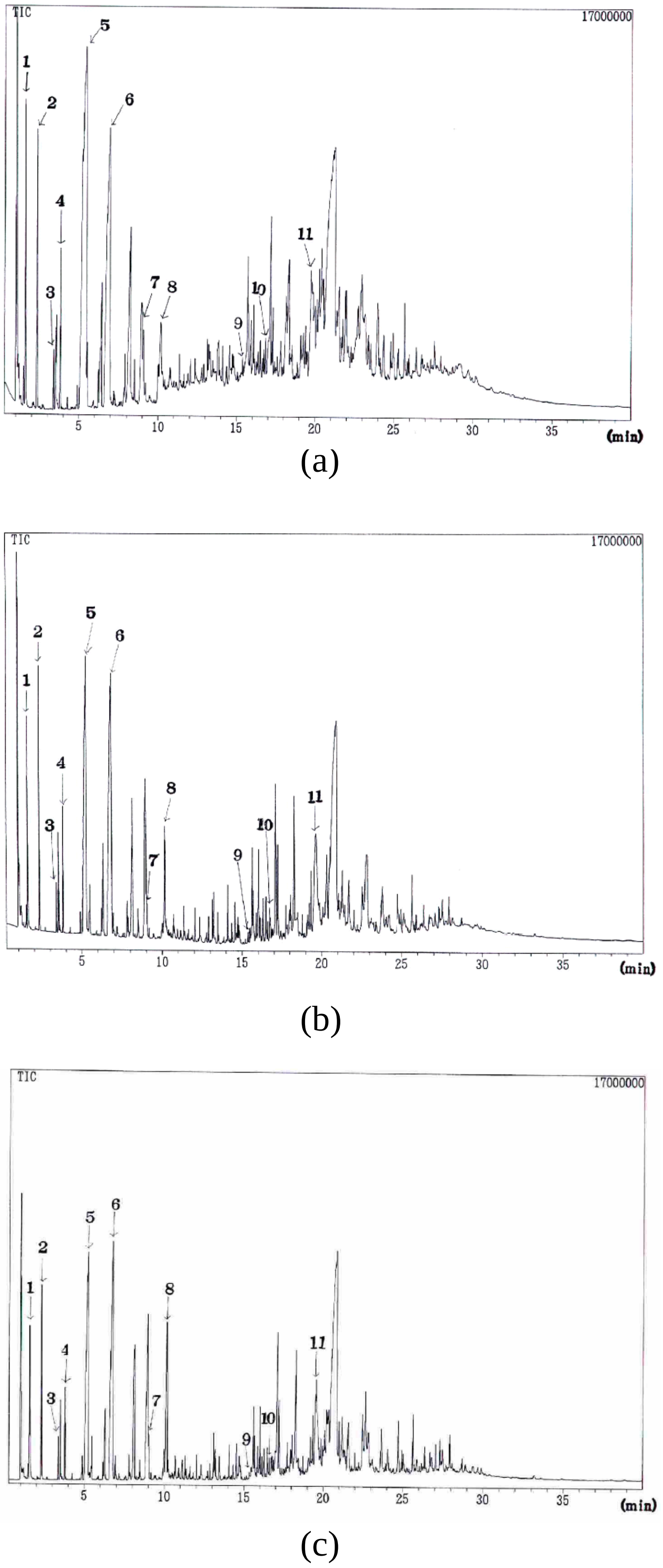


FIGURE 2-1-4 GC-MASS charts of (a) polycarbonate, (b) polycarbonate with 30 wt% fly ash, and (c) polycarbonate with 30 wt% spherical silica.

TABLE 2-1-5. Comparison of the amounts of thermal decomposition products measured by GC-MASS (800 ºC)

	Benzene	toluene	Benzene derivatives	Phenol	Cresol	Isopropyl phenol	Phenolic derivatives	Bis phenolic derivatives	Gas generation
Polycarbonate	100	100	100	100	100	100	100	100	100
Polycarbonate with 30% of fly ash	105	124	115	73	129	53	85	48	59
Polycarbonate with 30% of spherical silica	94	128	111	72	124	27	74	54	67

(5) Thermal degradation

Thermogravimetric analysis to investigate the effect of fly ash on the thermal degradability of the polycarbonate was shown in Figure 2-1-5. The results of thermal decomposition onset temperatures of polycarbonate and polycarbonate with fly ash showed that the fly ash improves resistance to the degradability. This reason was mainly proposed as follows; the fly ash stabilizes the carbonate group of the polycarbonate through the strong hydrogen bond between the hydroxyl group on the fly ash surface and the carbonate group.

(6) Proposed flame-retarding mechanism of fly ash

Based on the above results, a mechanism to explain the flame-retarding effect that fly ash has on polycarbonate was proposed. Of the inorganic fillers, only those including fly ash and silica, which have hydroxyl groups on their surfaces, made polycarbonate more flame retardant. It was also showed that the fly ash increased the thermal degradation resistance of polycarbonate. Furthermore, because fly ash and silica reduced the middle-molecular-weight component in the thermal decomposition of the polycarbonate, they accelerated the dehydration condensation between the phenols and the bisphenol-A to promote the carbonization of the polycarbonate [17-18]. Therefore, it is suggested that the hydrogen bond between the hydroxyl group on the fly ash surface and the carbonate group of the polycarbonate is the cause of the flame retardancy of the polycarbonate as shown in Figure 2-1-6. That is, this bond thermally stabilizes the polycarbonate on the fly ash surface, thus improving heat resistance; it also isomerizes the polycarbonate, promoting carbonization through which the fly ash improves the polycarbonate flame retardancy.

The present studies demonstrated that the flame-retarding mechanism of the polycarbonate added fly ash consists mainly of the two following steps.

I. The hydrogen bond between the hydroxyl group on the fly ash surface and the carbonate group of the polycarbonate stabilizes the combination in the polycarbonate, thus improving its heat resistance, while also isomerizing the polycarbonate.

II. The isomerized polycarbonate is condensed during dehydration with the phenols in the decomposition product, becoming carbonized to form a material like char, which is advantageous for flame retardation.

Figure 2-1-3 shows that the polycarbonate flame retardancy is more improved by fly ash than by the silica and alumina, which also have the hydroxyl group. This effect can be

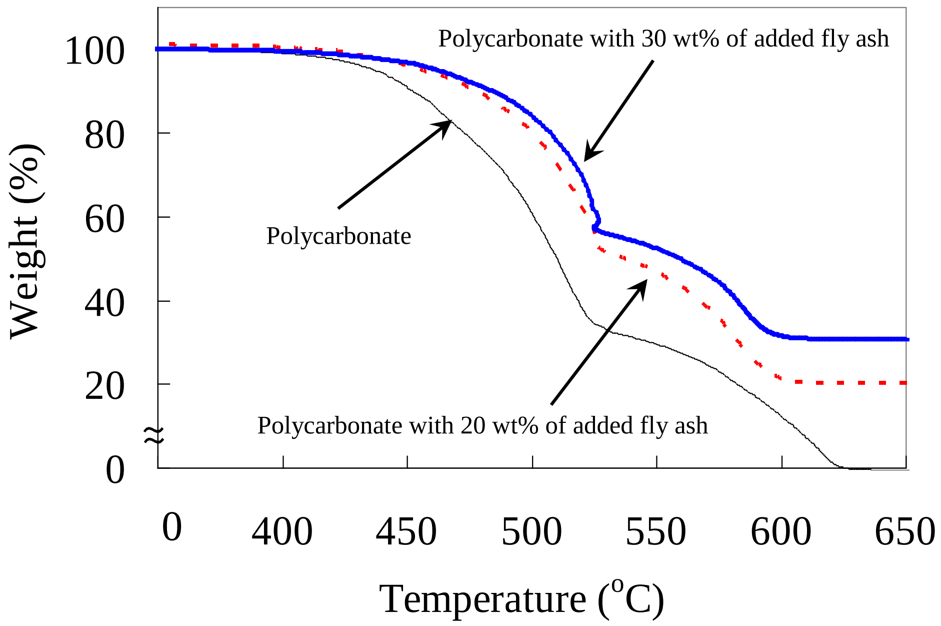


FIGURE 2-1-5 Thermogravimetric analysis of polycarbonate containing fly ash (air: 200 ml/min, 10 °C/min).

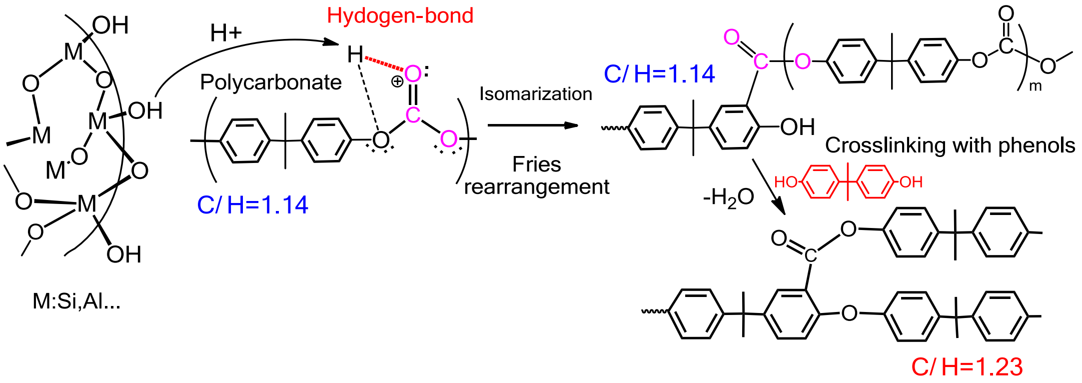


FIGURE 2-1-6 Scheme of isomerization and the cross-linking reaction of polycarbonate.

expected even if the flame retardancy is actually improved by a different factor specific to the fly ash; for example, if the silica-alumina composite included in the fly ash showed higher acidity than plain silica and alumina, thus increasing its effect as a solid acid catalyst to promote charring of the polycarbonate [19].

(7) Mechanical properties and moldability of polycarbonate with fly ash

Figure 2-1-7 shows the flexural properties of polycarbonate with fly ash, and Figure 2-1-8 shows its impact strength and fluidity. The flexural modulus improved with increasing fly ash content. While the flexural strength was maintained at comparatively low contents of fly ash, it fell sharply when the content exceeded 30 wt%. Adding too much fly ash to the polycarbonate also lowered its impact strength. These properties of the polycarbonate with 25 wt% of added fly ash were almost equal, however, to those of a polycarbonate with 10 wt% glass fiber, which is currently used as a housing material for electronics such as desktop computer, etc. Though fluidity is lowered with this quantity of fly ash added to the polycarbonate, this was improved by adding a plasticizer with comparatively high heat resistance, such as trioctyl trimellitate, while maintaining its flame retardancy, as shown in Table 2-1-6.

The appearance of the polycarbonate with fly ash was somewhat dark color owing to the original color of fly ash, which can retard the use in products required to be clear colors.

2-1-4. Conclusion

Fly ash, a by-product of thermal power plants, greatly was found to enhance the flame retardancy of polycarbonate and thus decreases the amount of energy required to manufacture flame-retardant polycarbonate. The flame retardancy of the polycarbonate with fly ash results from the hydrogen bond between the hydroxyl group on the fly ash surface and the carbonate group of the polycarbonate. This bond thermally stabilizes the polycarbonate on the fly ash surface and thus improves its heat resistance. In addition, it isomerizes the polycarbonate and then promotes carbonization, which improves flame retardancy. Though adding a large amount of fly ash degrades the mechanical properties and moldability of the material, the properties of polycarbonate with 25 wt% of fly ash were equal to those of polycarbonate with 10 wt% glass fiber, which is used as a housing material for electronics such as desktop computers, etc. In addition, combining this material with a plasticizer having high heat resistance drastically improves its fluidity, while maintaining its flame retardancy.

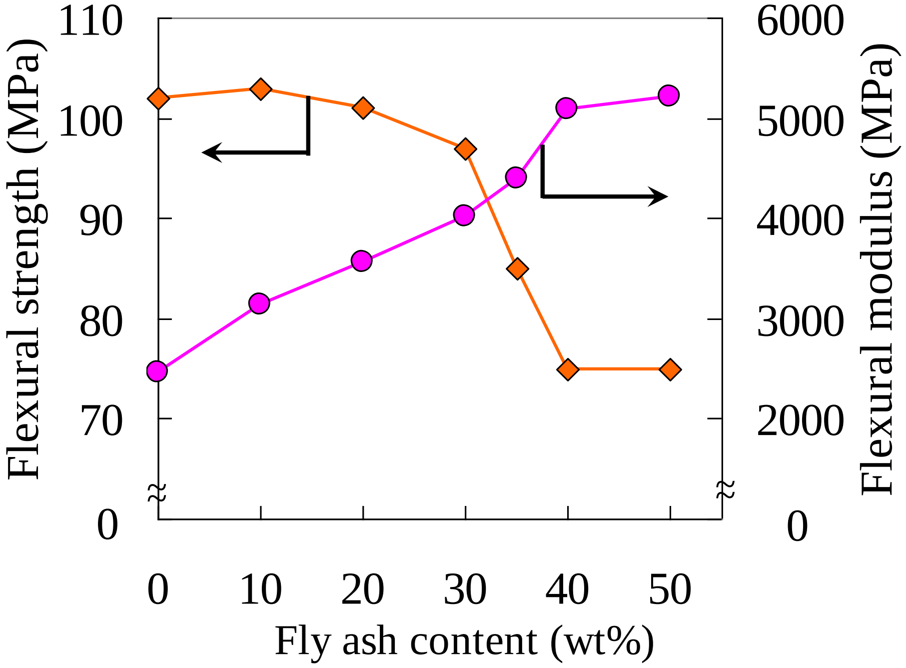


FIGURE 2-1-7 Flexural properties of polycarbonate containing fly ash.

TABLE 2-1-6. Properties of polycarbonate compounds containing fly ash

	Unit	Polycarbonate	PC with 10% glass fiber*	PC with 25% fly ash	PC with 25% fly ash and 5% plasticizer
Flame retardant (UL-94. 1/16 in.)	—	V-2	V-0	V-0	V-0
HDT (°C)	°C	134	132	128	98
Spiral flow (280°C, 1 mm-t)	mm	120	110	100	157
Flexural strength	MPa	90	98	99	108
Flexural modulus	MPa	2250	2940	3401	3862
Impact strength	kJ/m^2	75	8	7	5

*Flame-retardant polycarbonate with a silicone flame retardant and glass fiber (10 %)

References

[1] Iji M. and Serizawa S., *Polym. Advan. Technol.* **1998**, 9, 593.

[2] Gilman J.W. and Kashiwagi T. *Int. Conf. Addit.* **2000**, 55.

[3] Kashiwagi T. and Shields J. R. *J. Appl. Polym. Sci.* **2003**, 87, 1541.

[4] Chand N. and Vashishtha S. R. *B. Mater. Sci.* **2000**, 23, 103.

[5] Nikkesi S. and Ishiyama H. *Jpn. Soc. Polym. Process.* **1998,** 10, 891.

[6] Kashiwagi T. and Gilman J. W., *Fire. Mater.* **2000**, 24, 277.

[7] Levchik G. F. and Levchik S. V., *Polym. Degrad. Stabil.*, **1996**, 54, 361.

[8] Nagataki S, Tomosaka F, Kanazu T and Yamamoto T., *JIS A 6201-1999. Spec. Publ. Am. Concr. Inst.*, **2001**, 1, 29.

[9] Kondoh M. and Mori S., *J. Chem. Eng. Jpn.,* **1999**, 25, 374.

[10] Fuji M., *Sure. Sci. Soc. Jpn.* **2003**, 24, 625.

[11] Ballistreri A. and Montaudo G., *J. Polym. Sci. Part A1.*, **1988**, 26, 2113.

[12] Ishikawa T. and Maki I., *J. Macromol. Sci. Pure.,* **2004**, 41, 523.

[13] McNeil I. C. and Rincon A., *Polym. Degrad. Stabil.*, **1993**, 39, 13.

[14] Montaudo G. and Puglisii C. *Polym. Degrad. Stabil.*, **1992**, 37, 91.

[15] Marks M. J. and Erskine J. S., *Macromolecules*, **1994**, 27, 4114.

[16] Ito Y. and Ogasawara H., *Polym. J.,* **1996**, 28, 1090.

[17] Tesoro G. C., *ACS. Sym. Ser.,* **1990**, 425, 241.

[18] Davies A. and Golden J. H., *Macromol. Chem.* **1967**, 110, 180.

[19] Shiba T, Sato M, Hattori H, and Yoshida K., *Catalysts and Catalysis*, **1964**, 6, 80

Section 2-2.

Flame retardancy and heat resistance of phenol-biphenylene-type epoxy resin compound modified with benzoguanamine

2-2-1. Introduction

Epoxy resin compounds are widely used as insulating, building, painting and adhesive materials because of their excellent heat resistance, insulating, adhesive and strength properties that mainly result from their network structures formed by the crosslinking reaction between the epoxy resin and hardener. As a fire prevention measure, epoxy resin compounds as well as other plastics, especially those used as insulating materials in electronics and building materials, generally contain flame-retarding additives, most commonly halogen compounds [1, 2]. Some claim problems with such halogen compounds. During burning, halogen compounds may generate corrosive or toxic substances that create environmental hazards [3, 4].

In recent years, attempts have been made to replace halogen compounds with other flame-retarding additives, either phosphorus compounds such as red phosphorus and phosphoric ester or metal hydrates such as aluminum hydroxide [1, 2, 5–9]. Nitrogen compounds such as triazine derivatives have also been tried [1, 2], and in particular, a benzoguanamine-modified phenol novolac resin has been commercially produced. However, these materials themselves often adversely affect the useful properties of the epoxy resin compounds, such as heat resistance, water resistance, etc.

Another approach used to improve flame retardancy has been to increase the heat resistance of epoxy resin compounds by restraining the movement of the molecular segments in epoxy resin hardener networks under high temperature. One method to achieve this was to increase the crosslink density (i.e. the density of crosslinking points between epoxy resin and hardener in the network) through the use of a multifunctional epoxy resin and hardener [10–14]. Another method was to insert bulky substituents, such as condensed aromatic groups including fluorene derivatives and anthrone derivatives, into the networks [15, 16]. While these methods can increase the glass transition temperatures of the epoxy resin compounds, they have not resulted in the development of highly flame-resistant compounds.

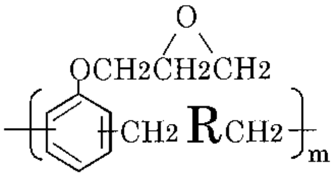
Flame-resistant epoxy resin compounds without flame-retarding additives were previously reported [17]. The compounds contained phenolaralkyl type epoxy resins and hardeners, both of which include an aromatic moiety, such as biphenylene and phenylene, in the main chain of the novolac resin structure as shown in Figure 2-2-1. In particular, the resulting epoxy resin compound including biphenylene moiety in the novolac structure (phenol- biphenylene-type epoxy resin compound) showed excellent flame retardancy with no flame-retarding additives.

Figure 2-2-2 showed that the significant improvement in flame retardancy results from a unique flame-retarding mechanism: during ignition stable foam layers consisting mainly of the resin compounds and volatile materials (carbon oxides, hydrocarbons) generated by pyrolysis of the resin compounds form on their surfaces. These foam layers effectively retard the transfer of heat to the insides of the compounds and the flames are thus extinguished. The foam layers are formed because of the low elasticity of the compounds at high temperatures due to the low crosslink densities of their network structures. The high stability of the foam layers during ignition is a result of the high thermal degradation resistance of the compounds due to the inclusion of the aromatic moieties in the structures. A new epoxy molding compound without any flame-retarding additives for electronic parts by using the phenol-biphenylene-type epoxy resin compound (PB-type epoxy resin compound), silica particle filler, and other additives was developed. The molding compound is highly safe during combustion and after disposal, showing excellent flame retardancy and demonstrating other good properties, such as solder-heating resistance and humidity resistance [18].Therefore, the PB-type epoxy resin compound is used as an insulating material in various electronic components such as IC packages.

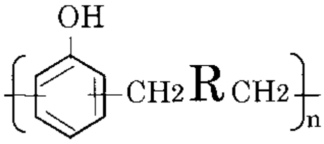
However, the PB-type epoxy resin compound's flame retardancy and heat resistance are insufficient for use in extremely thin electronic devices and in film products. Furthermore, the epoxy resin compound has lower heat distortion resistance indicated by lower glass transition temperature when compared with conventional epoxy resin compounds, because of its low crosslink density.

Here the improvement of flame retardancy and heat resistance of the PB-type epoxy resin compound and the increase of its glass transition temperature by adding a benzoguanamine-modified phenol biphenylene resin (BG- modified PB resin), newly produced was reported. Furthermore, its effectiveness was compared with that of a reference benzoguanamine- modified phenol novolac resin, which is a commercially available flame-retarding additive.

a) Phenol aralkyl-type epoxy resin



b) Phenol aralkyl resin



(R: biphenylene, phenylene)

FIGURE 2-2-1 Structures of phenol aralkyl resin derivatives.

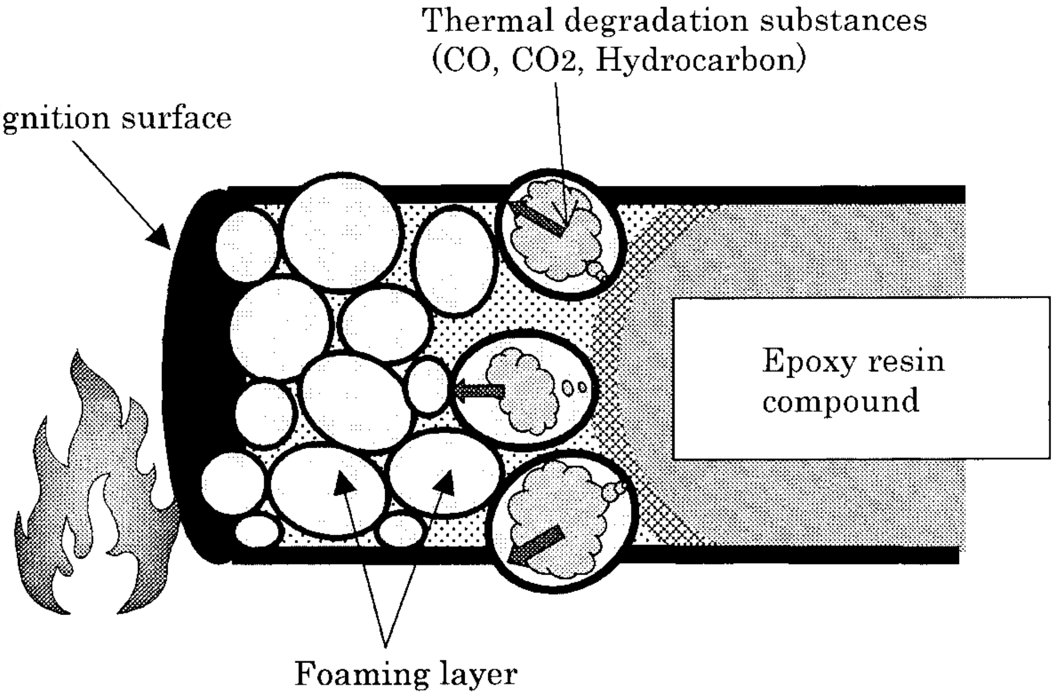


FIGURE 2-2-2 Flame retardant mechanism of phenol aralkyl-type epoxy resin compounds.

2-2-2. Experimental

(1) Materials

The sample epoxy resin compounds consisted of epoxy resin, phenol derivative resin or benzoguanamine-modified phenol derivative resin (as a hardener), fused silica powder (as a filler, average particle size: 15 mm, 70 wt%, Denkikagaku Kougyo Co.), triphenylphosphine (as a curing promoter, 0.20 wt%, Kantou Kagaku Co.), and carnauba wax (as a releasing agent, 0.25 wt%, Nikkou Fine Products Co.).

The epoxy resin was phenol 4, 40- dimethylbiphenylene-type epoxy resin (phenol biphenylene-type epoxy resin, softening temperature: 57 °C, epoxy equivalent: 270, Nippon Kayaku Co.). The phenol resin derivative hardener was phenol 4, 40- dimethyl biphenylene resin (phenol biphenylene resin, softening temperature: 120 °C, hydroxyl equivalent: 203, Meiwa Kasei Co.).

Benzoguanamine-modified phenol biphenylene resin was produced; benzoguanamine (2,4-dia- mino-6-phenyl-sym-triazine, 22.5 g, 1.0 mol, Japan Union Carbide Co.), phenol biphenylene resin (65.1 g, hydroxyl group: 1.0 mol, Nippon Kayaku Co.), formaldehyde(12.5 g of 37 wt% solution, 1.3 mol, Wakou Co.), and ammonia (0.2 g of 29 wt% solution, Kantou Kagaku Co.) were blended and the mixture was heated at 100 °C for 5 hr. The generated water was removed by heating at 180 °C for 2 hr, and the materials that did not react were removed under vacuum at the same temperature for 1 hr. Benzoguanamine-modified phenol novolac resin (softening temperature: 100 °C, hydroxyl equivalent: 220, nitrogen content: 19 wt%, KA-7055-L, Dainippon Ink Chemical Co.) was used as a reference.

The epoxy resin compounds were produced by blending the above components in a roll blender heated to 110–115 °C and molding them in a metal mold by using a conventional transfer molding machine under a curing condition of 170 °C for 5 min, and then post-curing them at 170 °C for 6 hr.

(2) Methods

The benzoguanamine-modified phenol biphenylene resin's and the benzoguanamine-modified phenol novolac resin's melting temperatures were measured according to the method described in JIS K7234. Their hydroxyl contents were determined by dissolving the resins in pyridine, acetylating them by adding to the solutions an excess of acetic anhydride, and measuring the remaining acetic anhydride based on titration with a sodium hydroxide solution. The nitrogen contents of the resins were determined by using a carbon-hydrogen-nitrogen (CHN) analyzer (2400 type, Perkinelmer Co.). The degraded substances generated from the resins (0.1 g, pulverized under 75 mm in diameter) in a tube-type electric furnace during heating at 850 °C for 10 min in air (0.5 l/min) were measured by using the methods specified in JIS K 7217. Hydrogen cyanide in the exhaust gases was absorbed in a solution containing sodium hydroxide (2.0 wt %), and its concentration was measured by using a spectrophotometer (UV-1200, Shimazu Co.). Ammonia in the gases was absorbed in a solution containing boric acid (0.5 vol %), and its concentration was measured by using an ion chromatography analyzer (HIC-10A, Simazu Co.). Nitrogen oxides in the gases were determined by using the Salzman reagent method described in JIS K 0104. Nitrogen oxides were absorbed in a solution including sulfuric acid (0.5 wt %) and naphthylenediamine (5 vol %) and their concentrations were measured by using an absorptiometry analyzer (UV-1200, Shimazu Co.).

Flame retardancy of the molded epoxy resin compounds was determined by using the UL94 method of Underwriters Laboratories Inc. In this method, a vertically clamped sample of molded compound is ignited by the gas burner flame applied twice for 10 sec to the bottom of the sample. The flame retardancy of the material is classified according to extinguishing time of the flame after ignition and on whether combustion occurs with dripping of flaming particles, which are capable of igniting surgical cotton placed underneath the specimen. The time of extinguishment increases from class V-0 (total time of five samples is within 50 sec) to V-1 (total time of five samples is within 250 sec). Ignition of the cotton within the time of V-1 leads to V-2 classification. Otherwise, the sample material is not classified (not V-2). In this study, the thickness of the samples was 1.6 mm. The width (13 mm) and length (120 mm) were specified in the UL method. The cross sections of the molded epoxy resin compounds (13 mm width, 50 mm length, 1.6 mm thickness) after being ignited with a flame for 10 sec were observed by using a microscope (MH90, Nippon Kougaku Co.). The ignition method was the same as UL94.

The glass transition temperatures of the molded compounds were measured at a heating rate of 5 °C/min by thermal mechanical analysis using the method specified in JIS K 7197. The mechanical properties of the molded compound samples, such as flexural modulus, were measured according to JIS K 6911. The water absorption ratios were measured by boiling the samples in water for 24 hr. Heat resistance (thermal degradation resistance) of the molded compounds was measured in air (0.2 l/min) at a heating rate of 10 °C/min by thermogravimetric analysis (TG/DTA6200, Seiko Instruments Co.).

2-2-3. Results and discussion

(1) Characterization of benzoguanamine modified phenol biphenylene resin

The structure of the BG-modified PB resin produced is shown in Figure 2-2-3. Benzoguanamine was selected as a suitable triazine derivative because of its adequate reactivity provided by its amino groups and its relatively hydrophobic properties owing to a phenyl group in addition to its generation of non-flammable degradation substances including nitrogen compounds during ignition, which retard plastics' flaming. One of the amino groups in benzoguanamine was reacted with phenol biphenylene resin via formaldehyde. The other amino group, which remained during the reaction by adjusting the blending ratio of benzoguanamine, phenol biphenylene resin, and formaldehyde, is able to react with a glycidyl group in the PB-type epoxy resin when the BG-modified PB resin is mixed with the epoxy resin. The reactivity owing to the amino group increases the crosslink density in the cured epoxy resin compound, as will be described later. Furthermore, the BG-modified PB resin contains biphenylene units, which maintains the hydrophobic property and thermal degradation resistance of the resin.

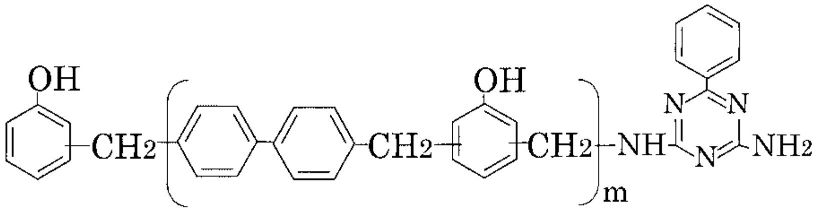
However, the reference benzoguanamine-modified phenol novolac resin (BG-modified PN resin) includes benzoguanamine inside the resin structure as shown in Figure 2-2-3. All of the amino groups are bound with the resin, suggesting that it has a lower reactivity with the epoxy resin compared with the BG-modified PB resin. Moreover, it does not include units such as biphenylene, which the BG-modified PB resin contains.

The properties of both the BG-modified resins are listed in Table 2-2-1. Their melting temperatures were sufficiently low to be mixable with the epoxy resin when heated. The hydroxyl group content of the BG-modified PB resin was lower than that of the BG-modified PN resin because the former resin includes biphenylene units. The nitrogen content (9.7 wt %) of the BG-modified PB resin revealed that most of the phenol biphenylene resin was bound with one benzoguanamine unit. The nitrogen content of the BG-modified PB resin was lower than that of the reference BG-modified PN resin (19 wt %), which contains a larger number of benzoguanamine units.

Figure 2-2-4 shows the thermal degradation behavior of the BG-modified resins. The resins decomposed in several steps as the heating temperature increased. The first step around 400 °C mainly resulted from the ease of degradation of benzoguanamine units in the modified resins, and the other steps were caused by the degradation of the other units. The thermal degradation resistance of the BG-modified PB resin was higher than that of the BG-modified PN resin. This seems to be due to the smaller number of easily decomposed benzoguanamine units and the inclusion of biphenylene units that have high pyrolysis resistance and accelerate charring (it was reported that such aromatic compounds in polymers accelerate charring [19].

The nitrogen compound amount, especially inorganic compounds, generated from these modified phenol derivative resins during heating and identified them were measured. The BG-modified PB resin generated the smaller amount of nitrogen compounds, which can be attributed to its lower benzoguanamine content. The main inorganic nitrogen compounds originating from the benzoguanamine units in the modified resins were nitrogen oxides, ammonia, and hydrogen cyanide (Table 2-2-2). The other nitrogen compounds appear to be organic nitrogen compounds.

a) Benzoguanamine-modified phenol biphenylene resin
(BG-modified PB resin)



b) Benzoguanamine-modified phenol novolac resin
(BG-modified PN resin)

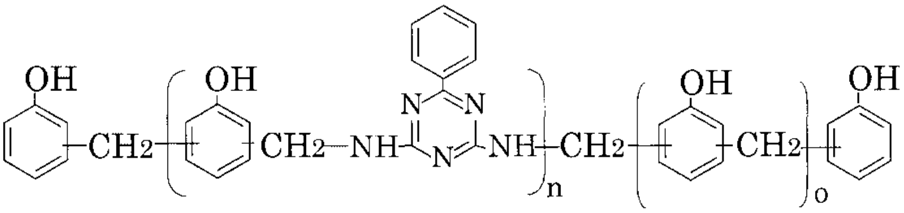


FIGURE 2-2-3 Structures of benzoguanamine-modified phenol derivative resins.

TABLE 2-2-1. Properties of benzoguanamine-modified phenol derivative resins

	BG-modified PB resin	BG-modified PN resin
Melting temperature (°C)	120	110
Hydroxyl group content (g/eq)	260	194
Nitrogen content (wt %)	9.7	19

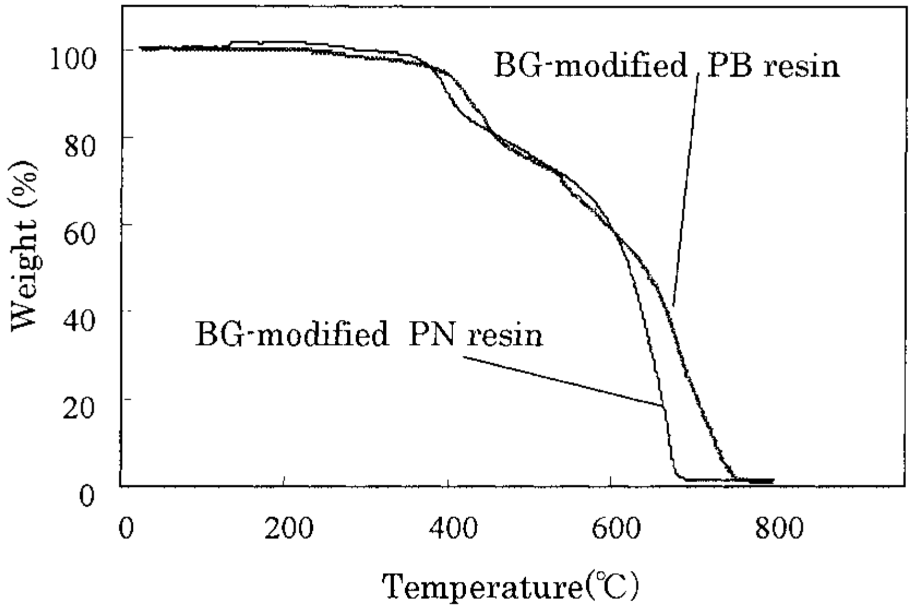


FIGURE 2-2-4 Thermogravimetric analysis of benzoguanamine-modified phenol derivative resins.

(2) Flame retardancy

Adding the BG-modified phenol derivative resins to the PB-type epoxy resin compound greatly improved its flame retardancy as shown in Figure 2-2-5. These resins were very effective in relatively small amounts and were most effective when they made up around 20 wt% of the resin part (without filler) of the epoxy resin compound. The flame retardancy was adversely affected at more than 40 wt%. The effectiveness of the BG-modified PB resin was almost the same as that of the BG- modified PN resin.

As suggested by the thermal degradation behavior of the BG-modified PB resin, the flame-retarding effect is mainly due to the generation of the nearly non-flammable substances containing nitrogen compounds through the degradation of the benzoguanamine unit during ignition. The released substances promoted the formation of the foam layer over the PB-type epoxy resin compound during ignition, as shown in Figure 2-2-6(a). Such foam layer effectively retards heat transfer during ignition, as previously reported. An excess of the BG-modified PB resin retarded the formation of the foam layer as shown in Figure 2-2-6(b), by increasing the crosslink density of the epoxy resin compound, which resulted in a decrease in the flame-retarding effect.

However, the BG-modified PN resin had a similar flame-retarding mechanism to the BG-modified PB resin at relatively low concentrations (under 30 wt %). The resin also promoted the formation of the foaming layer over the epoxy resin compound at these concentrations by releasing nearly non-flammable substances. The flame resistance was adversely affected at high concentrations, but the mechanism was different from that of the BG-modified PB resin because the crosslink density of the epoxy resin compounds including the BG-modified PN resin decreased, as will be described later. This adverse effect appeared to be caused by the lower thermal degradation resistance of the epoxy resin compound containing the BG- modified PN resin, as will be mentioned later.

TABLE 2-2-2 Generation of nitrogen compounds from benzoguanamine-modified phenol derivative resins during heating.

	BG-modified PB resin	BG-modified PN resin
NH_3 (mg/g)	2.2	4.1
HCN (mg/g)	4.6	7.6
NO_2 (mg/g)	0.085	0.047
NO (mg/g)	0.48	0.42
Total (mg /g)	7.37	12.17

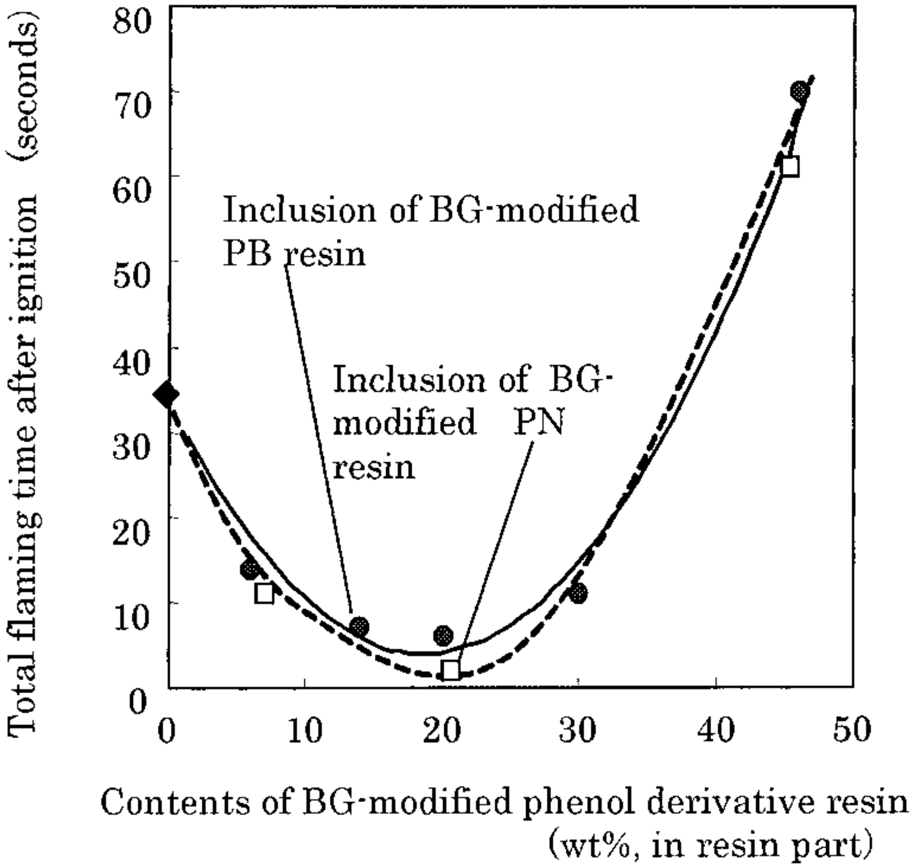
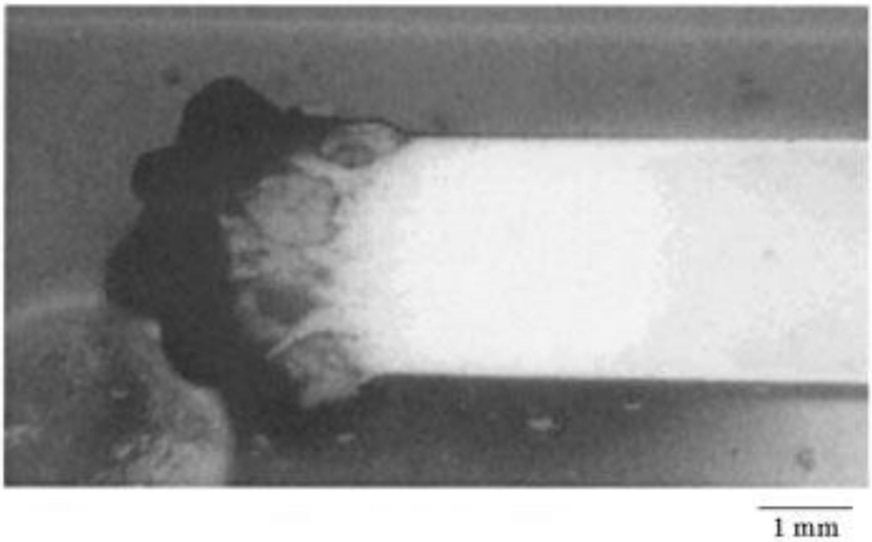


FIGURE 2-2-5 Flame retardancy of phenol biphenylene-type epoxy resin compounds including benzoguanamine-modified phenol derivative resins.

a) Inclusion of BG-modified PB resin of 20wt% in resin part



b) Inclusion of BG-modified PB resin of 45wt% in resin part

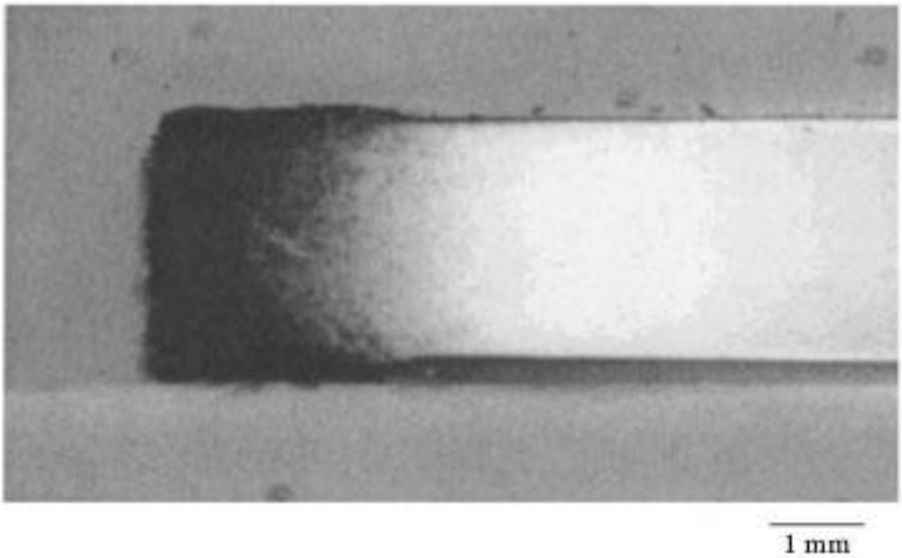


FIGURE 2-2-6 Cross sections of molded phenol biphenylene-type epoxy resin compounds including benzoguanamine-modified phenol biphenylene resin after ignition.

(3) Glass transition temperature

The inclusion of the BG-modified PB resin increased the glass transition temperature of the PB-type epoxy resin compound as shown in Figure 2-2-7. This result was attributed to an increase in the crosslink density within the network by adding the BG-modified PB resin because the amino group in the benzoguanamine unit is able to react with the epoxy resin.

However, the inclusion of the BG-modified PN resin decreased the glass transition temperature. This change appeared to result from the resin's lower reactivity with the epoxy resin due to its lack of the reactive amino group.

(4) Heat resistance

As shown in Figure 2-2-8, the inclusion of the BG-modified PB resin improved the thermal degradation resistance of the PB-type epoxy resin compound due to the increase of the crosslink density within the network. The inclusion of the BG-modified PN resin decreased the resistance of the epoxy resin compound at relatively low temperatures when compared with the BG-modified PB resin's resistance. This was mainly caused by the lower pyrolysis resistance of the BG-modified PN resin. However, the weight loss at high temperatures was smaller than that of the original epoxy resin compound. The charring of the epoxy resin compounds including these BG-modified resins seemed to be accelerated after the decomposition of the benzoguanamine unit in the resins.

(5) Influence of other properties

Other important properties of the PB-type epoxy resin compound with the BG-modified PB resin were evaluated and compared with those of the original epoxy resin compound and those of the epoxy resin compound with the BG-modified PN resin.

While adding the BG-modified PB resin had a slightly adverse effect on the water resistance of the PB-type epoxy resin compound, due to the inclusion of the polar triazine moiety in the benzoguanamine unit, the epoxy resin compound still had excellent water resistance as shown in Figure 2-2-9. However, the addition of the BG-modified PN resin caused a greatly adverse effect on the water resistance, which resulted from the lack of hydrophobic units such as biphenylene.

Figure 2-2-10 showed that the flexural modulus of the epoxy resin compound with the BG-modified PB resin at a room temperature and high temperatures was comparable to that of the original epoxy resin compound. However, the modulus of the epoxy resin compound with the BG-modified PN resin was lower, especially at high temperature, because of its low crosslink density.

As suggested by the thermal degradation test results of the BG-modified PB resin (Table 2-2-2), the epoxy resin compound containing the modified resin can generate nitrogen compounds during ignition. However, since the epoxy resin compound contains a large amount of filler (70 wt%), as well as general epoxy resin compounds, the total nitrogen content of the compound (0.6 wt%: calculated from maximum 20 wt% of the BG-modified PB resin in the resin part) is much smaller than that of the conventional nitrogen-containing resins, such as polyamide (about 14 wt%), polyurethane (about 12 wt%) and polyacrylonitrile (about 31 wt%).

2-2-4. Conclusion

The flame retardancy and heat resistance of a PB-type epoxy resin compound used in electronic components were increased by adding to it a BG-modified PB resin. The BG-modified PB resin, produced as a new additive, includes a benzoguanamine unit, which releases non-flammable substances containing nitrogen compounds during ignition and increases the modified resin's reactivity toward epoxy resins owing to its reactive group (the amino group). The BG- modified PB resin also includes biphenylene units to help maintain the resin's thermal degradation resistance and water resistance. Adding the BG-modified PB resin in the PB-type epoxy resin compound increased the compound's flame retardancy, heat resistance, and glass transition temperature. Other important properties, such as water resistance and mechanical properties, were almost unaffected by the addition of the BG-modified PB resin. However, adding the BG-modified PN resin as a reference decreased the epoxy resin compound's heat resistance, glass transition temperature, water resistance, and mechanical properties because of the modified resin's low reactivity, low thermal degradation resistance, and high hydrophilic property.

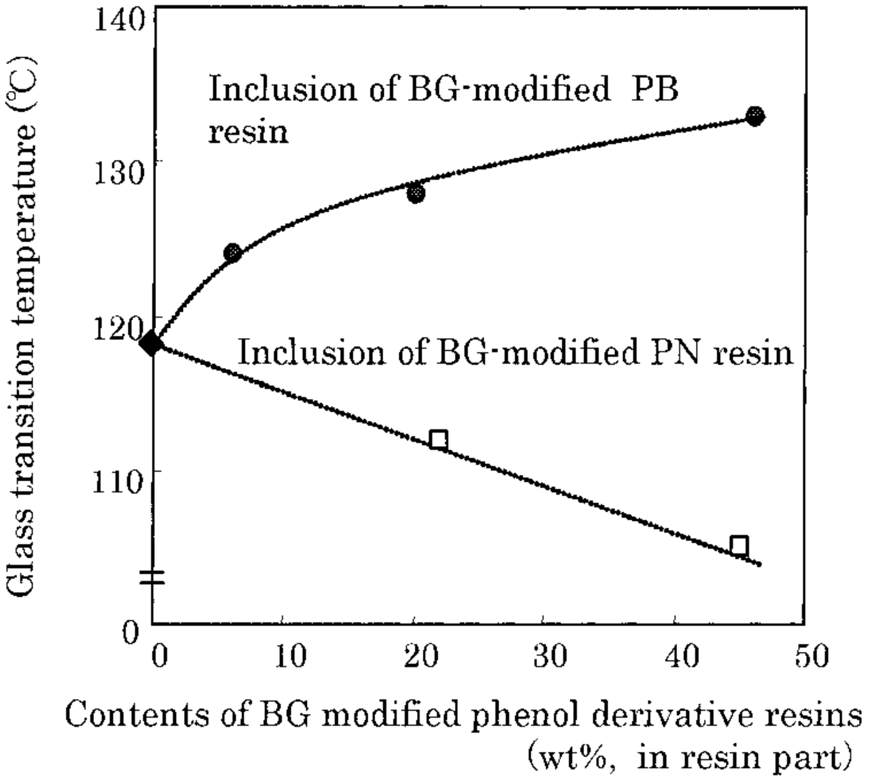
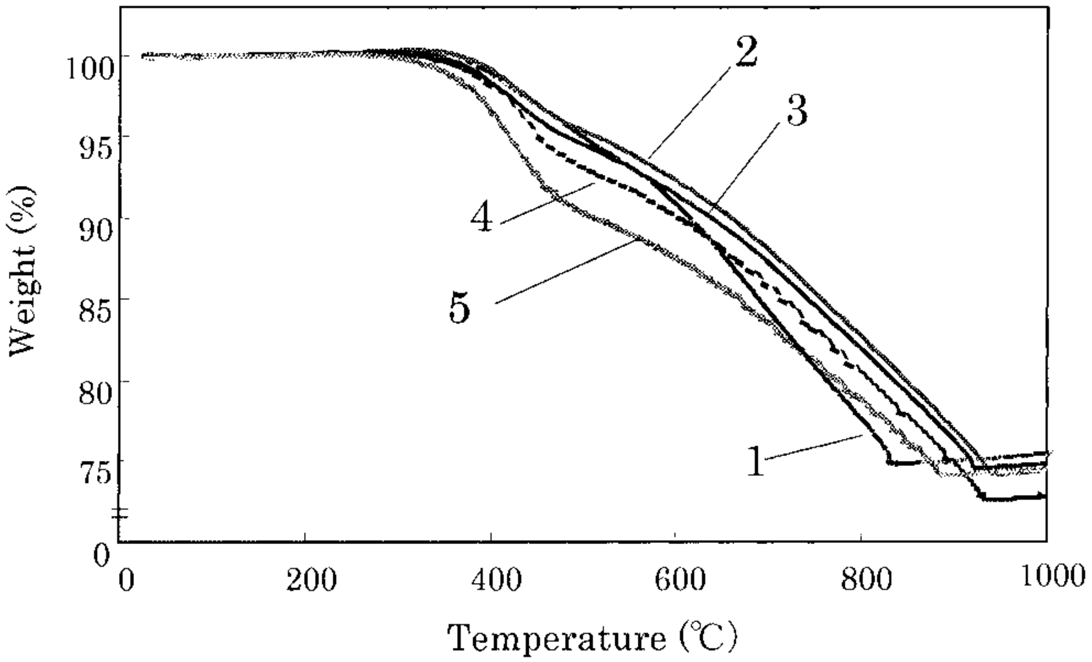


FIGURE 2-2-7 Glass transition temperatures of phenol biphenylene-type epoxy resin compounds including benzoguanamine-modified phenol derivative resins.



1. PB-type type epoxy resin compound
2. Inclusion of BG-modified PB resin (20wt% in resin part)
3. Inclusion of BG-modified PB resin (45wt% in resin part)
4. Inclusion of BG-modified PN resin (20wt% in resin part)
5. Inclusion of BG-modified PN resin (45wt% in resin part)

FIGURE 2-2-8 Thermogravimetric analysis of phenol biphenylene-type epoxy resin compounds including benzoguanamine-modified phenol derivative resins.

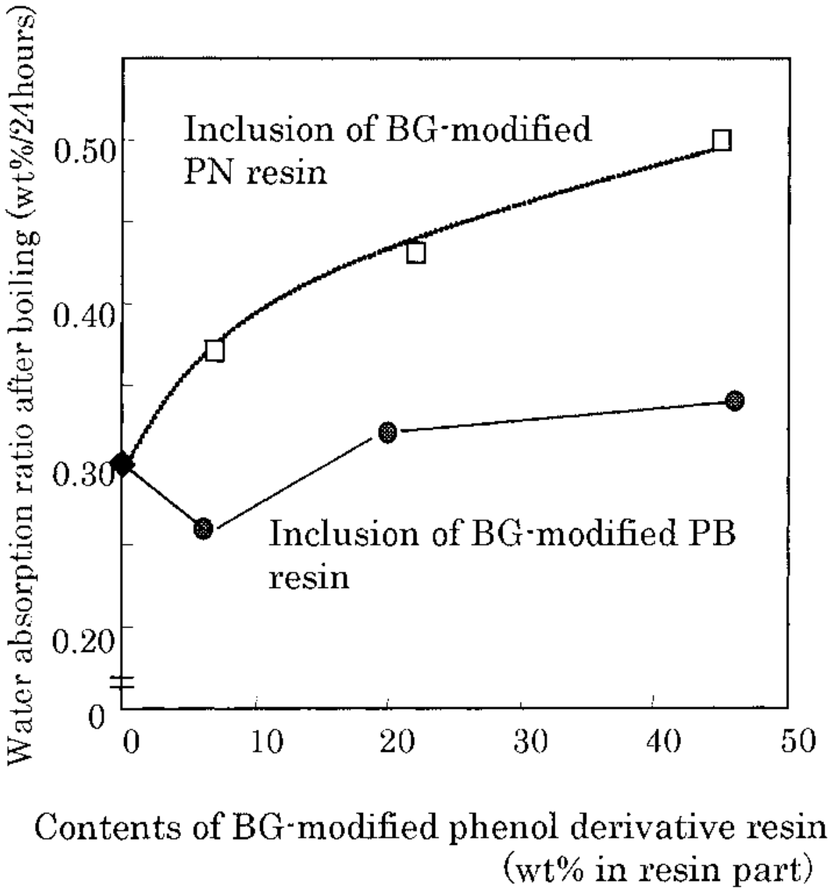


FIGURE 2-2-9 Water resistance of phenol biphenylene-type epoxy resin compounds including benzoguanamine-modified phenol derivative resins.

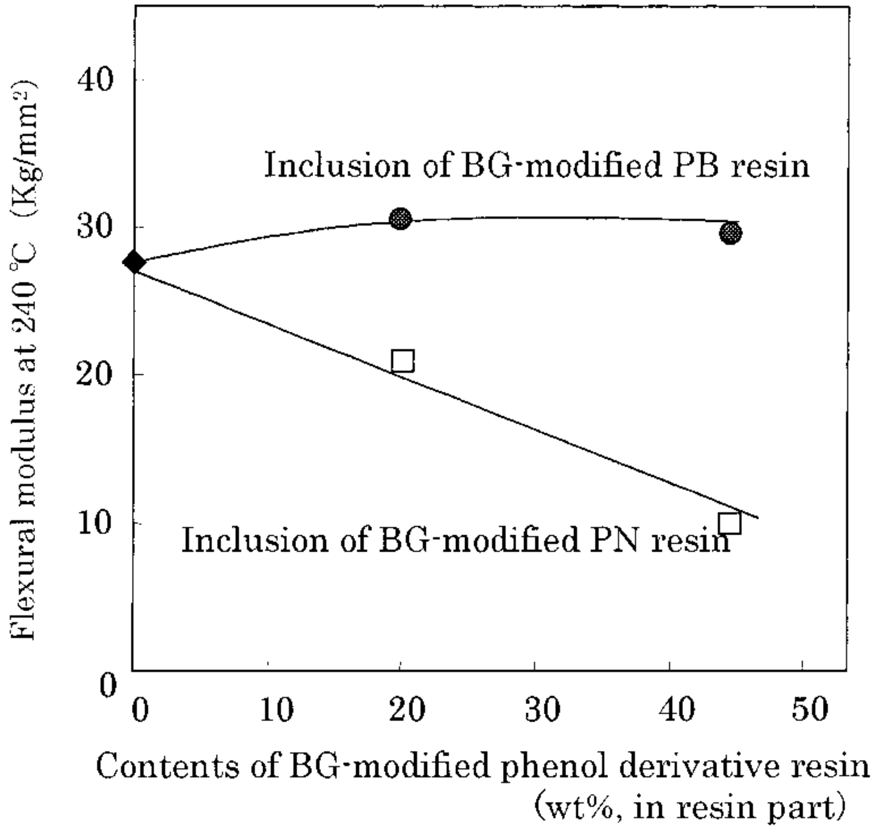


FIGURE 2-2-10 Flexural modulus of phenol biphenylene-type epoxy resin compounds including benzoguanamine-modified phenol derivative resins (240 °C).

References

[1] Camino G., Costa L., *Polym. Deg. Stab.* **1988**, 20, 271.

[2] Cullis CF., *J. Analyt. Pyroly.* **1987**, 11, 451.

[3] Dumler R., Thoma H., and Hutzinger O., *Chemosphere,* **1989**,19, 1–6, 305.

[4] Luijk P., Govers HAJ., Eijkel GB. and Boon JJ., *J. Appl. Pyroly.,* **1991**, 20, 303.

[5] Termine EJ. and Taylor KG., *Reinforced Plastics* **1990,** 34, 12, 28.

[6] Termine EJ. and Taylor KG., *SPI Compos. Inst. Annu. Conf. Expo. Proc.* **1990**, 45: 17C1.

[7] Huggard MT., *Soc. Plast. Eng. Annu. Tech. Conf.* **1993**, 51(2): 1753.

[8] Zhu W., Weil ED. and Mukhopadhyay S., *J. Appl. Polym. Sci.* **1996**, 62(13): 2267.

[9] Chiu S-H. and Wang W-K., *J. Appl. Polym. Sci.* **1998**, 67(6):989.

[10] Hasegawa K,, Fukuda A. and Tonogi S., *J. Appl. Polym. Sci.*, **1989**, 37, 3423.

[11] Chen HH and Nixon AC., *SPE Trans.*, **1965**, 5(2), 90.

[12] Brown LE. and Harshman JB., *AEC Accession,* **1964**, No. 35935, Rept. No. MLM-CF-64-8-1.

[13] Cizmecioglu M., Gupta A. and Fedors RF., *J. Appl. Polym. Sci.,* **1986**, 32, 6177.

[14] Danieley ND. and Long ER., *J. Polym. Sci. Chem. Ed.,* **1981,** 19, 2443.

[15] Korshak VV., Soloveva LK. and Kamenskh IV., *Vysokomol. Soedin.,* **1970**; 13: 150.

[16] Chen CS., Bulkin BJ. and Pearce EM., *J. Appl. Polym. Sci.,* **1982**, 27, 3289.

[17] Iji M. and Kiuchi Y., *Polym. Adv. Technol.* **2001**, 12: 393.

[18] Iji M. and Kiuchi Y., *J. Mater. Sci. Mater. Electronics*, **2001**, 12, 715.

[19] Ouchi K., *Carbon*, **1966**, 4, 59.

Chapter 3.

Improvement of mechanical properties and flame retardancy of modified cardanol-bonded cellulose resin by adding specific additives

3-1. Introduction

Biomass–based plastics derived from renewable biomass resources are expected to be environmentally friendly materials to ameliorate petroleum depletion and carbon dioxide emissions that are causing global warming. [1] In recent years, mass–produced bioplastics such as poly(lactic acid) (PLA) [2] and bio–polycarbonate (PC) and their composites have been used in durable products for automobiles and electronic devices as well as in consumer products such as textiles and tableware. [3] As most of these bioplastics are made using starch produced from edible plants, anxiety about food shortages in the future has increased interest in making bioplastics from inedible plants and the inedible parts of edible plants.

Cellulose, the main component of plant fiber, is the most abundant inedible plant material on Earth, [4] but the strong hydrogen bonds between its molecules make it difficult to thermally plasticize and mold.

Substantial research efforts have therefore been devoted to facilitating its thermal plasticization by synthesizing cellulose derivatives such as cellulose diacetate (CDA) [5, 6] and by adding large amounts of plasticizers [7] (e.g., di–n–hexyl phthalate, diethyl sebacate, triethyl citrate) to them. These cellulose derivatives have short–chain fatty acids such as acetic acid, propionic acid, and nitric acid [8] bonded to hydroxyl groups of cellulose and, however, these derivatives absorb large amounts of water, making their hydrophobicity insufficient. Furthermore, adding large amounts of plasticizers reduces the rigidity and heat resistance of these cellulose derivatives. These issues have limited their use in durable products; therefore, cellulose derivatives with long alkyl chains have been developed. The long alkyl chains used include carboxylic acids and their derivatives, such as carboxylic anhydrides and carboxylic acid chlorides, [9, 10] and alkyl halides with alkalis [11], and they were bonded with the hydroxyl groups on the glucose units of cellulose or cellulose bonded with short chain acids. [12-14] An advanced CDA resin-bonded with cardanol to improve water absorption, rigidity and heat resistance of cellulose derivatives have been developed.[15] Cardanol extracted from the shells of cashew nuts is a uniquely structured phenol derivative with a linear alkyl side long–chain, and it is hydrophobic and flexible. [16]

Esterification of the modified cardanol, 3–pentadecylphenoxy acetic acid (PAA) and CDA (Figure 3-1) results in a thermoplastic PAA–bonded CDA resin with excellent rigidity and good water resistance. The impact strength of the resin, however, was insufficient for use in durable products such as electronics. Furthermore, achieving high flame retardancy was required to be used in various parts in electronics.

The author subsequently demonstrated that adding specific olefin resins (section 3-3-1) [17] and polyether silicones (section 3-3-2) efficiently improves the impact strength of PAA-bonded CDA [18] and also adding a flexible polyester, glass-fiber and complexed flame retardants greatly improves its impact strength as well as flame retardancy while maintaining other important practical characteristic for use in electronics (section 3-3-3).

In section 3-3-1, with the objective of simultaneously achieving impact strength and flexural properties (flexural strength and breaking strain) of PAA-bonded CDA, adding relatively flexible resins was attempted. First, the addition of general petroleum plastics (ABS, acrylonitrile-styrene: AS, polyamide 6: PA6) was investigated. Second, olefin resins (polyethylene: PE, polypropylene: PP), which are expected to show high affinities to hydrophobic cardanol side chains were added. Finally, to investigate the effect of the interfacial state between PAA-bonded CDA and olefin resins, the effect of adding several types of PP with different concentrations of maleic anhydride was verified.

In section 3-3-2, enhancement of the impact strength of PAA-bonded CDA by using modified silicones that have various polarities by including polar groups (polyether, amino and epoxy groups) with various concentrations and viscosities were studied. Furthermore, the dispersed particle diameter of polyether silicone in PAA-bonded CDA, effects on impact strength of the composites was investigated. The optimized polyether silicone in terms of their amount (up to 5 wt %), polarities, and viscosities increased the impact strength of the PAA–bonded CDA composites through crazing [19] and shearing deformations. [20]

In section 3-3-3, adding a flexible polyester, glass-fiber and complexed flame retardants to PAA-bonded CDA was investigated to greatly improve its impact strength as well as flame retardancy and maintain other important properties to be used in electronics. First, incorporating various polyester resins with different polarities and structures—especially branched polyester resins and linear polyester resins—was attempted to increase the impact strength of the PAA–bonded CDA. Adding glass fiber to the PAA–bonded CDA composites with PBSA was also examined to improve rigidity including the bending strength and bending modulus. Finally, using aluminum hydroxide, cresyl diphenyl phosphate (CDP) and polytetrafluoroethylene (PTFE) as complex flame retardants in the PAA-bonded CDA composite was tried to enhance its flame retardancy while maintaining its impact strength and other practical properties.

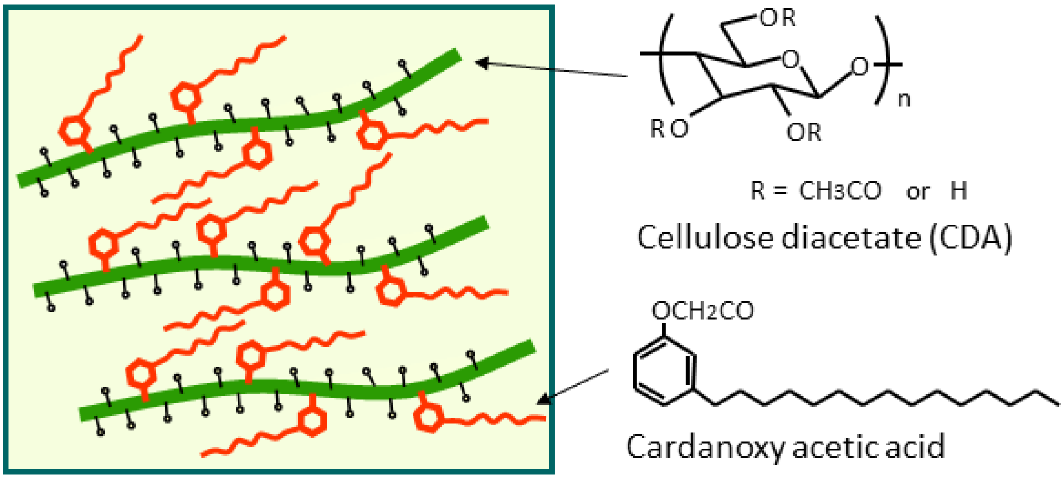


FIGURE 3-1 Hypothesized structure of PAA-bonded CDA.

3-2. Experimental

(1) Materials

Cellulose diacetate (CDA: LM-80, degree of substitution (DS) of acetic acid: 2.1, viscosity: 200 mPa・s/ 6 weight (wt) % in acetone) was supplied by Daicel Corporation (Japan).

Cardanol-bonded cellulose (PAA-bonded CDA) was produced as follows.

Hydrogenated cardanol (3-pentadecyphenol), in which the unsaturated bonds in the alkyl side chain were changed to saturated ones, was purchased from ACROS Organics Co. (USA) and used as received. The change ratio was more than 99 wt %, as measured by ACROS Organics. Chloroacetic acid, chloroform, acetone, 1,4-dioxane, methanol, hexane, diethyl ether, triethyl amine, sodium hydroxide, hydrochloric acid, oxalyl chloride, and N,N-dimethylformamide were the analytical reagents and used as received from Kanto Chemical Co., Inc. (Japan) without further purification.

The synthesis process of PAA-bonded CDA is shown in Figure 3-2-1. The method of preparing PAA chloride is the same at that used by Iji et al. [21]. The charge-in quantities of each material for obtaining PAA chloride were 1.5 times those presented in their study. PAA-bonded CDA was synthesized using the same method as that used by Iji et al. The charge-in quantities of each material to obtain PAA-bonded CDA were 25 times those presented in their study. The final product (PAA-bonded CDA) resulted using a 1H-NMR spectrometer. The DS of PAA was calculated using the ratio between the area corresponding to the proton resonance of the methyl protons of the acetate group (δ1.80-2.20) and the corresponding resonance for the methyl protons of CDA (δ0.86). As a result, the DS of PAA was 0.53 (the ratio of bonded PAA content calculated using the 1H-NMR spectrometer as mentioned above was 42 wt %). The molecular weight of PAA-bonded CDA was estimated using gel permeation chromatography (GPC: Shimadzu LC-VP system with Shim-pack GPC-8025C and GPC-80MC column, Shimadzu Co., Japan) calibrated using polystyrene standards (solvent: chloroform). The number-average molecular weight (*Mn*) of PAA-bonded CDA was about 120,000.

To compare with the resulting resins and composites, reference plastics were prepared. ABS resin (GA-701) was supplied by Nippon A&L Inc. (Japan). AS resin (SAVREX) was supplied by Techno Polymer Co., Ltd. (Japan). PA6 (Amilan CM1007) was supplied by Toray Industries, Inc. (Japan). PA11: poly11−aminoundecanoic acid (product name Rilsan BMFO) was supplied by Arkema Japan, Ltd. (Japan).

In section 3-3-1, three types of PE, which were manufactured by Japan Polyethylene Corporation (Japan), were used as impact modifiers, high-density PE (HDPE; product name: HJ490; density: 0.96 g/cm^3; melting point (m. p.): 133 °C; melt flow rate (MFR): 20 g/10 min), low-density PE (LDPE; product name: UJ370; density: 0.92 g/cm^3; m. p.: 120 °C ; MFR: 16 g/10 min), and Branched-PE (product name: KS560T; density: 0.90 g/cm^3; m. p.: 90 °C; MFR: 16.5 g/10 min). Furthermore, three types of PP, which were manufactured by SunAllomer Ltd.

(Japan), were used as another impact modifier, high-flow-type PP (HFlow-PP; product name: PM900A; density: 0.90 g/cm^3; MFR: 30 g/10 min), low-flow-type PP (LFlow-PP; product name: PM600A; density: 0.90 g/cm^3; MFR: 7.5 g/10 min), and middle-flow-type PP (MFlow-PP; product name: PM801A; density: 0.90 g/cm^3; MFR: 13 g/10 min). Furthermore, PP with different concentrations of maleic anhydride (MAH-PP) supplied by Sanyo Chemical Industries Ltd. were tested. MAH7-PP (product name: Umex 110TS; acid value: 7; softening point: 149 °C) and MAH52-PP (product name: Umex 1010; acid value: 52; softening point: 148 °C) were applied for investigating the effect of the interfacial state between cardanol-bonded cellulose thermoplastic and olefin resins. Incidentally, the above acid values indicate the weights of potassium hydroxide (KOH), which were needed for neutralizing the acid ingredients in 1 g of MAH-PP; therefore, MAH-PP with higher acid values show higher polarities.

In section 3-3-2, modified silicones (dimethyl silicones modified with polyether, amino, and epoxy groups) and a dimethyl silicone were prepared with the structure outlined in Figure 3-2-2 and the properties listed in Table 3-2-1. Dimethyl silicones (polydimethylsiloxane : D-Si), dimethyl silicones modified with polyether group (PE-Si 5, 6, 7a, 7b, 8, 13, 14) and dimethyl silicone modified with amino group (A-Si-M) were produced by TORAY Dow Corning Silicone Co, Ltd. Dimethyl silicones modified with polyether group (PE-Si 10), dimethyl silicones modified with epoxy group (E-Si-H, L), and dimethyl silicones modified with amino group (A-Si-H, A-Si-L) were produced by Shin-Etsu Chemical Co., Ltd. The hydrophile-lipophile balance (HLB), which shows the polarity of a polyether silicone, was calculated by using Formula 1. The epoxy and amino equivalents were measured in accordance with the ISO 3001 and ISO 3771 standard test method.

$$\mathrm{HLB} = 20 * \mathrm{Mh} / \mathrm{M} \qquad \text{(Formula 1)}$$

Mh: sum of molecular mass of the hydrophilic portion of the molecule

M: molecular mass of the whole molecule (polyether silicone)

In section 3-3-3, linear polyester resins poly(butylene succinate) (PBS), poly(butylene succinate adipate) (PBSA), and poly(caprolactone) (PCL) with the structures were described in Figure 3-2-3 were used in this study. The branched polyester resins poly(lactic acid) (PLA) and poly(hydroxybutyrate) (PHB) with the structures were shown in Figure 3-2-4. PBS (Bionole 1001MD: M_n=61,000, M_w=150,000) and PBSA (Bionole 3001MD: M_n =48,000, M_w=128,000), in which 20 mol % of the succinic acid in PBS was replaced by adipic acid, were supplied by Showa Denko Co., Ltd. (Japan). PCL (CELGREEN PH7: M_n=11,000, M_w=30,000) was supplied by Daicel Co. (Japan). PLA (TE−4000: M_n=31,000, M_w=72,000) was manufactured by Unitika Ltd. (Japan). PHB (Biogreen™: M_n=200,000, M_w=622,000) was supplied by Mitsubishi Gas Chemical Co. (Japan). M_n and M_w represent number−average and weight−average molecular weight of the polyester resins in terms of polystyrene. The chemical structure of the polyesters was identified using an 1H-NMR spectrometer. 1H-NMR spectrometers of the polyesters were shown in supporting information. The glass fibers used (03JAFT792) was supplied by Owens Corning Japan LLC. The aluminum hydroxide used as a flame retardant (HIGILITE HP-350) was produced by Showa Denko Co., Ltd. (Japan). Phosphate in the form of cresyl diphenyl phosphate (CDP) was supplied by Daihachi Chemical Industry Co., Ltd. Moreover, polytetrafluoroethylene (Daikin Industries, Ltd., Polyflon MPA FA-500H) was added to prevent dripping during heating.

The plasticizer triethyl citrate (TEC) was supplied by Pfizer Inc. (USA).

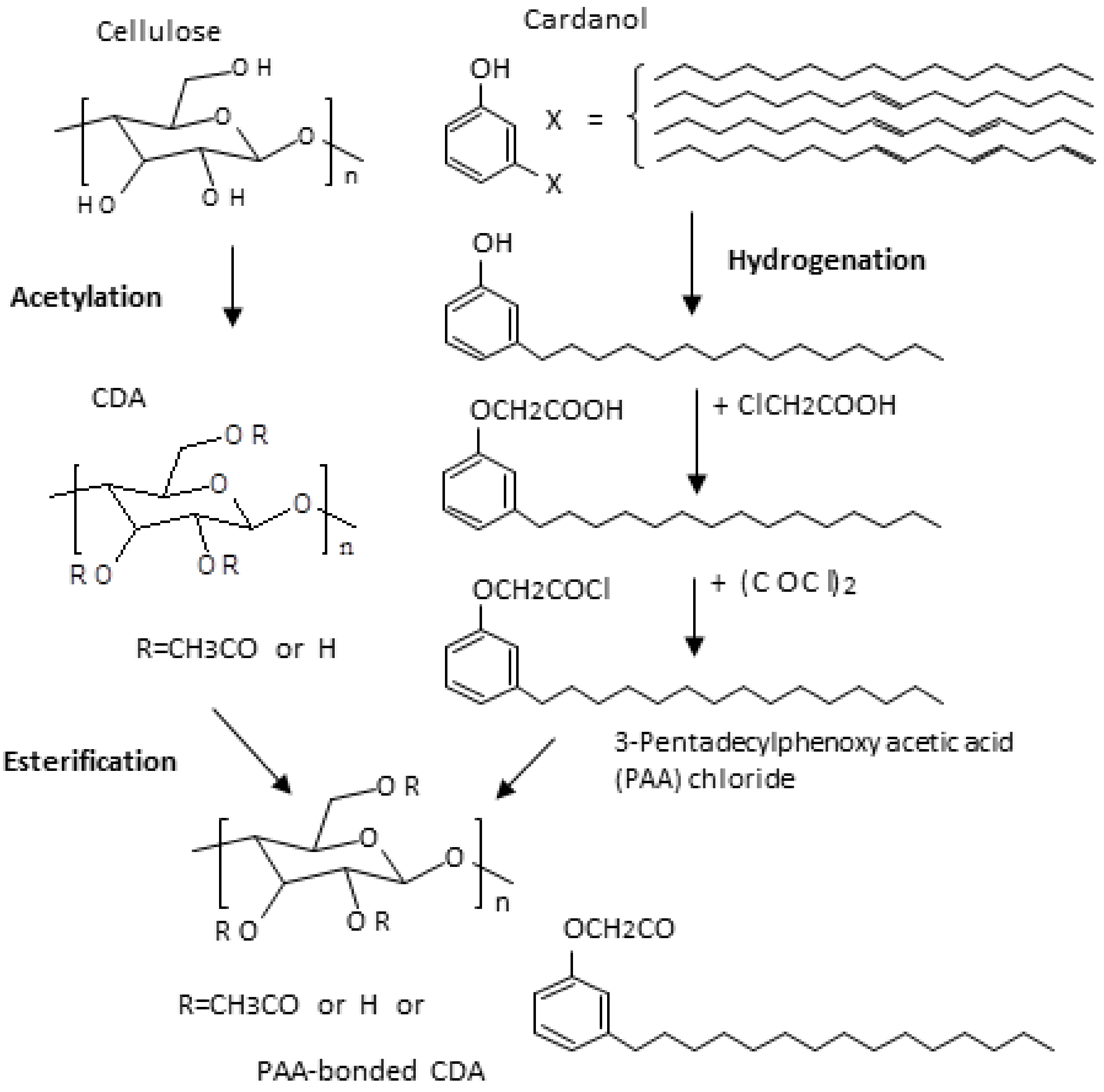
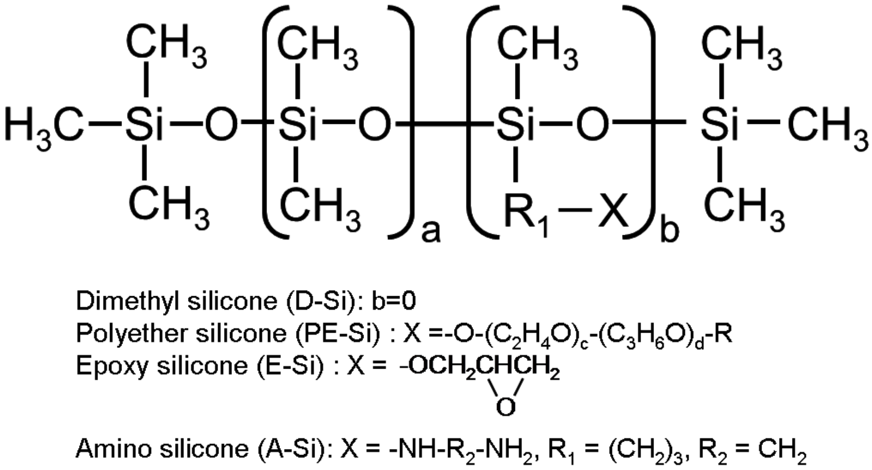


FIGURE 3-2-1 Preparation process of PAA-bonded CDA.



Dimethyl silicone (D-Si): $b=0$

Polyether silicone (PE-Si) : $X = -O-(C_2H_4O)_c-(C_3H_6O)_d-R$

Epoxy silicone (E-Si) : $X = -OCH_2CHCH_2$ O

Amino silicone (A-Si): $X = -NH-R_2-NH_2$, $R_1 = (CH_2)_3$, $R_2 = CH_2$

FIGURE 3-2-2 Structures of tested silicones.

TABLE 3-2-1. Properties of tested silicones

Silicone Name*	Viscosity [25^oC] (mm^2/s)	Hydrophile-Lipophile Balance (HLB)	Functional equivalent (g/mol)	Functional group
D-Si	200	-	-	none
PE-Si5	900	5	-	Polyether
PE-Si6	110	6	-	Polyether
PE-Si7-1	1100	7	-	Polyether
PE-Si7-2	1200	7	-	Polyether
PE-Si7-3	1300	7	-	Polyether
PE-Si7-4	1500	7	-	Polyether
PE-Si7-5	1600	7	-	Polyether
PE-Si7-6	2900	7	-	Polyether
PE-Si8-1	300	8	-	Polyether
PE-Si8-2	3500	8	-	Polyether
PE-Si10	920	10	-	Polyether
PE-Si13	390	13	-	Polyether
PE-Si14	1000	14	-	Polyether
A-Si-H	70	-	350	Amino
A-Si-M	1300	-	600	Amino
A-Si-L	1500	-	3800	Amino
E-Si-H	1500	-	350	Epoxy
E-Si-L	17000	-	3500	Epoxy

*D-Si,PE-Si5,6,7-1~3,7-6,8-1~2,13,14,A-Si-M were produced by TORAY Dow Corning silicone Co ltd.
PE-Si7-4~5,10,E-Si-H,L,A-Si-H,A-Si-L were produced by Shin-Etsu Chemical Co., Ltd.

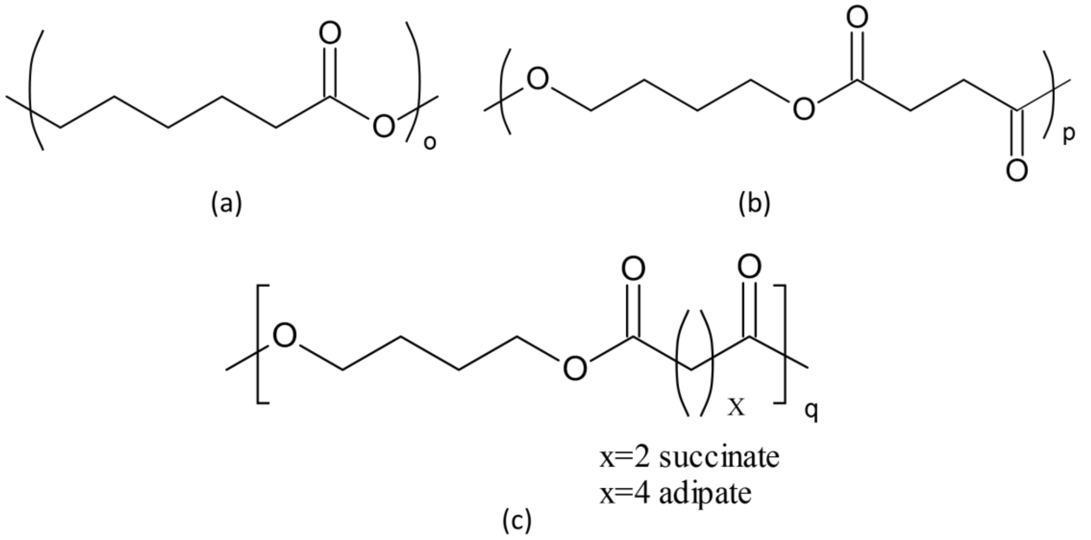


FIGURE 3-2-3 Structures of tested linear polyester resins: (a) poly(caprolactone), PCL; (b) poly(butylene succinate), PBS; (c) poly(butylene succinate adipate), PBSA.

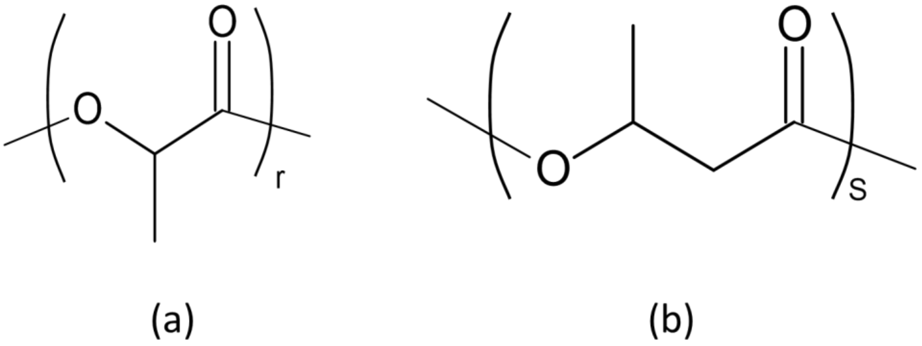


FIGURE 3-2-4 Structures of tested branched polyester resins: (a) poly(lactic acid), PLA; (b) poly(hydroxybutyrate), PHB.

(2) Methods

Sample composites were prepared using an extruder (Haake MiniLab, Thermo Fisher Scientific Co., Germany), mechanically kneading PAA−bonded CDA and olefin resins, polyether silicone, polyester resins and glass fiber at 200±10 °C. Each sample was kept at 80 °C for 5 hours before injection−molding to remove moisture. For the mechanical tests, PAA−bonded CDA and its derivatives with additional components, such as polyester resins and glass fiber, were molded into test pieces using an injection−molding machine (Haake Mini Jet II, Thermo Fisher Scientific Co., Germany). The temperature of the molten pellets was 200–220 °C, and the temperature of the mold was 80–110 °C. The injection pressure was 70–120 MPa, and the pressure was subsequently kept at 40 MPa for 5–10 s. The test pieces of the molded samples were 2.4 mm thick, 80 mm long, and 12.4 mm wide.

The mechanical characteristics of the molded samples were measured at room temperature in bending tests conducted in accordance with the ASTM D790 on a universal testing machine (Instron 5567, Instron Co., USA; cross−head speed: 0.85 mm/min; span: 32 mm). The test pieces in the bending test were 2.4 mm thick, 80 mm long, and 12.4 mm wide. Izod impact tests were conducted in accordance with the JIS K7110 by using an impact testing instrument (Universal Impact Tester C1, Toyo Seiki Seisaku−sho, Ltd., Japan; pendulum: 2.75 J; upswing angle: 150°). The impact resistance was calculated in accordance with the JIS K7110 standard test method.

The fracture surfaces of the molded samples after the impact test were observed with a scanning electron microscope (KEYENCE, VE−7800).

Water absorption was calculated by measuring the finite difference of weights before and after dipping specimens in distilled water at room temperature for 24 H.

The melt flow rate (MFR), which is the weight of melted sample passing through a capillary (10 mm long and 2 mm in diameter) in 10 minutes, was measured using a capillary rheometer (CFT−500D, Shimadzu Co., Japan) at 200 °C with a 500−kgf/cm^2 load. Each sample was kept at 80 °C for 5 hours before the MFR test in order to remove moisture.

The molecular weight of PAA-bonded CDA in terms of polystyrene was measured using gel permeation chromatography (liquid chromatograph; product name: LC-10ADvp; manufactured by SHIMADZU CORPORATION (Japan)) with columns for chloroform (product name: GPC-80MC, GPC-80M, GPC-8025C; manufactured by SHIMADZU CORPORATION (Japan)).

The turbidity (or haze) of the PAA−bonded CDA composites was evaluated by using a haze meter (HM−150, Murakami Color Research Laboratory Co., Ltd.) The haze was calculated in accordance with the JIS K7136 standard test method. The test pieces for the haze measurements were 2.4 mm thick, 80 mm long, and 12.4 mm wide, and the turbidity values are the haze values obtained in the thickness direction.

To measure the glass transition temperature (Tg) of the resulting resin samples and the heat of fusion of crystallized polyester in the resulting resin samples, differential scanning calorimetric (DSC) analysis of the samples was conducted using a differential scanning calorimeter (DSC 6200/EXSTAR6000, Seiko Instrument Inc., Japan). The same thermal history as before the measurement was performed by heating each sample from -100 to 230 °C at a scanning rate of 10 °C per minute and then measuring the heat of fusion of the crystallized polyester, and finally quenching it to room temperature.

The appearance of the molded samples was observed with a digital microscope (KEYENCE, VHX–500F)

The flame retardancy of the molded compounds was measured by the oxygen index method (JIS-K-7201) and the UL94V method of Underwriters Laboratories (UL) Inc. In the UL94V method, a vertically clamped sample of the molded compound is ignited by a gas burner flame applied to the bottom of the sample for 10 s twice. For a material to be classified as V-0 requires that burning stops within 10 s after both ignitions. The V-1 and V-2 classifications both require that burning stops within 60 s after the two ignitions, but V-2 allows a flaming drip. A sample that burns out does not meet the conditions required for any of the classifications.

3-3. Results and discussion

3-3-1. Improvement in impact strength of modified cardanol-bonded cellulose thermoplastic resin by using olefin resins

(1) Addition of general petroleum plastics

The impact strength and flexural properties of compounds consisting of PAA-bonded CDA with 5 weight (wt) % of general petroleum plastics such as ABS, AS and PA6 were measured. As shown in Table 3-3-1-1, the compounds obtained by adding these plastics could not simultaneously exhibit high impact strength and good flexural properties. Additionally, these plastics exhibited low dispersibilities in PAA-bonded CDA; therefore, these compounds were opaque. When adding PA6, the outside appearance of this compound was marblelike, and continuous layers of PA6 were clearly observed. The impact strength of the compound with PA6 was improved, while those of the compounds with ABS or AS were decreased.

The fracture surface of the PAA-bonded CDA with PA6 was more rugged and had a larger specific surface area than those of the compounds with ABS or AS. The increase in impact strength by adding PA6 was thought to be due to the forming of continuous layers of PA6. These layers, which originated from low dispersibilities of PA6 in PAA-bonded CDA, show excellent fracture toughness and would prevent the progress of destruction cracks; therefore, a large amount of energy during the impact test was spent to form this fracture surface. In contrast, fracture surfaces of the PAA-bonded CDA with ABS or AS were less rugged and flatter than that of the PAA-bonded CDA with PA6. From these results, the addition of ABS or AS, which could not form continuous layers, would not be able to improve impact strength.

On the other hand, the addition of PA6 drastically decreased the breaking strain. Too weak interfacial coherency between PAA-bonded CDA and PA6 resulted in low breaking strain. The weak coherency was derived from the large difference in the intermolecular force between PAA-bonded CDA and PA6 with higher polarity than those of ABS or AS. Destruction began at a smaller strain than that of PAA-bonded CDA alone because stresses were concentrated on the weak interfaces between PAA-bonded CDA and PA6. During the bending test of the compound with PA6, the beginnings of fracture was observed around 4% of strain.

TABLE 3-3-1-1 Properties of PAA-bonded CDA with polymers.

a DS of acetic acid: 2.1

Sample content	Izod impact Strength (kJ/m^2)	Bending test			Water absorption (%)	Melt flow rate (g/10min)
		Strength (MPa)	Modulus (GPa)	Breaking strain (%)		
Cellulose diacetate (CDA)[a]	-	-	-	-	17.0	-
PAA-bonded CDA (DS of PAA: 0.53, 42wt%)	3.8	72	2.3	8.2	0.85	1.50
PAA-bonded CDA + **ABS 5wt%**	3.4	59	1.9	9.2	0.80	15.2
PAA-bonded CDA + **AS 5wt%**	3.7	61	2.0	9.1	0.76	16.1
PAA-bonded CDA + **Nylon6 5wt%**	9.6	52	1.9	4.0	0.88	11.0
PAA-bonded CDA + **Branched-PE 5wt%**	7.7	53	2.3	>10	0.69	15.6
PAA-bonded CDA + **Mflow-PP 5wt%**	7.3	55	2.3	>10	0.65	16.4

(2) Addition of olefin resins

As previously mentioned, the addition of three types of general petroleum resins (ABS, AS, or PA6) could not simultaneously exhibit high impact strength and flexural properties. The reason for these results was derived from insufficient dispersibilities of the three resins in PAA-bonded CDA.

Based on the above results and considering a proper structure of PAA-bonded CDA, which is different from conventional cellulose resins such as CDA, adding resins that can disperse in PAA-bonded CDA. The center structure of PAA-bonded CDA is hydrophilic resembling CDA, while the periphery structure of PAA-bonded CDA is extremely hydrophobic by adding alkyl long chains of the modified cardanols. Therefore, the total polarity of PAA-bonded CDA is hydrophobic (Figure 3-1). As shown in Table 3-3-1-1, the hydrophobicity of PAA-bonded CDA is obvious from its low water absorption (0.85 wt %), which is one-twentieth of that of CDA (17.0 wt %).

For improving impact strength, therefore, the addition of hydrophobic olefin resins was investigated because it is expected to show high affinities to hydrophobic cardanol side chains. Several types of PE and PP were used as olefin resins. Table 3-3-1-1 lists the best results of adding representative olefin resins (Branched-PE, middle-flow-type PP: MFlow-PP), which showed high effectiveness in improving impact strength. In the near future, PE and PP will be able to be produced from plant sources; therefore, these resins have potential for use in the manufacture of bioplastics. The detail results and discussions were described as follows.

(3) Addition of several types of PE

The impact strength of compounds consisting of PAA-bonded CDA and 5 wt % of PE (HDPE, LDPE, Branched-PE) was drastically increased (Figure 3-3-1-1, >7 kJ/m^2). The outside appearances of these compounds were observed. The appearance of the compound with HDPE was opaque, and those of the compounds with LDPE and Branched-PE were translucent. Dispersibilities of LDPE and Branched-PE in PAA-bonded CDA were the most favorable.

When the fracture surfaces were observed after the impact tests as shown in Figure 3-3-1-2, the dispersing of PE particles could be observed for all three types of PE added to PAA-bonded CDA. Furthermore, many exfoliated interfaces between PAA-bonded CDA and PE particles were observed. From these images, Branched-PE showed the most uniform dispersibility in PAA-bonded CDA. The average diameters of the dispersed Branched-PE were under 2.5 μm.

Next, the impact and flexural strength by changing the amount of Branched-PE, which showed the most uniform dispersibility among the three types of PE were estimated in Figure 3-3-1-3. When the amount of Branched-PE was over 5 wt %, the impact strength tended to slightly decrease. Furthermore, by increasing the amount of Branched-PE, flexural strength also tended to decrease.

Two effects for increasing impact strength by adding PE were discussed. The first is PE's deformation consuming the impact energy as heat, which is well-known for adding elastomer and rubber particles in resins. The second is from moderate weak interfaces between PAA-bonded CDA and PE; therefore, the shearing deformation of PAA-bonded CDA prominently increased. This was obviously from the relatively high breaking strain (8 %) of PAA-bonded CDA, and traces of shearing deformation on the surface of PAA-bonded CDA alone fractured by impact test were observed in Figure 3-3-1-2a. Finally, the moderate adhering strength between PAA-bonded CDA and low modulus PE particles mainly resulted in the increase in shearing deformation of the matrix resin (PAA-bonded CDA).

In contrast, with increases in the amounts of Branched-PE and the other PE resins, the bending strength of the compounds with these PE resins decreased. These decreases were derived from the increases in the shearing deformations of PAA-bonded CDA by including deformable PE resins.

(4) Addition of several types of PP

The impact strength of compounds consisting of the PAA-bonded CDA with several types of PP (high-flow-type: HFlow-PP, low-flow-type: LFlow-PP, and middle-flow-type: MFlow-PP) were measured. All these PP improved the impact strength of the compounds (Figure 3-3-1-4, > 6 kJ/m^2). Furthermore, the outside appearances of these compounds with PP were transparent, and the dispersibilities were observed to be good.

By observing the fracture surfaces of compounds after the impact tests, dispersed liner PP domains can be seen on all three PP cases. Figure 3-3-1-5 shows the typical fracture surfaces of the compounds observed using SEM. From Figure 3-3-1-5, the same as with the compounds with PE, exfoliated-like interfaces between PAA-bonded CDA and the liner PP were clearly observed at many points of the fractured surfaces.

From these results, two effects for increasing the impact strength by adding PP were considered. The first is deformations of PP using the impact energy as heat. The Second is from moderate weak interfaces between PAA-bonded CDA and PP; therefore, the shearing deformation of PAA-bonded CDA prominently increased. From the dispersing morphology of PP, which is liner in PAA-bonded CDA, the liner PP behaved as rubber-like reinforced fibers.

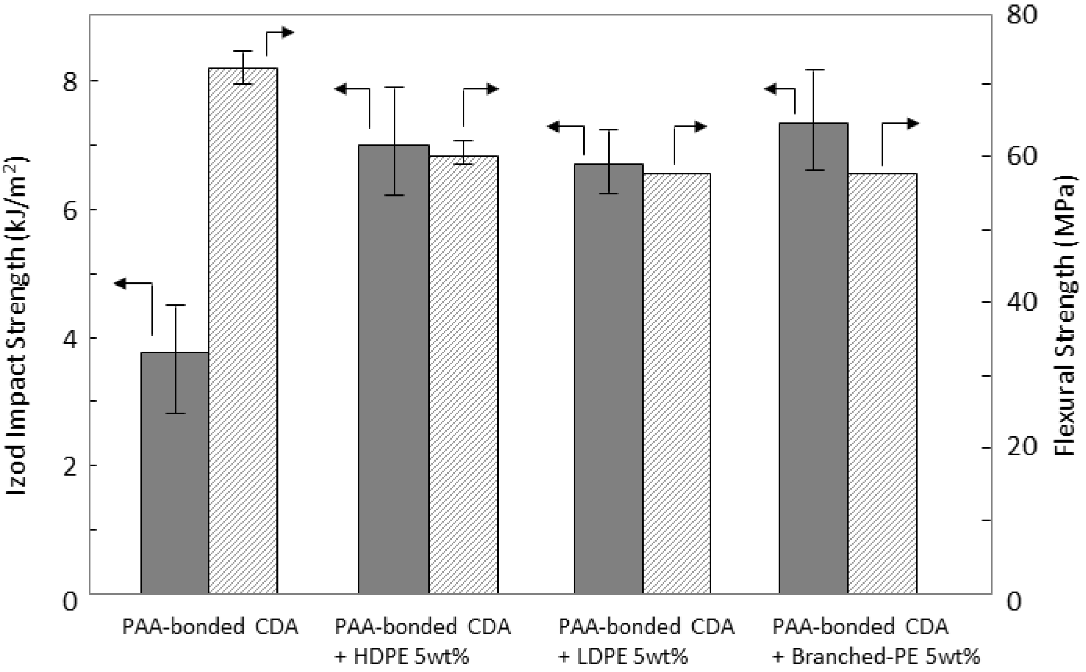


FIGURE 3-3-1-1 Impact strength and flexural strength of PAA-bonded CDA with PE.

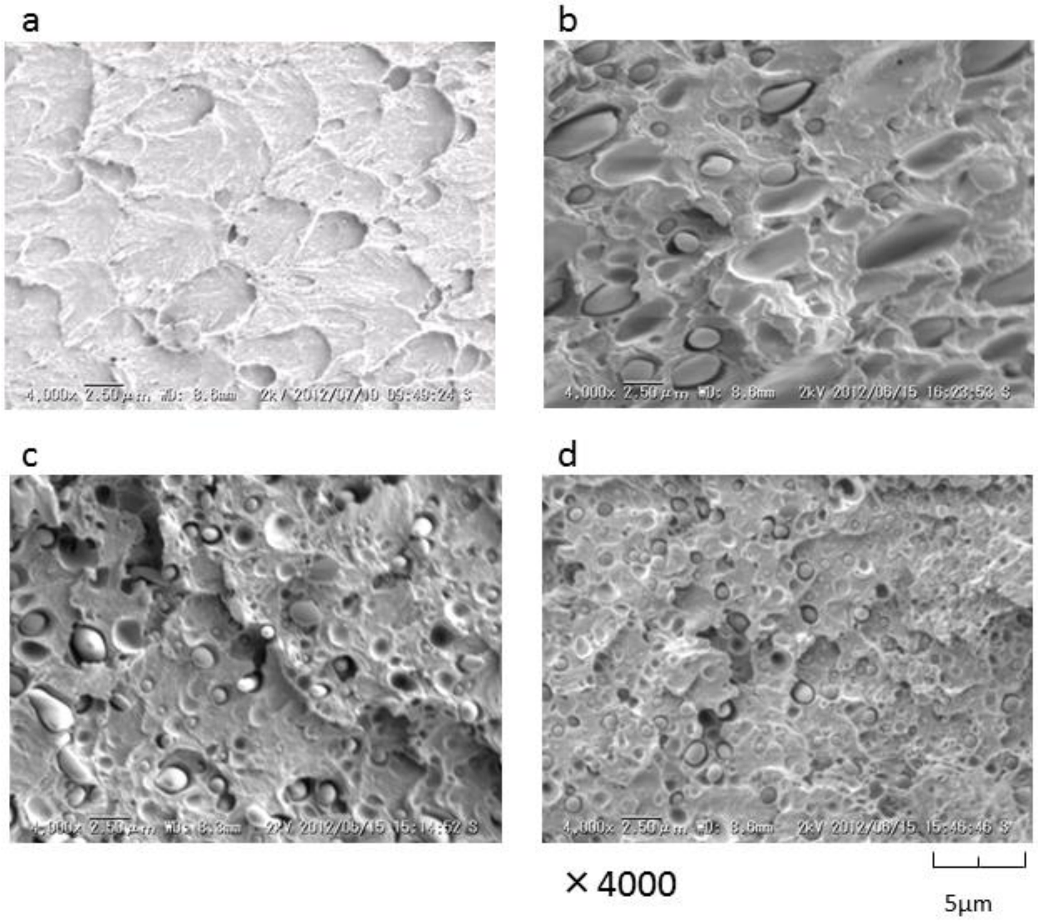


FIGURE 3-3-1-2 SEM images of fracture surfaces of PAA-bonded CDA with PE after impact tests.

a PAA-bonded CDA. b PAA-bonded CDA + HDPE 5 wt %.

c PAA-bonded CDA + LDPE 5 wt %. d PAA-bonded CDA + Branched-PE 5 wt %.

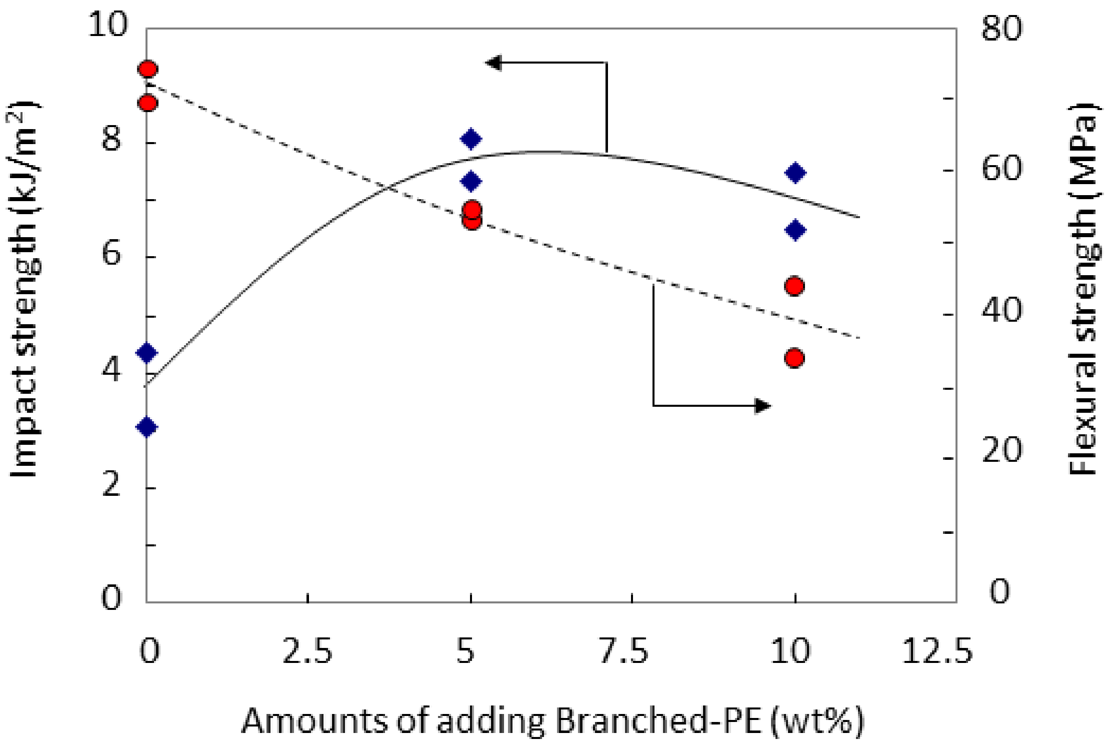


FIGURE 3-3-1-3 Impact strength and flexural strength of PAA-bonded CDA with Branched-PE.

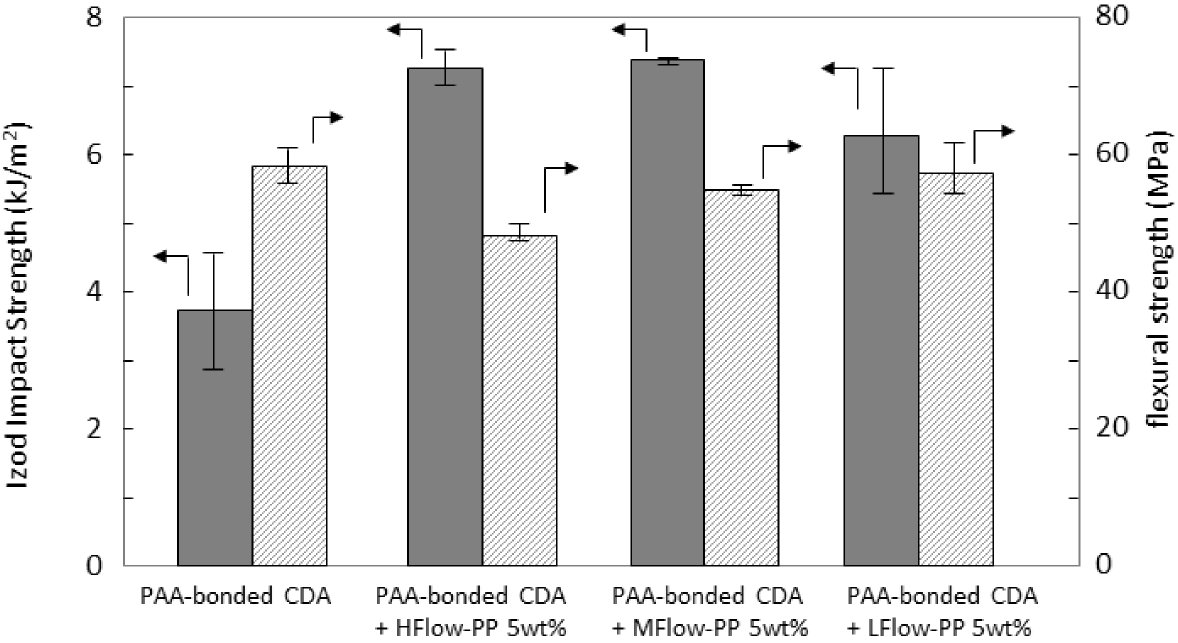


FIGURE 3-3-1-4 Impact strength and flexural strength of PAA-bonded CDA with PP.

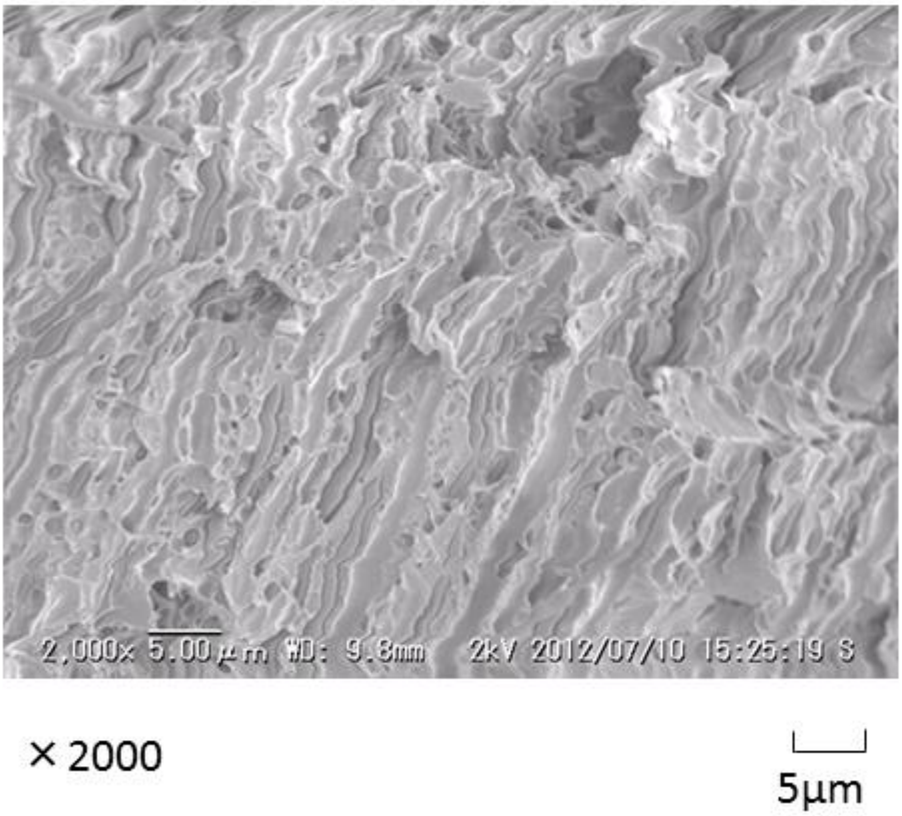


FIGURE 3-3-1-5 SEM image of fracture surface of PAA-bonded CDA with MFlow-PP after impact test.

(5) Effect of interfaces between PAA-bonded CDA and olefin resins

As mentioned above, compounds that consisted of PAA-bonded CDA and olefin resins, such as PE or PP, showed higher impact strength than that of PAA-bonded CDA alone. At the many points of fracture surfaces of the compounds, exfoliated interfaces between PAA-bonded CDA and olefin resins could be observed using SEM. To investigate the effect of the interfacial adhesiveness between PAA-bonded CDA and olefin resins, the impact strength was estimated and the fracture surfaces of compounds consisting of PAA-bonded CDA and PP with different concentrations of maleic anhydride (MAH-PP), which can react with the residual hydroxyl groups (OH) of PAA-bonded CDA were observed. Therefore, interfacial adhesiveness between PAA-bonded CDA and MAH-PP can be regulated as shown in Figure 3-3-1-6. In a previous study, to improve impact strength of an alloy of PA6 and AS, as a compatibilizer, a copolymer of styrene and maleic anhydride (SMA) was added to PA6 and AS for reinforcing the interfacial adhesiveness between PA6 and AS. [18] However, there were no examples for investigating the effect of interfacial adhesiveness between cardanol-bonded cellulose resin and additive resins.

As shown in Figure 3-3-1-7, with an increase in polarities (acid values) of MAH-PP (MAH7-PP; acid value: 7, MAH52-PP; acid value: 52), the points of the exfoliated interfaces between PAA-bonded CDA and MAH-PP disappeared. Consequently, as shown in Figure 3-3-1-8 the impact strength and breaking strains of the PAA-bonded CDA with MAH-PP decreased.

The reason for the disappearance of the exfoliated interfaces as the polarities of MAH-PP increased was discussed. The disappearance was derived from an increase in interfacial adhesiveness due to partially reaction of the residual OH with MAH-PP; therefore, the dispersibilities of MAH-PP increased. As a result, it was difficult to observe shearing deformation in the PAA-bonded CDA with MAH-PP. Additionally, finer particle sizes of MAH-PP than that of PP alone decreased the effect for using impact energy by deformation, mainly resulting in that the impact strength of the PAA-bonded CDA with MAH-PP decreased.

With an increase in the polarities of MAH-PP, the breaking strains of compounds consisting of PAA-bonded CDA and MAH-PP decreased. As shown in Figure 3-3-1-6, hydrophilic parts such as ester bonding and carboxyl groups were generated by reacting residual OH of the PAA-bonded CDA with MAH-PP. These hydrophilic parts resulted in the increase in intermolecular interaction, such as hydrogen bonding; therefore, local areas, which show high intermolecular forces, can be created. Hence, bending stress is probably concentrated at the local areas.

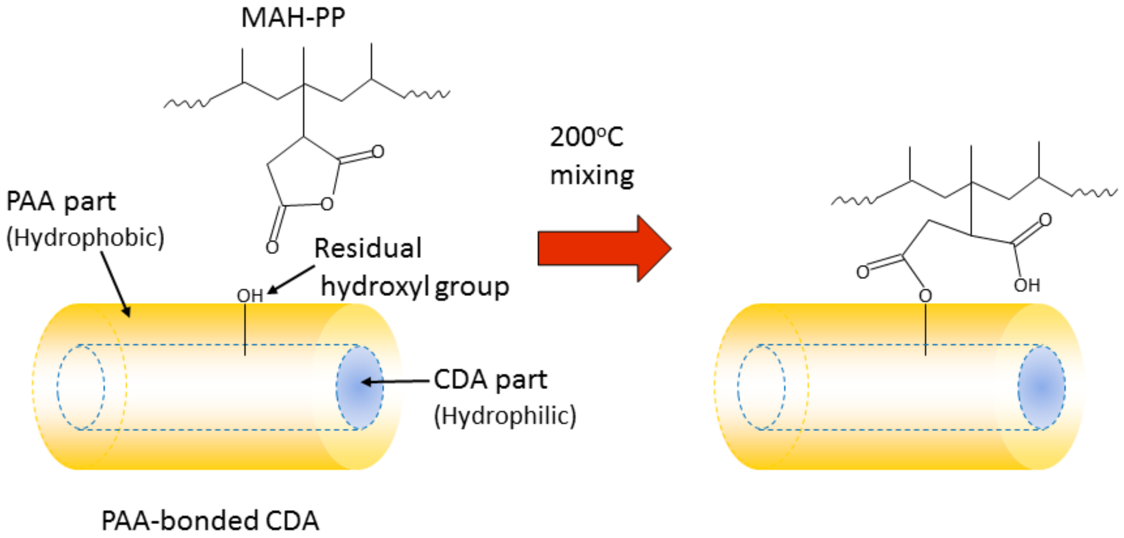


FIGURE 3-3-1-6 Reaction scheme of MAH-PP with residual hydroxyl group in PAA-bonded CDA.

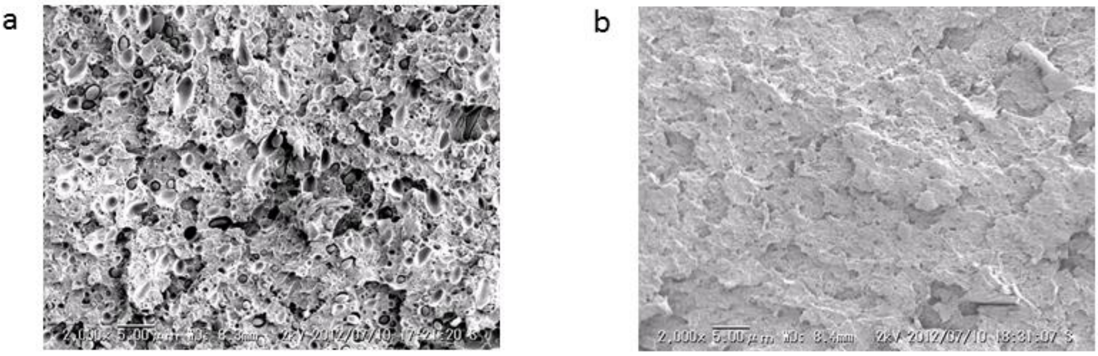


FIGURE 3-3-1-7 SEM images of fracture surfaces of PAA-bonded CDA with MAH-PP after impact tests.

a PAA-bonded CDA + MAH7-PP 5 wt%.

b PAA-bonded CDA + MAH52-PP 5 wt %.

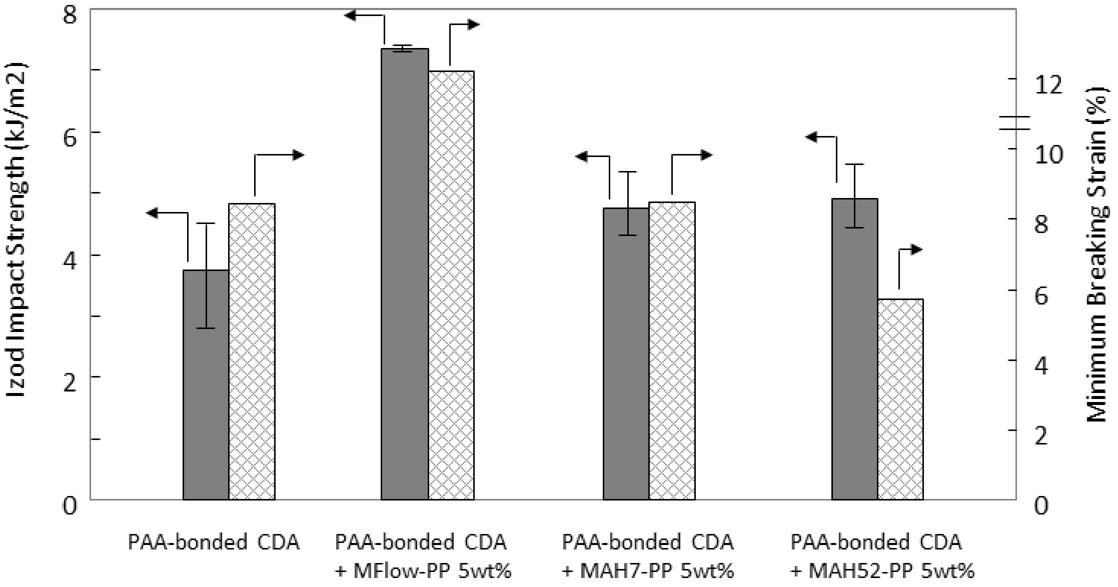


FIGURE 3-3-1-8 Impact strength and flexural strain of PAA-bonded CDA with MAH-PP.

(6) Effects on water absorption and fluidity by adding olefin resins

The water absorption of the PAA-bonded CDA with 5 wt % of olefin resins was measured. As shown in Figure 3-3-1-9, the addition of hydrophobic olefin resins showed the lowest water absorption and good water resistance. In contrast, only 5-wt-% addition of PA6 with high polarity showed higher water absorption than that of PAA-bonded CDA alone.

As shown in Table 3-3-1-1, the compounds with all types of tested resins showed higher fluidity than that of PAA-bonded CDA alone. As shown in Figure 3-3-1-10, the fluidity at low load (5 kgf) was about ten times higher than that of PAA-bonded CDA alone. The higher fluidity resulted from the resins' behavior as plasticizers at high temperatures (around 200 °C) for measuring MFR.

(7) Conclusion

The impact strength of cardanol-bonded cellulose diacetate (PAA-bonded CDA) was drastically increased by adding a small amount of olefin resins. In our past studies, PAA-bonded CDA indicated high practical properties such as bending strength, heat resistance, and water resistance. In contrast, its impact strength was not sufficient for use in durable products. In this study, improvement in the impact strength of PAA-bonded CDA was achieved by using hydrophobic olefin resins such as PE or PP, while satisfying good bending strength and breaking strain.

Moreover, the addition of olefin resins improved water resistance and fluidity of the PAA-bonded CDA with olefin resins. The PAA-bonded CDA with olefin resins are thus promising cellulose-based bioplastics for use in various durable products requiring high impact strength and other practical properties.

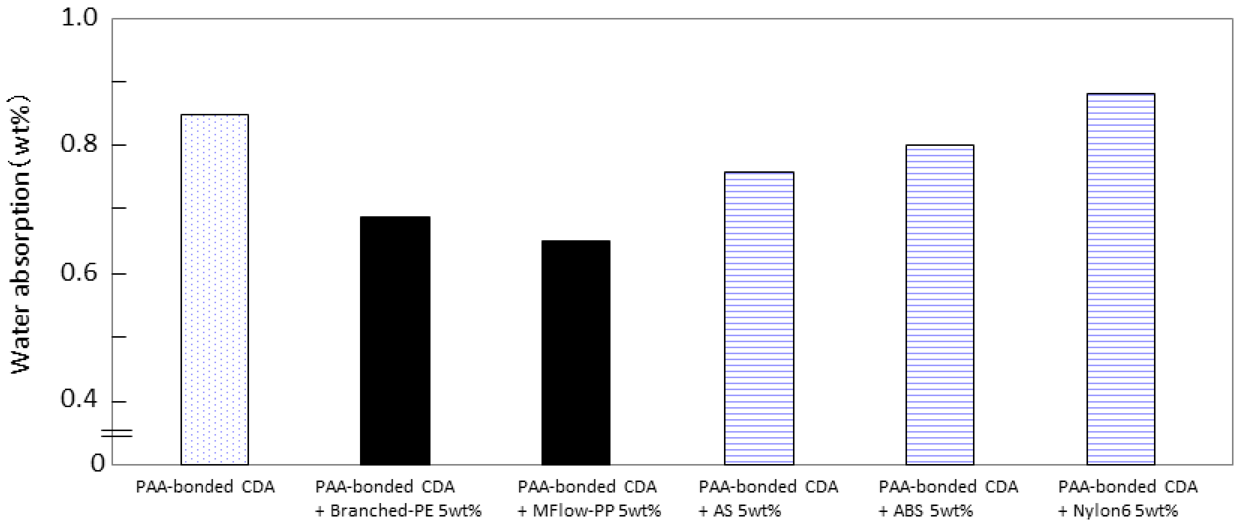


FIGURE 3-3-1-9 Water absorption of PAA-bonded CDA with polymers.

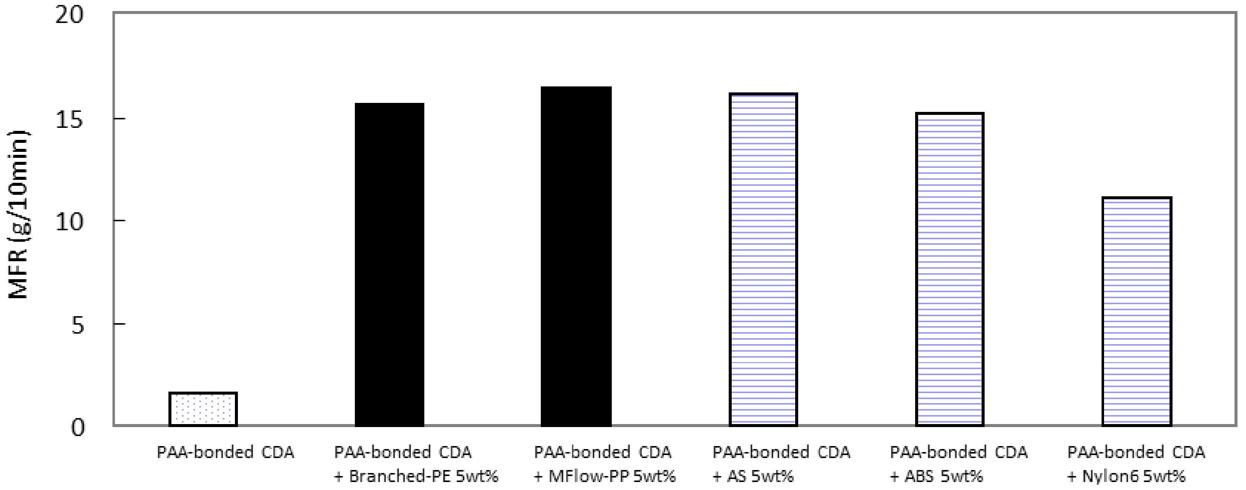


FIGURE 3-3-1-10.　Fluidity（MFR）of PAA-bonded CDA with polymers.

3-3-2. Improvement in impact strength of modified cardanol-bonded cellulose thermoplastic resin by modified silicones.

(1) Characteristics of PAA-bonded CDA after adding modified silicones with various polar groups

As the characteristics of PAA-bonded CDA composites with modified silicones, their mechanical properties (impact strength and maximum bending strength), and the dispersion of these silicones in the PAA-bonded CDA composites were investigated. A dimethyl silicone (polydimethylsiloxane: D-Si: 5 wt %) without a polar group migrated to the surface of the PAA-bonded CDA composite with D-Si (Table 3-3-2-1). Since the dimethyl silicone was lower in polarity than the PAA-bonded CDA, the dimethyl silicone could not be uniformly dispersed in the PAA-bonded CDA composite. Modified silicones composed of dimethyl silicone and functional groups such as polyether, amino, and epoxy groups were used to enhance the dispersion of the silicones. As a result, adding dimethyl silicones with polyether group (polyether silicones: PE-Si) with relatively high polarity tended to disperse uniformly in the PAA-bonded CDA composite and greatly improved the impact strength of the PAA-bonded CDA. The silicones did not migrate to the surfaces of the PAA-bonded CDA composites with PE-Si during molding the composites. The dispersion of PE-Si in PAA-bonded CDA composite was affected by the polarity of PE-Si, which depended on the concentration of the polyether group in the PE-Si. That is, PE-Si with relatively higher polarity became highly dispersed in the PAA-bonded CDA composite. In particular, adding PE-Si 7 (an HLB of 7) and PE-Si 8 (an HLB of 8) improved the impact strength of the PAA-bonded CDA the most (Table 3-3-2-1).

Adding amino silicones with middle and high concentrated amino group, i.e., A-Si-M with an amino equivalent of 600 g/mol and A-Si-H with an amino equivalent of 350 g/mol, improved the impact strength of PAA-bonded CDA. However, the amino silicone with low concentration of amino groups, i.e., A-Si-L with an amino equivalent of 3800 g/mol, bled to the surface of the PAA-bonded CDA composite with A-Si-L. The reason is that the polarity of A-Si-L was not as high as that of PAA-bonded CDA. In comparison, epoxy silicones migrated to the surfaces of the PAA-bonded CDA composites with the epoxy silicones, regardless of the concentrations of epoxy group, i.e., E-Si-H with an epoxy equivalent of 350 g/mol and E-Si-L with an epoxy equivalent of 3500 g/mol. This occurred because the epoxy group had low polarity compared with the polyether or amino group.

TABLE 3-3-2-1. Properties of PAA-bonded CDA composites with silicones

Sample	Compatibility of compound*	Impact strength (kJ/m^2)	Bending Strength (MPa)
PAA-bonded CDA	-	3.5	68
PAA-bonded CDA with 5wt% of D-Si	Bleed	IM**	IM**
PAA-bonded CDA with 5wt% of PE-Si5	Bleed	IM**	IM**
PAA-bonded CDA with 5wt% of PE-Si6	Poor	4.8	47
PAA-bonded CDA with 5wt% of PE-Si7-1	Moderate	6.7	49
PAA-bonded CDA with 5wt% of PE-Si7-2	Moderate	8.0	49
PAA-bonded CDA with 5wt% of PE-Si7-3	Moderate	7.5	48
PAA-bonded CDA with 5wt% of PE-Si7-4	Moderate	6.6	49
PAA-bonded CDA with 5wt% of PE-Si7-5	Moderate	7.0	47
PAA-bonded CDA with 5wt% of PE-Si7-6	Moderate	6.3	48
PAA-bonded CDA with 5wt% of PE-Si8-1	Moderate	7.2	49
PAA-bonded CDA with 5wt% of PE-Si8-2	Moderate	7.3	50
PAA-bonded CDA with 5wt% of PE-Si10	Good	5.2	51
PAA-bonded CDA with 5wt% of PE-Si13	Good	5.2	47
PAA-bonded CDA with 5wt% of PE-Si14	Poor	IM**	IM**
PAA-bonded CDA with 5wt% of A-Si-H	Moderate	5.4	55
PAA-bonded CDA with 5wt% of A-Si-M	Poor	6.2	54
PAA-bonded CDA with 5wt% of A-Si-L	Bleed	IM**	IM**
PAA-bonded CDA with 5wt% of E-Si-H	Bleed	IM**	IM**
PAA-bonded CDA with 5wt% of E-Si-L	Bleed	IM**	IM**

*Good: <0.1 μm, Moderate: 0.1~0.5 μm, Poor: >0.5 μm, Bleed: Silicone migration
**IM: Impossible to measure

(2) Effects of amounts and structure of polyether silicones on impact strength of PAA-bonded CDA

The polyether silicones that were optimized in terms of their amount, polarity, and viscosity enhanced the impact strength of the PAA-bonded CDA composites. Figures 3-3-2-1 and 3-3-2-2 show the mold surface and the impact strength of PAA-bonded CDA composites after adding the polyether silicones with different polarities (HLBs: from 5 to 14). These results indicate that adding the polyether silicones with HLBs from 6 to 13 (PE-Si6 to PE-Si 13) enhanced the impact strength of the PAA-bonded CDA and there was no silicone migration on the composites' surfaces. Adding PE-Si 7 and PE-Si 8 (polyether silicones with HLBs of 7 and 8) improved the impact strength of the PAA-bonded CDA the most, and its appearance was translucent.

It is known that crazing and shearing deformations enhance the impact strength of polymers. The impact strength of polymers, such as acrylonitrile-butadiene-styrene (ABS), has been enhanced by the inclusion of fine flexible domains made of elastomeric particles [22]. Crazing deformations tend to occur when elastomeric particles with moderate particle diameters (0.3 - 1.5 μm) are dispersed in polymers. In comparison, smaller elastomeric particles (< 0.3 μm) are more likely to induce shearing deformation.

Therefore, the dispersion of the polyether silicones (5 wt %) with HLBs from 6 to 13 (PE-Si 6 to PE-Si 13) in the PAA-bonded CDA composites was studied.

The polyether silicone with an HLB of 6 (PE-Si 6) was of micron-order size (> 0.5 μm) in the PAA-bonded CDA composite. The appearance of the PAA-bonded CDA composite with PE-Si 6 was translucent and it had a relatively low impact strength (Figures 3-3-2-1(b) and 3-3-2-2(a)). The particles of polyether silicones with moderate concentration of polyether groups (PE-Si 7 with an HLB of 7 and PE-Si 8 with an HLB of 8) were also of submicron-order size (0.1 - 0.5 μm) as shown in Figure 3-3-2-3(a). These composites were almost transparent and had high impact strength (Figures 3-3-2-1(c) and 3-3-2-2(b)). In addition, although the fracture cross sections of the PAA-bonded CDA before adding the silicones had a flat surface (Figure 3-3-2-4(a)), those of the PAA-bonded CDA composites with 5 wt% of PE-Si 7 (Figure 3-3-2-4(b)) and PE-Si 8 had corrugated surfaces due to shearing deformations. Moreover, whitened areas were observed in these fracture cross sections. It showed that when the test pieces were destroyed, stress concentrated on the silicones with low elasticity and crazing deformations occurred. These results suggest that adding 5 wt% of PE-Si 7 and PE-Si 8 to PAA-bonded CDA resulted in both shearing and crazing deformations and increased the impact strength of the composites.

The polyether silicones with the high concentrated polyether group (PE-Si 10 with an HLB of 10 and PE-Si 13 with an HLB of 13) were highly dispersed (< 0.1 μm) as shown in Figure 3-3-2-3(b). These composites were transparent. However, fracture cross sections did not have any whitened or flat surfaces (Figures 3-3-2-1(d) and 3-3-2-4(c)). That is, crazing and shearing deformations rarely occurred in the fracture cross sections of these composites. The

PAA-bonded CDA composites with PE-Si 10 and PE-Si 13 had relatively low impact strength (Figure 3-3-2-2(c)). In comparison, the polyether silicone with an HLB of 5 (PE-Si 5), in which the concentration of the polyether group was low, bled to the surface of the PAA-bonded CDA composite (Figure 3-3-2-1(a)). The polyether silicone with an HLB of 14 (PE-Si 14), in which the concentration of the polyether group was high, could not disperse uniformly in the PAA-bonded CDA composite (Figure 3-3-2-1(e)).

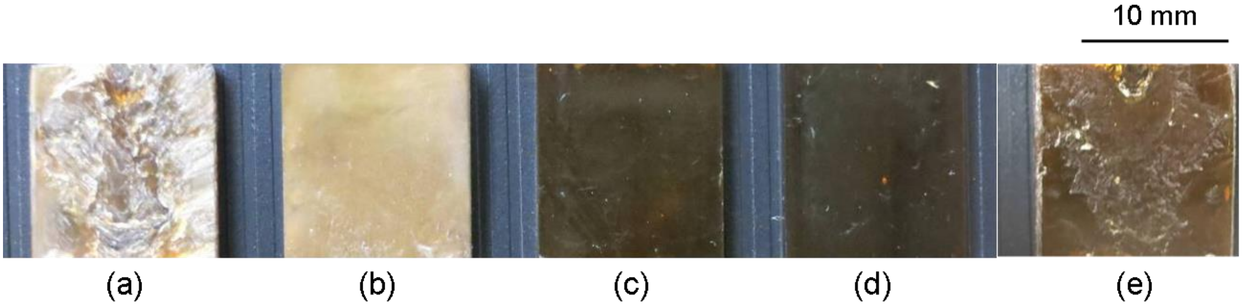


FIGURE 3-3-2-1 Appearance of PAA-bonded CDA composites with polyether silicones.

a PAA-bonded CDA composite with 5 wt% of PE-Si5: HLB=5. b with 5 wt% of PE-Si6: HLB=6.

c with 5 wt% of PE-Si7: HLB=7. d with 5 wt% of PE-Si13: HLB=13.

e with 5 wt% of PE-Si14: HLB=14.

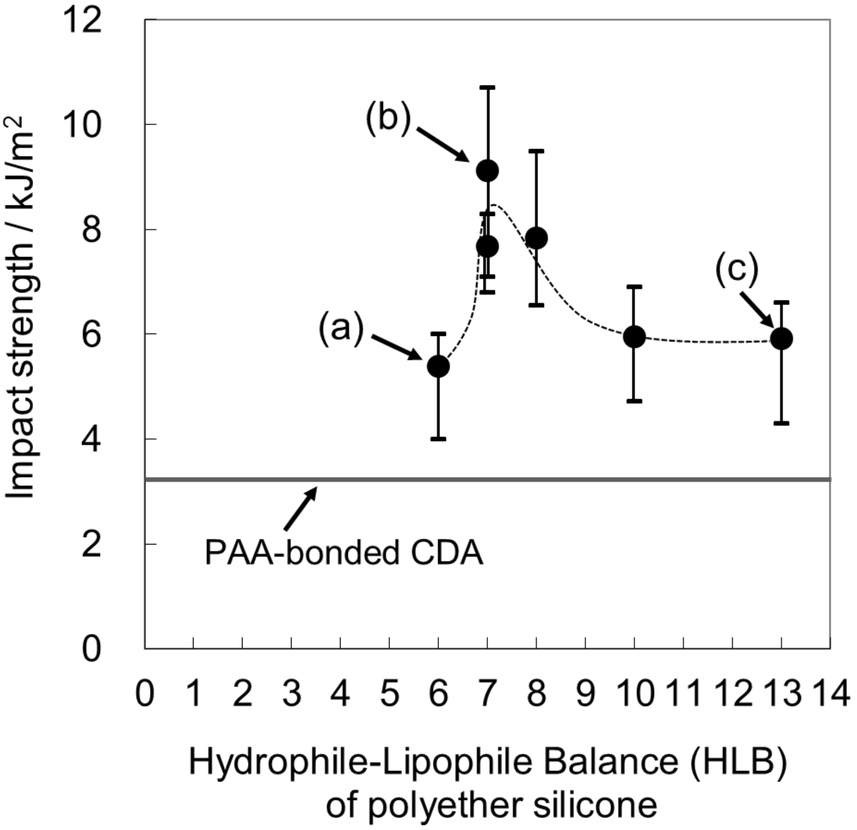


FIGURE 3-3-2-2 Effects of HLB of polyether silicone on impact strength of PAA-bonded CDA composites with polyether silicones.

a PAA-bonded CDA composite with 5 wt% of PE-Si6: HLB=6.

b with 5 wt% of PE-Si 7a: HLB=7.

c with 5 wt% of PE-Si13: HLB=13.

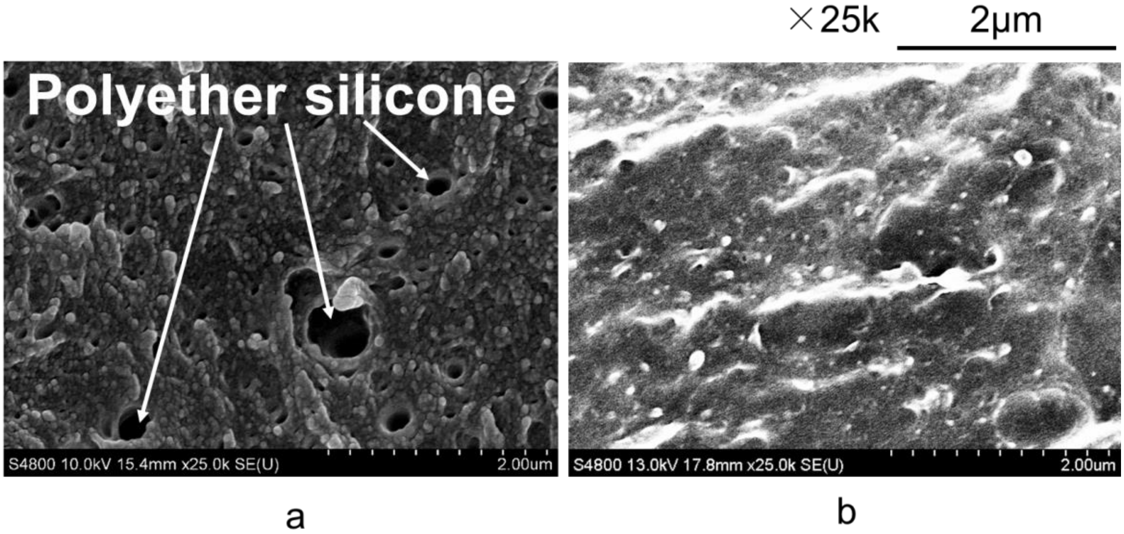


FIGURE 3-3-2-3 Scanning electron microscope image of PAA-bonded CDA composite with polyether silicones.

a PAA-bonded CDA composite with 5 wt% of PE-Si 7a: HLB=7.

b with 5 wt% of PE-Si13: HLB=13.

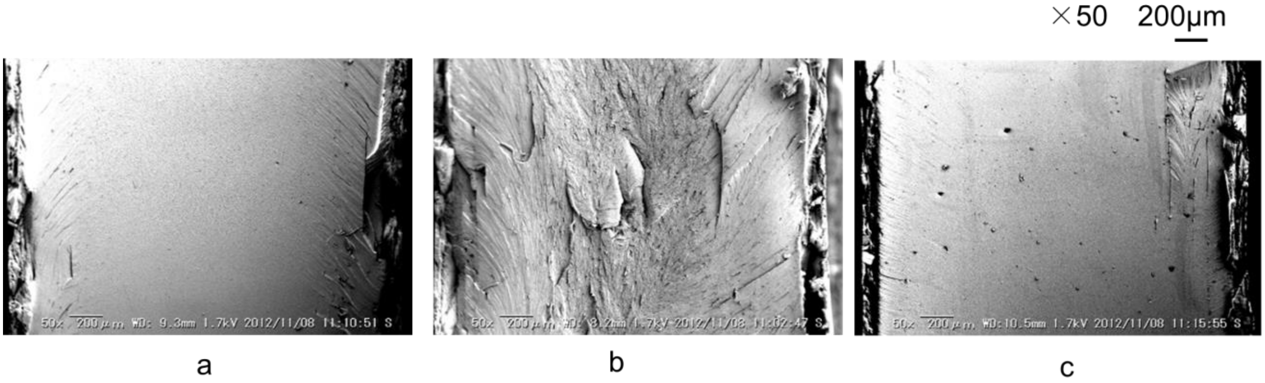


FIGURE 3-3-2-4 Scanning electron microscope images of fracture surfaces.

a PAA-bonded CDA (3 kJ/m^2). b PAA-bonded CDA composite with 5 wt% of PE-Si 7a: HLB=7 (8 kJ/m^2). c with 5 wt% of PE-Si13: HLB=13 (5 kJ/m^2).

The effect of varying the amount of the most effective polyether silicone (PE-Si 7a: polyether silicones with an HLB of 7 and viscosity of 1200 mm^2/s) on the impact strength, maximum bending strength, elastic modulus, elongation, thermoplasticity (in terms of melt flow rate), and water resistance (in terms of water absorption ratio) were investigated. As shown in Table 3-2-2 and Figure 3-2-5, adding even 1 wt% of the polyether silicone (PE-Si 7a) improved the impact strength of PAA-bonded CDA. Additionally, reducing the amount of the polyether silicone suppressed the decrease in the bending strength and modulus of the PAA-bonded CDA composites. Although no whitened areas were observed in the fracture cross section of the composite with 1 wt% of PE-Si 7a, in which the silicone particles were 0.1 μm, there were a large number of corrugations. These results indicate that adding 1 wt% of PE-Si 7a resulted in shearing deformation but no crazing deformation. The impact strength of the PAA-bonded CDA increased as the result of the shearing deformation.

The PAA-bonded CDA composites containing the polyether silicone were compared with reference current plastics, including a CDA composite with plasticizer (TEC), PLA: a mass-produced bioplastic derived from corn starch, Polyamide 11 (PA11): a bioplastic derived from castor beans used in durable products, and acrylonitrile-butadiene-styrene (ABS) resin: a petroleum-based plastic used in durable products.

Table 3-2-2 lists the impact strength, glass transition temperature (Tg), water resistance (water absorption), maximum bending strength, and thermoplasticity (melt flow rate) of the PAA-bonded CDA composites with 0–5 wt% of PE-Si 7a, the CDA composite with plasticizer (29 wt%), PLA, PA11, and ABS resin. Although the PAA-bonded CDA without PE-Si had a lower impact strength compared with PLA, the PAA-bonded CDA composites with 1–5 wt% of PE-Si 7a were higher in impact strength than PLA and were nearly equal in strength to PA11 and the CDA composite with plasticizer. The glass transition temperature (Tg) of the PAA-bonded CDA composites with 1–5 wt% of PE-Si 7a was particularly higher than that of the CDA composite with plasticizer and the other reference plastics. Their water resistance was superior to those of CDA and the CDA composite with plasticizer, as previously reported [21]. Moreover, the maximum bending strength of the PAA-bonded CDA composites with 1-2 wt% of PE-Si 7a was near that of PA11. Their thermoplasticity was comparable to those of the CDA composite with plasticizer and ABS resin.

TABLE 3-3-2-2. Characteristics of PAA-bonded CDA with polyether silicone: PE-Si 7a (HLB=7, 1200mm^2/s) and references

Sample	Compatibility of compound**	Impact strength (kJ/m^2)	Bending test			Water absorption (%)	Melt flow rate (g/10 min)
			Strength (MPa)	Modulus (GPa)	Breaking Strain (%)		
Cellulose diacetate (CDA)	-	-	-	-	-	17.0	-
PAA-bonded CDA	-	3.5	68	1.9	10	1.0	1011
PAA-bonded CDA with polyether silicone* 1wt%	Good	6.2	58	1.7	>10	1.0	1040
PAA-bonded CDA with polyether silicone* 2wt%	Good	7.5	55	1.6	>10	1.1	1073
PAA-bonded CDA with polyether silicone* 3wt%	Good	7.4	52	1.5	>10	1.1	1072
PAA-bonded CDA with polyether silicone* 5wt%	Moderate	8.0	49	1.5	>10	1.1	1094

* PE-Si7-2:HLB=7, 1200mm^2/s

**Good:<0.1 μ m, Moderate:0.1~0.5 μ m

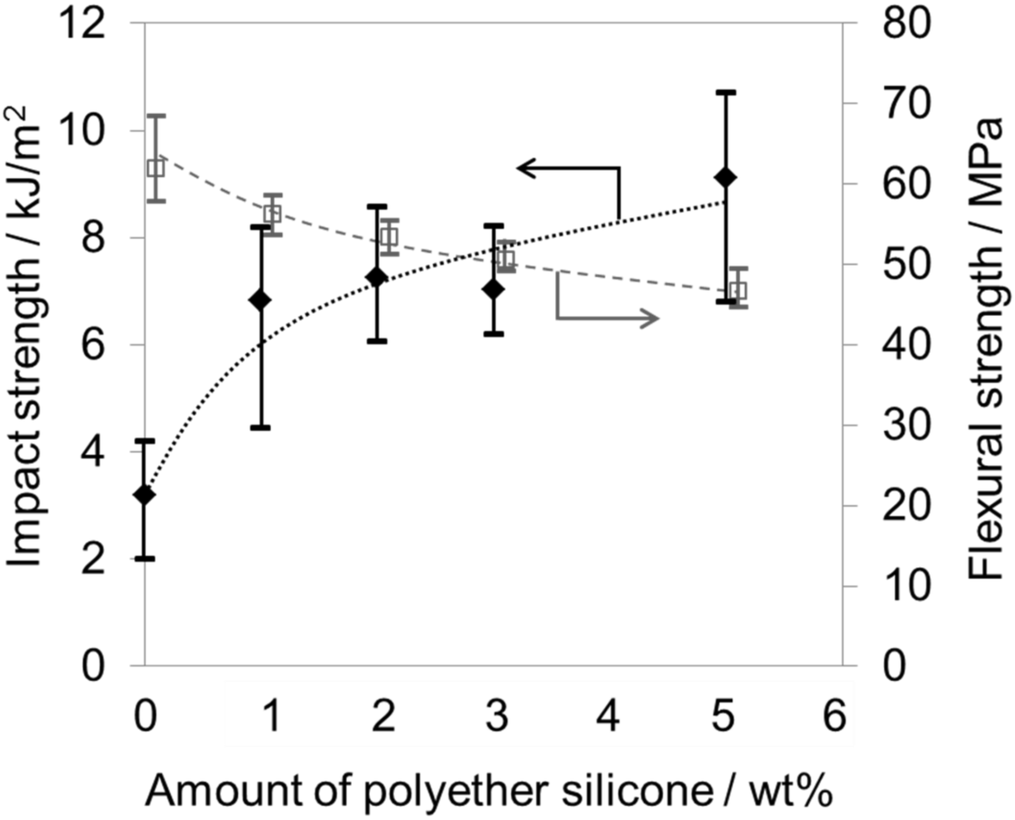


FIGURE 3-3-2-5 Effects of amount of polyether silicone: PE-Si 7a (HLB=7, 1200mm²/s) on mechanical properties of PAA-bonded CDA composites with polyether silicones.

3-3-3 Improvement of impact strength and flame retardancy of modified cardanol-bonded cellulose resin by adding complex additives containing polyester, glass fiber, and aluminum hydroxide

(1) Effect of adding polyester resins on impact strength of PAA–bonded CDA

The impact strength of the PAA–bonded CDA composites with 20 wt% of polyester resins with branched monomers (PLA and PHB) and with linear monomers (PCL, PBS and PBSA) were measured (Figure 3-3-3-1). Among all polyesters, PBSA was the most effective as an impact modifier of the PAA–bonded CDA. The dispersion of the polyester resins in the composites and the heat of fusion and crystallization rate of the polyester resins in the composites as well as fracture cross sections of the composites after impact testing were investigated (Table 3-3-3-1, Figure 3-3-3-2). Adding PLA and PHB as branched monomers was examined to enhance the impact strength of the PAA–bonded CDA. The composite with PLA had a weak impact strength and opaque appearance. Adding PLA to the PAA–bonded CDA formed a weak layered structure in the composites (Figure 3-3-3-2(b)) and PLA was not dispersed in the composite. Moreover, the composite with PHB had relatively high impact strength and a translucent appearance; therefore, the added PHB seemed to disperse relatively well in the composite. However, adding PHB to the PAA–bonded CDA formed a layered structure, as did adding PLA (Figure 3-3-3-2(c)). This result indicated that PHB was not uniformly dispersed in the composite.

The polyester resins with linear monomers (PCL, PBS and PBSA) did not form a layered structure (Figure 3-3-3-2(d), 3-3-3-2(e) and 3-3-3-2(f)). However, the composites with PCL and PBS showed high turbidity, indicating that these resins did not disperse uniformly in the composite, as shown in Table 3-3-3-1. As a result, adding these resins did not increase the impact strength of PAA–bonded CDA. By contrast, PBSA, in which 20 mol % of the succinic acid in PBS was replaced by adipic acid, resulting in lower polarity than PBS, was especially uniformly dispersed; PBSA appeared almost transparent in the PAA–bonded CDA composites, and greatly improved their impact strength.

The heat of fusion of crystallized polyester resins in PAA–bonded CDA composites was examined by DSC analysis. As shown in Table 3-3-3-1, the degree of crystallization of PBS and PCL in the PAA–bonded CDA composites were larger than that of PBSA, and the crystallized parts of these polyesters, which were fragile and were not finely dispersed, did not improve the impact strength. Based on our previous research [18], adding polyether-modified silicones, which were finely dispersed in the PAA–bonded CDA composites, greatly improved impact strength through shearing-induced deformations. Therefore, that the reason why PBSA enhanced the impact strength of the composites compared to the other polyester resins was deduced its compatibility with the PAA-bonded CDA and the high amounts of flexible amorphous PBSA in the PAA–bonded CDA composites. As shown in Figure 3-3-3-3, the highest impact strength was obtained when 30 wt% PBSA was added.

Figure 3-3-3-3 and Table 3-3-3-2 indicate the effect of adding PBSA on the turbidity and heat of fusion of PAA–bonded CDA composites. The addition of more than 30 wt% PBSA to the PAA–bonded CDA composites increased its turbidity and reduced its impact strength. As shown in Table 3-3-3-2, adding large amounts of PBSA tended to crystallize PBSA in the PAA–bonded CDA composites.

Consequently, the crystallized PBSA, which is fragile and not finely dispersed, would reduce the impact strength. That is, the high impact strength of the PAA–bonded CDA composites containing 20–30 wt% PBSA was due to amorphous PBSA, which is flexible and finely dispersed in the composites. In addition, the fracture cross-section of PAA–bonded CDA without PBSA had a flat surface (Figure 3-3-3-2(a)), whereas the fracture cross-section of a composite with 20 wt% PBSA (Figure 3-3-3-2(f)) had a corrugated surface due to shearing-induced deformation caused by the finely dispersed flexible PBSA in the composites. By contrast, the fracture cross-sections of PAA–bonded CDA with PCL and PBS had fewer concavities and convexities than the fracture cross-sections of the composites with PBSA (Figure 3-3-3-2(d) and 3-3-3-2(e)).

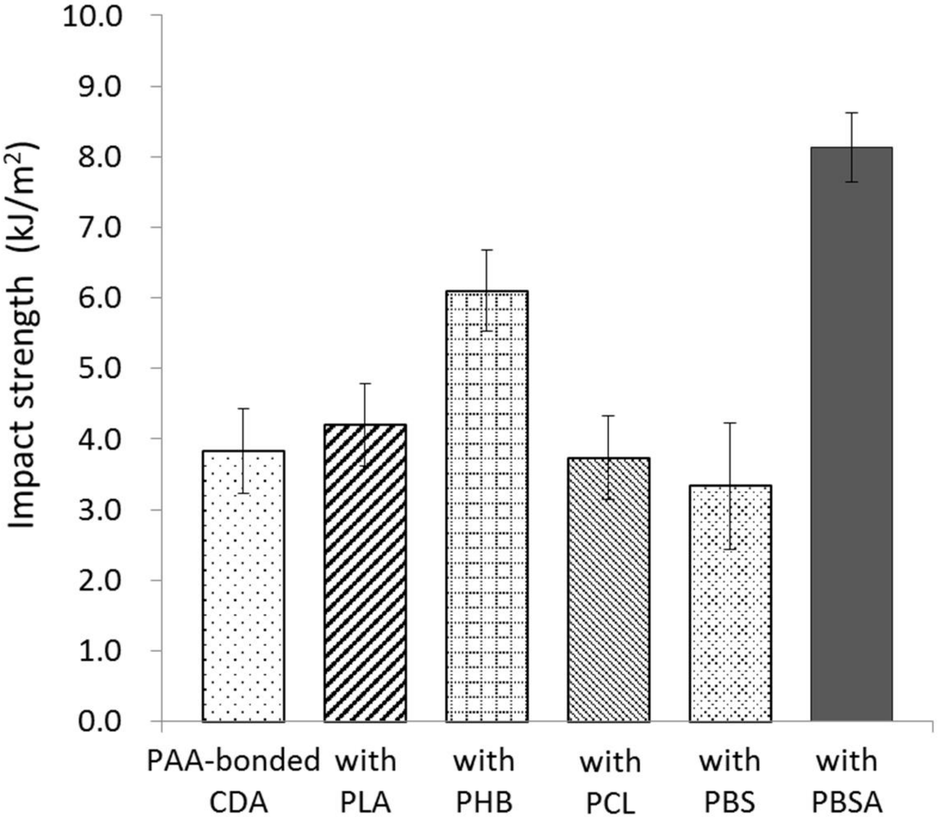


FIGURE 3-3-3-1 Effect of adding 20 wt% polyester resins on impact strength of PAA–bonded CDA composites.

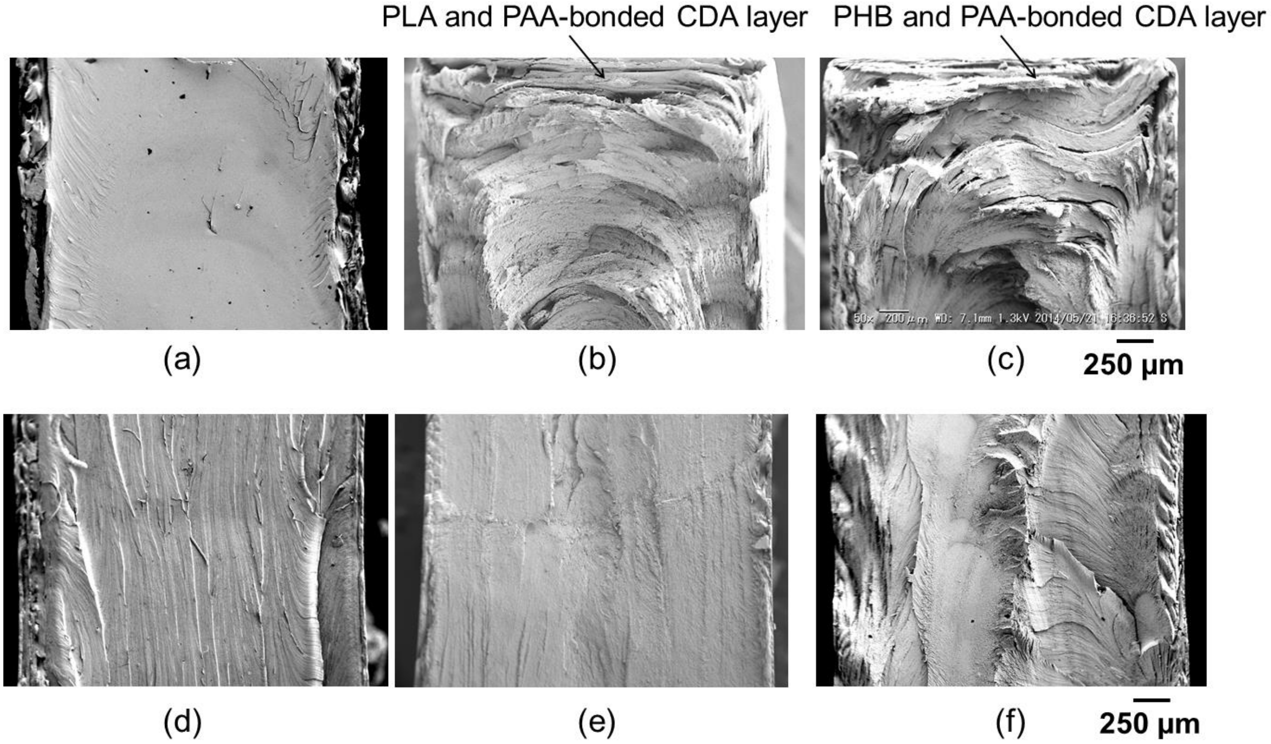
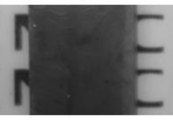
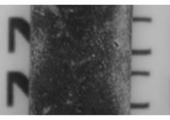
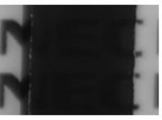
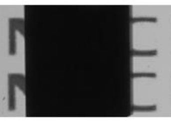
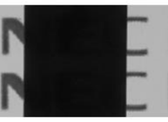
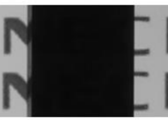


FIGURE 3-3-3-2 Scanning electron microscope images of fracture surfaces of PAA–bonded CDA with 20 wt% polyester resins after impact test: (a) PAA–bonded CDA, (b) with PLA, (c) with PHB, (d) with PCL, (e) with PBS, (f) with PBSA.

TABLE 3-3-3-1 Effect of adding each polyester resin on turbidity and impact strength of PAA-bonded CDA composites and on heat of fusion and crystallization rate of polyester in the composites

	PAA-bonded CDA	PAA-bonded CDA with 20 wt% polyester				
		PLA	PHB	PCL	PBS	PBSA
Appearance						
Transparency						
Turbidity (%)	23	ND*	68	94	89	36
Impact strength (kJ/m^2)	4.0	4.2	6.1	3.6	3.3	8.1
Heat of fusion of polyester (mJ/mg-polyester)	-	-	-	35	32	19
Crystallization rate of polyester (%)	-	-	-	46	59	35

*ND = Not Detected

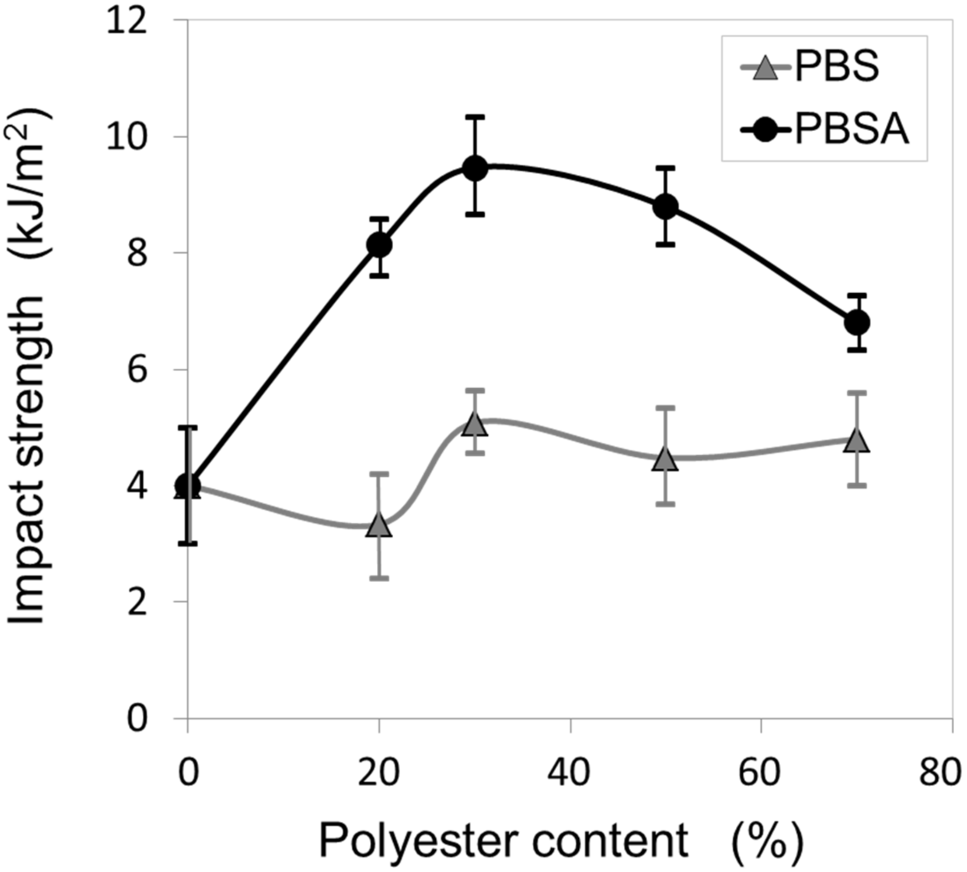
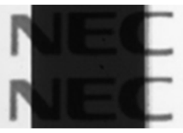


FIGURE 3-3-3-3 Effect of adding PBSA and PBS on impact strength of PAA−bonded CDA composites.

TABLE 3-3-3-2 Effect of adding PBSA on turbidity and impact strength of PAA–bonded CDA composites and on heat of fusion and crystallization rate of PBSA in the composites

	PAA-bonded CDA	PAA-bonded CDA with PBSA (wt %)			
		20	30	50	70
Transparency					
Turbidity (%)	23	36	43	84	99
Impact strength (kJ/m^2)	4.0	8.1	9.5	8.8	6.8
Heat of fusion of PBSA (mJ/mg-PBSA)	-	19	30	41	56
Crystallization rate of PBSA(%)		35	54	73	100

(1) Enhancing bending strength of PAA–bonded CDA composites with PBSA by adding glass fiber

The PAA-bonded CDA composites with PBSA and glass fiber exhibited high bending strength as well as high impact strength. The bending strength of the PAA–bonded CDA composites with highly flexible PBSA was relatively low (Figure 3-3-3-4), but the strength is preferably required to be at least 60 MPa, as mentioned above, when the composites are used in durable products such as electronic devices. Therefore, adding glass fiber was investigated to improve the bending strength of the composites. As shown in Figure 3-3-3-4 and Table 3-3-3-3, the glass fiber–reinforced PAA–bonded CDA composites had higher bending strength and a larger bending modulus than the corresponding composites without glass fiber. Adding 20 wt% glass fiber to the PAA–bonded CDA composite with 30 wt% PBSA increased its impact strength and bending strength. Figure 3-3-3-5 (a) and (b) show scanning electron microscope images of fracture surfaces of PAA–bonded CDA composites containing 10 wt% glass fiber, (a) without PBSA and (b) with PBSA after impact testing. The length of glass fiber withdrawn from the PAA–bonded CDA composite containing only glass fiber was shorter than the length drawn from the composite containing both glass fiber and PBSA. Therefore, the inclusion of PBSA in the composites with glass fiber in particular tended to enhance its impact strength, as the flexibility of PBSA facilitated withdrawal of the glass fiber and suppression of its breaking when the composites were fractured, in addition to shearing-induced deformation of the resin parts. The energy loss caused by pulling out the glass fibers enhanced the impact strength of the composites. Indeed, holes caused by pulling out the glass fibers were observed at the fracture cross–section. Meanwhile, adding the glass fiber to the rigid composites without PBSA hardly enhanced its impact strength, as the glass fibers were easily broken without shearing-induced deformation of the resin parts.

The PAA–bonded CDA composites with PBSA and glass fiber were compared to current representative plastics, including the following: a CDA composite with a plasticizer (TEC); PLA, a mass–produced bioplastic derived from corn starch; Polyamide 11 (PA11), a bioplastic derived from castor beans and used in durable products; and acrylonitrile–butadiene–styrene (ABS), a petroleum–based plastic used in durable products. Table 3-3-3-3 lists the impact strength, water resistance (water absorption), maximum bending strength, and thermoplasticity (melt flow rate) of the PAA–bonded CDA composites with 0–50 wt% PBSA and 0–25 wt% glass fiber, a CDA composite with 29 wt% plasticizer (TEC), PLA, PA11, and ABS. PAA–bonded CDA had lower impact strength than PLA, but the PAA–bonded CDA composites with 20–50 wt% PBSA were significantly stronger than the one with PLA and nearly equal to PA11 and the CDA composite with the plasticizer. The water resistance of the PAA–bonded CDA composites was superior to the water resistance of CDA and the CDA composite with plasticizer. Furthermore, the impact strength and the maximum bending strength of the PAA–bonded CDA composites with 20–50 wt% PBSA and 10–25 wt% glass fiber were higher than for PA11. The thermoplasticity of the PAA–bonded CDA composites was comparable to the thermoplasticity of the CDA composite with the plasticizer and of ABS.

(2) Improving flame retardancy of PAA-bonded CDA composites

The flame retardancy of PAA-bonded CDA composites with PBSA and glass fiber was greatly enhanced by adding aluminum hydroxide, phosphate, and polytetrafluoroethylene (PTFE) as complex flame retardants. As shown by the values listed in Table 3-3-3-4, the PAA-bonded CDA with the flame retardants had high flame retardancy (2.4mmt UL94V-1) but its impact strength was low (2 kJ/m^2). PBSA and glass fiber were therefore included in the composite increased its impact strength and maximum bending strength. As also shown by the values listed in Table 3-3-3-4, the flame-retardant PAA-bonded CDA composites with these flame retardants, PBSA, and glass fiber showed high flame retardancy—up to 2.4mmt UL94V-0—yet still performed good levels of impact and bending strength, water resistance, and thermoplasticity to be used in durable products.

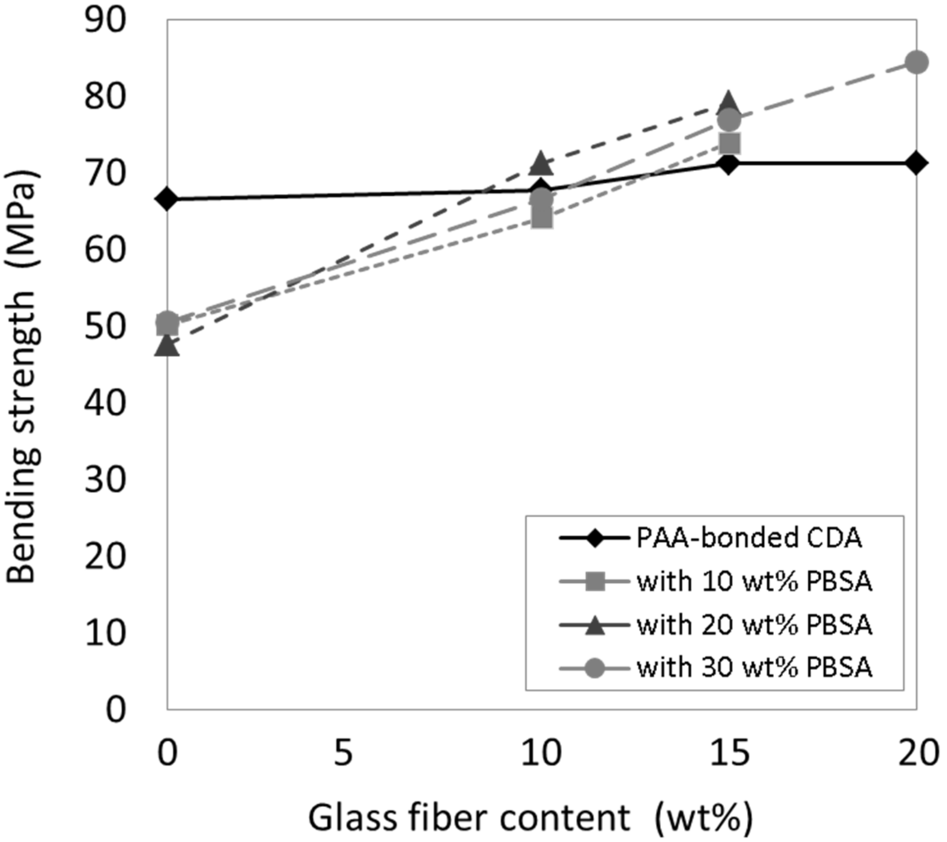


FIGURE 3-3-3-4 Effect of adding glass fiber on bending strength of PAA−bonded CDA composites with PBSA.

TABLE 3-3-3-3 Characteristics of PAA–bonded CDA with PBSA and glass fiber

No.	Sample	Impact strength (kJ/m^2)	Standard deviation of the impact strength	Bending strength (MPa)	Bending modulus (GPa)	MFR 200°C, 500 kgf/m^2 (g/10 min)	Water absorption (%)
1	PAA-bonded CDA	4.0	1.41	67	2.1	1050	0.83
2	No. 1 + glass fibers (90+10)*	6.5	0.39	68	2.8	1030	0.81
3	PAA-bonded CDA composite with 20 wt% PBSA	8.1	0.85	51	1.4	1140	0.81
4	No. 3 + glass fibers (90+10)*	8.0	0.20	71	2.0	1060	0.71
5	PAA-bonded CDA composite with 30 wt% PBSA	9.5	1.67	50	1.2	1200	0.79
6	No. 5 + glass fibers (90+10)*	10.3	1.47	67	1.9	1120	0.69
7	No. 5 + glass fibers (80+20)*	11.2	1.41	85	3.1	1030	0.63
8	PAA-bonded CDA composite with 50 wt% PBSA	7.5	0.57	43	1.0	1200	0.78
9	No. 8 + glass fibers (75+25)*	10.5	0.40	75	2.8	1090	0.62
10	CDA composite with added plasticizer (29 wt%)	8.7	0.54	70	2.7	960	2.7
11	Polylactic acid (PLA)	4.4	0.48	93	4.4	1320	4.4
12	PA11	7.7	2.99	65	1.2	1340	1.2
13	ABS resin	23.5	1.53	78	2.5	1040	2.5

* wt% ratio

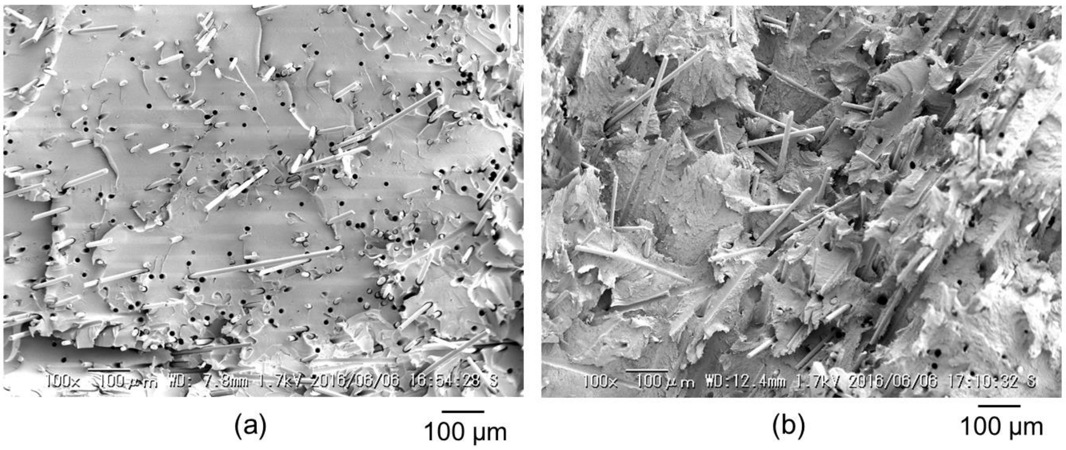


FIGURE 3-3-3-5 Scanning electron microscope images of fracture surfaces of (a) PAA–bonded CDA with 10 wt% glass fiber and (b) PAA–bonded CDA composite with 30 wt% PBSA and 10 wt% glass fiber after impact test.

TABLE 3-3-3-4 Characteristics of PAA-bonded CDA with PBSA, glass fibers and flame retardant (FR)

No.	Sample	UL94V	Impact strength (kJ/m^2)	Standard deviation of the impact strength	Bending strength (MPa)	MFR 200 °C, 500 kgf/m^2 (g/10 min)	Water absorption (%)
1	PAA-bonded CDA	notV-2	4.0	1.41	68	1050	0.83
2	PAA-bonded CDA composite with FR[a]	V-1	2.0	0.14	33	1140	0.58
3	PAA-bonded CDA composite with 10 wt% PBSA + FR[a] + 10 wt% glass fibers	V-1	6.3	0.14	35	1090	0.54
4	PAA-bonded CDA composite with 20 wt% PBSA + FR[a] + 10 wt% glass fibers	V-1	6.8	0.71	39	1170	0.39
5	PAA-bonded CDA composite with 20 wt% PBSA + FR[a] + 15 wt% glass fibers	V-1	7.3	0.42	44	1080	0.42
6	PAA-bonded CDA composite with 30 wt% PBSA + FR[a] + 15 wt% glass fibers	V-1	8.2	1.13	43	1120	0.47
7	PAA-bonded CDA composite with 30 wt% PBSA + FR[a] + 20 wt% glass fibers	V-0	6.8	0.90	47	1120	0.35

[a] 29 wt% aluminum hydroxide,12 wt% phosphorus and 0.5 wt% PTFE

3-4. Conclusion

In the past studies, a modified cardanol-bonded cellulose thermoplastic resin was developed, using inedible plant resources: 3−pentadecylphenoxy acetic acid (PAA)-bonded cellulose diacetate (PAA-bonded CDA), which indicated high practical properties such as bending strength, heat resistance, and water resistance. In contrast, its impact strength and flame retardancy were not sufficient for use in durable products such as electronics. Therefore, in this study, these characteristics were improved by adding specific additives and the mechanisms were investigated

Improvement in the impact strength of PAA-bonded CDA was achieved by using hydrophobic olefin resins such as PE or PP, while satisfying good bending strength and breaking strain, which were due to high affinities of the olefin resins to hydrophobic cardanol side chains of the PAA-bonded CDA. Moreover, the addition of the olefin resins improved water resistance and thermoplasticity of PAA-bonded CDA composite.

Adding polyether silicones to PAA-bonded CDA achieved sufficient impact strength and other good properties such as glass transition temperature (Tg), water resistance and thermoplasticity while suppressing a decrease in bending strength. The polyether silicones with relatively high polarity became highly dispersed in the PAA-bonded CDA composites. The polyether silicones that were optimized in terms of their amount, polarity, and viscosity enhanced the impact strength of the PAA-bonded CDA composites.

Furthermore, to simultaneously achieve the strength properties and flame retardancy of the PAA-bonded CDA composites was investigated. The composites with poly(butylene succinate adipate) (PBSA) had high impact strength, good water resistance and sufficient thermoplasticity (melt flow rate), equivalent to ABS resin. Because flexible amorphous PBSA became highly dispersed in the PAA−bonded CDA composites, the impact strength increased as a result of shearing-induced deformation. Adding glass fiber to the composites prevented a decrease in the maximum bending strength by adding PBSA and enhanced the impact strength by withdrawing the glass fiber when the composites fractured. Moreover, the flame retardancy of the PAA-bonded CDA composites with PBSA and glass fiber was greatly enhanced by adding aluminum hydroxide, phosphate, and polytetrafluoroethylene (PTFE) as complex flame retardants. The composites achieved sufficient practical properties to be used in various parts in electronic devises.

References

1. Anastas P. T., Kirchhoff M. and M. Origins, *Acc Chem Res,* **2002**, 35, 686-694.

2. Li S., Ernst W and Martin P., *Biofuels, Bioproducts and Biorefining*, **2010**, 4, 25–40.

3. Auras R., Harte, B. and Selke, S., *Macromol. Biosci.*, **2004**, 4, 835–864.

4. Heinze T and Liebert T., *Prog. Polym. Sci.*, **2001**, 26, 1689-1762.

5. Sawai D., Nozoe Y., Yoshitani T. and Tsukada Y., *FUJI FILM Research & Development* , **2012**, 57, 55–58.

6. Mohanty A. K., Wibowo A., Misra M. and Drzal, L. T., *Polym. Eng. Sci.*, **2003**, 43, 1151–1161.

7. Park H. M., Misra M., Drzal L. T. and Mohanty A. K., *Biomacromolecules*, **2004**, 5, 2281–2288.

8. Zepnik S., Kesselring A., Kopitzky R. and Michels C., *Bioplastics Magazine*, **2010**, 5, 44–47.

9. Sealey J. E., Samaranayake G., Todd J. G. and Glasser W. G., *J. Polym. Sci.*, **1996**, Part B: Polym. Phys. 34, 1613-1620 (1996).

10. Edgar Kevin J., Pecorini Thomas J. and Glasser Wolfgang G., *American Chemical Society in cellulose*, **1998**, 38-60.

11. Isogai A., Ishizu A. and Nakano J., *J. Appl. Polym. Sci.*, **1986**, 31, 341-352.

12. Roy D., Semsarilar M., Guthrie J. T. and Perrier S., *Chem. Soc. Rev.,* **2009**, 38, 2046-2064.

13. Teramoto Y. and Nishio Y., *Polymer*, **2003**, 44, 2701-2709.

14. Enomoto-Rogers Y., Kamitakahara H., Takano T. and Nakatsubo F., *Biomacromolecules,* **2009**, 10, 2110-2117.

15. Iji M., Moon S. and Tanaka S., Hydrophobic, *Polym. J.*, **2011**, 43, 738–741.

16. Lubi M. C and Thachil E. T., *Designed Monom. Polym.*, **2000**, 3, 2, 123-153.

17. Kiuchi Y., Soyama M., Iji M., Tanaka S. and Toyama K., *J. Appl. Polym. Sci.*, **2014**, 131, 3, 39829.

18. Soyama M., Kiuchi Y., Iji M., Tanaka S. and Toyama K., *J. Appl. Polym. Sci.*, **2014**, 131, 40366.

19. Bucknall C. B. and Smith R. R., *Polymer*, 1965, 6, 437–446.

20. Seo Y., Hwang S. S., Kim U. K., Lee J. and Sung Hong II., *Polymer*, **1996**, 34, 1667–1676.

21. Iji M., Toyama K. and Tanaka S., *Cellulose*, **2013**, 20, 559-569

22. Athene M. D. and Edward J. K., *J Mater Sci*, **1982**, 17, 1765-1772

Chapter 4.

General conclusions

In this thesis, the author presented environmentally friendly technologies of plastic composites for use in electronics. Highly safe flame-retardant technologies without using organic halogen compounds and their application to flame-retardant plastics for the important components in electronics were described. These technologies can enable highly safe treatment of plastic waste and progress toward their reuse for other purposes. Furthermore, bioplastic composites produced from inedible plant sources have been developed for use in electronics. The bioplastic composites can contribute to conserving petroleum resources and reducing the generation of carbon dioxide that contributes to global warming.

In chapter 2, the author described safer flame-retardant technologies of petroleum-derived plastics used in electronics: a polycarbonate resin composite for use in housings and an epoxy resin compound for use in electronic components.

Section 2-1 reported on adding fly ash, a by-product of thermal power plants, that greatly enhances the flame retardancy of polycarbonate; thus, decreasing the amount of energy required to manufacture flame-retardant polycarbonate composites. The flame retardancy of polycarbonate with fly ash results from the hydrogen bond between the hydroxyl group on the fly ash surface and the carbonate group of the polycarbonate. This bond thermally stabilizes the polycarbonate on the fly ash surface; thus, improving its heat resistance. It also isomerizes the polycarbonate and promotes carbonization, which improves flame retardancy. The properties of the polycarbonate composite with fly ash are the same as those of polycarbonate composite with glass fiber, which is used as a housing material for electronics such as desktop computers.

Section 2-2 described the improvement of the flame retardancy and heat resistance of a phenol-biphenylene-type epoxy resin compound for electronic components by adding a benzoguanamine-modified phenol-biphenylene resin. This resin includes a benzoguanamine unit that releases non-flammable substances containing nitrogen compounds during ignition and increases the modified resin's reactivity toward epoxy resins due to its amino group. This resin also includes biphenylene units to help maintain the thermal-degradation and water resistance of the resin.

In chapter 3, the author argued that the impact strength and flame retardancy of a modified cardanol-bonded CDA (PAA-bonded CDA), which is a bioplastic from non-edible plant resources were improved. In previous studies, PAA-bonded CDA indicated high practical properties, such as bending strength, heat resistance, and water resistance but its impact strength was not sufficient for use in electronics. Its impact strength was improved by adding olefin resins, modified silicones, and polyesters after optimizing the structures. The flame retardancy of the PAA-bonded CDA composite with the polyesters was also improved by adding safe complex flame retardants.

Section 3-3-1 described improvement in the impact strength of PAA-bonded CDA through the addition of hydrophobic olefin resins. The addition of olefin resins, such as PE and PP, improved the impact strength, water resistance, and fluidity of PAA-bonded CDA.

As demonstrated in section 3-3-2, by adding polyether silicones, PAA-bonded CDA composites with sufficient impact strength and other important properties such as glass-transition temperature, water resistance, and thermoplasticity, while suppressing a decrease in bending strength were developed. The polyether silicones with relatively high polarity became highly dispersed in the PAA-bonded CDA composites. Adding polyether silicones that were optimized in terms of their amount, polarity, and viscosity enhanced the impact strength and other properties of the PAA-bonded CDA composites.

Section 3-3-3 described that the improvement in impact strength, flame retardancy, and other practical properties such as water resistance and thermoplasticity made PAA-bonded CDA composites applicable to electronics. Compounding PAA-bonded CDA with a polyester (a biopolymer), i.e., PBSA, glass fiber, and complex flame retardants, i.e., aluminum hydroxide and a phosphorus compound, achieved these properties. Since flexible amorphous PBSA became highly dispersed in the PAA-bonded CDA composite, its impact strength was increased as a result of shearing deformation when impacting the composite. Adding glass fiber to the composite suppressed the decrease in the maximum bending strength due to the PBSA and maintained its high impact strength by withdrawing the glass fiber when the composite was fractured. The addition of complex flame retardants resulted in high flame retardancy of the composites with other sufficient properties for use in electronics.

The technologies described in this thesis can offer certain advantages to overcome environmental problems including waste treatment, recycling, petroleum-resource depletion, and carbone dioxide generation, caused by plastic composites currently used in electronics. The author believes that this research will contribute to production of plastic composites with high functionality and environmental friendliness for use in electronics and other durable products and creation of a sustainable society while maintaining the convenience of electronics.

Acknowledgements

The author is deeply grateful to Dr. Masatoshi Iji, professor at Tsukuba University and research fellow of NEC Corporation, for giving the chance to carry out these studies and for his guidance. Also, the author gratefully acknowledges the help of his colleagues, especially Mr. Yukihiro Kiuchi, Mr. Shukichi Tanaka, Dr. Kiyohiko Toyama, and Mrs. Toshie Miyamamoto.

The author would like to express his gratitude to Dr. Junji Nakamura, Dr. Tatsuya Nabeshima, and Dr. Kazuya Saito, and Dr. Yasuhiro Tokura, professors and Dr. Tsuyoshi Yamamoto, associate professor at Tsukuba University for their leading the research in the university and critical reading of this thesis. Also, the author thanks to Dr. Tsuyoshi Nakamura of NEC Corporation for his critical reading of this thesis.

List of Author's Published Papers

1. Makoto Soyama and Masatoshi Iji, "Improving mechanical properties of cardanol−bonded cellulose diacetate composites by adding polyester resins and glass fiber", Polymer Journal, doi:10.1038/pj.2017.10
2. Kiyohiko Toyama, Makoto Soyama, Shukichi Tanaka, Masatoshi Iji," Development of cardanol-bonded cellulose thermoplastics: high productivity achieved in two-step heterogeneous process, Cellulose 22(3):1625-1639 (2015).DOI: 10.1007/s10570-015- 0601-7
3. Makoto Soyama, Yukihiro Kiuchi, Masatoshi Iji, Shukichi Tanaka, Kiyohiko Toyama, "Improvement in impact strength of modified cardanol-bonded cellulose thermoplastic resin by adding modified silicones", Journal of Applied Polymer Science, vol. 131, Issue 12, Article first published online 15 June 2014 (DOI: 10.1002/app.40366) (2014)
4. Yukihiro Kiuchi, Makoto Soyama, Masatoshi Iji, Shukichi Tanaka, Kiyohiko Toyama "Improvement in Impact Strength of Modified Cardanol-Bonded Cellulose Thermoplastic Resin by Using Olefin Resins", Journal of Applied Polymer Science, vol. 131, Issue 3, Article first published online: 26 AUG 2013 (DOI: 10.1002/app.39829) (2013)
5. Makoto Soyama, Kazuhiko Inoue, Masatoshi Iji," Flame Retardancy of Polycarbonate Enhanced by Adding Fly Ash", Polymers for Advanced Technologies, 18, 5, 386-391 (2007).
6. Masatoshi Iji, Yukihiro Kiuchi, and Makoto Soyama, "Flame Retardancy and Heat Resistance of Phenol-Biphenylene-Type Epoxy Resin Compound Modified with Benzoguanamine", Polymers for Advanced Technologies, 14, 9,638-644 (2003).
7. Takayuki Watanabe, Makoto Soyama, Atsushi Kanzawa, Akihiro Takeuchi, Mamoru Koike, "Reduction and separation of silica-alumina mixture with argon–hydrogen thermal plasmas", Thin Solid Films 05/1999; 345 (1):161-166.DOI:10.1016/S0040-6090(99)00071-1