Synthesis of poly[(methyl methacrylate)-*co*-acrylamide] modified by titanium-triisopropoxide and their thermal stability

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Abstract

Poly[(methyl methacrylate)-*co*-acrylamide] of various compositions were previously prepared by the radical copolymerization reaction of methyl methacrylate and the acrylamide monomer in a solvent. The copolymers were modified through a resonating salt by the addition reaction of a chlorotitanium-triisopropoxide; the modified resins are called Ti hybrid copolymers. The chemical structure of acrylamide side chain groups in the Ti hybrid copolymers was confirmed by the ash weight after combustion, the characteristic absorption band determined by Fourier transform infrared spectrophotometry (IR) and elementary analysis (EA). The curing temperature and time of the resins were determined from the change in the insoluble resin weight when the extraction was done with a mixture of acetone and methanol using the curing resin samples. The thermal stability of the Ti hybrid copolymers was evaluated using both the thermal-degradation temperature (T_x) measured by thermogravimetric analysis and the thermal degradation at 130 °C for 720 h. The cured resins improved the weight loss of the resins at the T_x, and exhibited a high thermal stability. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Methacrylic hybrid copolymer; Amide–titanium-triisopropoxide group; N–Ti bond

1. Introduction

Among the various former types of thermosetting acrylic coating resins (called thermosetting methacrylic coating resins), a self-thermosetting methacrylic coating resin is prepared by the addition reaction of formaldehyde with the terpolymer of ethyl acrylate, styrene and acrylamide [1–3]. This methacrylic coating resin has been employed as a high quality baked-finish coating because it has excellent surface hardness, scratch resistance, chemical stability and weather resistance.

Although the methacrylic coating resin has the aforementioned excellent properties, the resin had the following problems. The curing temperature and time of this coating resin are required to be higher than 170 °C and 30 min, respectively. An essential condition of the heat curing treatment for this resin is the greater energy expenditure than for the treatment of a melamine-alkyd type coating resin which is used for various coatings and is cured at 150 °C for 10 min. The thermal stability of this methacrylic resin coat-

ing film has better properties than a melamine-alkyd type resin, however, it begins to deteriorate when it is used in rigorous temperature situations of 80 °C or over. For example, it has been applied to the outside wall of a heating apparatus. Accordingly, an improved thermal stability was required for this use. Furthermore, the self-thermosetting methacrylic resin polluted the working atmosphere as it produced formaldehyde and by-products during the coating process and heat curing treatment.

On the other hand, Yano et al. [4] have prepared a methacrylic resin (Si hybrid resin) which has a triethoxysilane compound as the curing component. The Si hybrid resin, which has an improved thermal stability, does not produce formaldehyde during the coating process and heat curing treatment [5–7]. It is possible to carry out the curing process at less than 150 °C when curing accelerators such as hydrochloric acid and water are added to the Si hybrid resin [8]. When this Si hybrid resin along with the curing accelerator is applied to the outside wall of heating equipment, an after-cure occurs, and a discoloration and degradation of the cured coating film develops as the curing accelerator remains in the coating film.

Schmidt [9,10] has proposed a synthetic resin as a coating using an interrupted polycondensation reaction of $(RO)_3Si(CH_2)_3OCH_2CHCH_2O$, $Si(OR)_4$ and $Ti(OR)_4$ which

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decreases the curing temperature to 150 °C; the OR in the structural formula indicates an alkoxy group.

An objective of this study is to develop a formaldehydeless self-thermosetting methacrylic resin with an improved thermal stability using an alkoxytitanium compound as the curing component, and the methacrylic resin makes it possible to cure at a temperature lower than 150 °C in the absence of the curing accelerators. At first, various base copolymers were prepared by changing the molar ratios of methyl methacrylate and acrylamide monomer using a radical polymerization method in the solvents. The self-thermosetting methacrylic resins were synthesized through the formation of a resonating salt by the addition reaction of the chlorotitanium-triisopropoxide compounds with the amide groups of the base copolymers (called Ti hybrid copolymers). The curing temperature and thermal stability of the Ti hybrid copolymers were investigated by comparing them with the former type of methacrylic resins which were prepared by the addition reaction of the base copolymers with formalin. We now report the excellent characteristics of the synthesized Ti hybrid copolymer coating films.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA; 99%, Nakalai Tesque, Inc.) was distilled before use. Acrylamide (AAm; 99%, Nakalai Tesque) was dissolved in methanol, and recrystallized twice from xylene and then dried under vacuum. Chlorotitanium-triisopropoxide [ClTi(isoOC$_3$H$_7$)$_3$; 95%, Aldrich Co.] was used without purification.

Tetrahydrofuran (THF; 99%) and methanol were distilled and used as the copolymerization solvent. Dimethylformamide (DMF), 1-butanol, acetone and hexane (Nakalai Tesque) were distilled and dehydrated on silica gel. These solvents were used for the purification and cleaning of the resins.

Benzoyl peroxide (BPO; Kanto Chemical Co.) was dissolved in xylene, and recrystallized from methanol and then dried in vacuo. Triethylamine (99%, Nakalai Tesque)

was dehydrated with A-4 molecular sieves, and then used for the neutralization of the resonating salt. Formalin (37 wt% in water, Nakalai Tesque) was used for the preparation of the reference thermosetting resins.

2.2. Preparation of base copolymers

According to the blending ratios shown in Table 1, the base copolymers with various compositions were prepared using a free radical copolymerization technique in a mixed solvent of THF and methanol (monomer concentration: 30 wt%). For example, MMA (80.0 g, 80 mol%), AAm (14.2 g, 20 mol%), BPO (0.28 g), THF (146.5 g) and methanol (73.3 g) were simultaneously charged into a three-necked flask (1000 ml). The mixture was then agitated in the refluxed state for 3 h in dry nitrogen gas. BPO (0.14 g) was then added to the reaction mixture, and the copolymerization was continued for 12 h under the same conditions.

An excess amount of methanol was poured into the reaction mixture to separate the base copolymer. The precipitated resin was collected by filtration. The collected resin was washed three times with methanol (50 °C), and then dried at room temperature for 48 h in vacuo to obtain the base copolymer 20 (the number 20 indicates that AAm composition during the polymerization is 20 mol%). The yield of the base copolymer 20 was 65.8 g (69.9 wt% by weight of the initial composition). The blending ratios of the initial materials to prepare the other base copolymers and the yields of the base copolymers are summarized in Table 1.

The content of AAm (mol%) in the base copolymer 20 was determined by the following method. About 2 g of the base copolymer 20 was dissolved in THF (50 g). Methanol (50 g), potassium hydroxide (KOH = 2.5 g) and water (50 g) were added to the base copolymer 20 solution. This mixed solution was then refluxed for 4 h to convert the amide groups of AAm to carboxyl groups. The reaction solution was cooled to room temperature, and the solution was weakly acidified with an aqueous solution of sulfuric acid. The resin was separated from the solution with hexane, and dried after washing. The dried resin (1.00 g) was dissolved in the mixed solvent of THF, CH$_3$OH and H$_2$O (weight ratio = 1:1:0.5), and the solution was titrated with a

Table 1
Initial compositions and characteristics of various base copolymers

Experimental samples	MMA (g/mol%)	AAm (g/mol%)	BPO		Yield (wt%)	AAm[a] (mol%)	Molecular weights		$T_{x\text{-Base}}$[b] (°C)
			Initial (g)	After 3 h (g)			M_w	M_n	
Base copolymer 10	90.0/90	7.1/10	0.29	0.15	71.8	8.0	97,600	55,600	244
Base copolymer 15	85.0/85	10.7/15	0.29	0.15	71.0	11.0	–	–	245
Base copolymer 20	80.0/80	14.2/20	0.28	0.14	69.9	15.0	79,400	44,300	250
Base copolymer 25	75.0/75	17.8/25	0.28	0.14	65.4	20.0	–	–	252
Base copolymer 30	70.0/70	21.3/30	0.27	0.14	65.3	26.0	64,100	36,100	254
Base copolymer 35	65.0/65	24.9/35	0.27	0.14	64.2	30.0	–	–	255

[a] AAm content in the base copolymers.
[b] Decomposition temperature of the base copolymers.

methanol solution of 1N KOH (using phenolphthalein as the indicator), and the base copolymer 20s titer was obtained. It was suspicious that the base copolymer 20s titer contained both a conversed carboxylic acid value from AAm and that from MMA unit. Therefore, AAm (mol%) was obtained by the following method. The blank titration value by the reference PMMA was measured. The base copolymer 20s titer minus the blank titration value is the net AAms titer. AAm (mol%) was calculated using the net AAms titer. AAm (mol%) contents of the other base copolymers are shown in Table 1.

The weight-average molecular weight (M_w) and number-average molecular weight (M_n) of the base copolymer 20 were measured as the polystyrene conversion molecular weight by gel permeation chromatography (GPC; Chromatopac C-R4 A, Shimadzu Co.) with THF as the eluent. The obtained results are 79,400 (M_w) and 44,300 (M_n). The M_w and M_n of the other base copolymers are shown in Table 1.

The thermal degradation temperature ($T_{x\text{-Base}}$) of the base copolymer 20 was measured by thermogravimetric analysis (TGA, TG/DSC-6200; Seiko Instruments) in the temperature range 50–450 °C at the heating rate of 10 °C/min in air. The temperature at which the resin began to decompose by heating was adopted as the T_x value. The result was 250 °C. The $T_{x\text{-Base}}$ of the other base copolymers are shown in Table 1.

2.3. Synthesis of poly[(methyl methacrylate)-co-acrylamide] modified by titanium-triisopropoxide as side groups (Ti hybrid copolymers)

It is known that a resonating salt is produced by reacting hydrochloric acid (HCl) with the C=O of the amide group in a dehydrated solvent as like THF, xylene, DMF or acetone (Scheme A1) [11,12]. The Ti hybrid copolymers were synthesized through the formed resonating salt by the addition reaction of ClTi(isoOC$_3$H$_7$)$_3$ with amide groups in the base copolymers.

The base copolymer 20 (40.0 g), acetone (100 g) and DMF (100 g) were charged in a three-neck flask (1000 ml) to prepare the base copolymer 20 solution. The amount of ClTi(isoOC$_3$H$_7$)$_3$ (39.9 g), which corresponded to 2.2 mol relative to 1 mol of the amide content of the base copolymer 20, was mixed with acetone (50 g), the mixture was charged in the flask, and then it was agitated at room temperature for 20 min. The reaction solution was next poured into a beaker, and hexane was added to separate the resin. The separated resin is insoluble in acetone. The resin was cut into flaky pieces in acetone, and then repeatedly washed with acetone until no cloudiness appeared due to the insoluble ClTi(isoOC$_3$H$_7$)$_3$. Since the possibility of a by-product was expected from the radical copolymerization, the washed resin was immersed in acetone for the elimination of the soluble matter at room temperature for 1 h.

The purified flaky resin was removed from acetone, and dissolved in the mixed solvent of DMF and acetone (weight ratio = 1:1) to prepare resin solution (about 7 wt%). Triethylamine dissolved in the mixed solvent of DMF and acetone (weight ratio = 1:1) was then gradually added to the resin solution to adjust the pH to 6. The viscosity of the solution was increased with the extent of neutralization, and the solution had a jellified state at the end of the neutralization because the resin became insoluble in the mixed solvent during this process. The jellified state resins were washed by decantation using acetone in order to remove triethylamine hydrochloric acid salt. The separated resin was dissolved in the mixed solvent of methanol, 1-butanol, acetone and xylene (weight ratio = 1:1:1:1) to prepare a solution of the resin (15 wt%). The yield of the resin was determined after it was dried in vacuo, and the yield was 49.5 g (63.5 wt%). The amounts of ClTi(isoOC$_3$H$_7$)$_3$ used for the preparation of the other Ti hybrid copolymers and the yields of the synthesized resins are summarized in Table 2.

In order to estimate the composition of the side groups in the synthesized Ti hybrid copolymer 20, the amount of

Table 2
Initial compositions, yields and characteristics of the Ti hybrid copolymers (AAm in the base copolymers and ClTi(isoOC$_3$H$_7$)$_3$, 1.0/2.2 mol ratio)

Experimental samples	Base copolymer weights[a] (g)	ClTi(isoOC$_3$H$_7$)$_3$ weights[a] (g)	Yields[b] (g/wt%)	Ash weights[c] (g)	AAm–Ti(isoOC$_3$H$_7$)$_3$ calculated from ash weight[d] (mol%)	AAm–Ti(isoOC$_3$H$_7$)$_3$/ AAm (mol ratio)
Ti hybrid copolymer 10	40.0	20.8	38.6/64.5	0.069	10.4	1.30/1.00
Ti hybrid copolymer 15	40.0	28.8	43.5/64.5	0.078	12.1	1.10/1.00
Ti hybrid copolymer 20	40.0	39.9	49.5/63.5	0.089	14.2	0.95/1.00
Ti hybrid copolymer 25	40.0	54.0	55.1/60.4	0.112	19.3	0.97/1.00
Ti hybrid copolymer 30	40.0	71.6	62.3/57.7	0.131	24.1	0.93/1.00
Ti hybrid copolymer 35	40.0	83.6	66.0/55.2	0.139	26.4	0.88/1.00

[a] Initial compositions for syntheses of the Ti hybrid copolymers.
[b] Yields of nonvolatile matter.
[c] Ash weights of the Ti hybrid copolymers 1.00 g.
[d] Calculated by the following equations: (1) weight of AAm–Ti(isoOC$_3$H$_7$)$_3$ in the Ti hybrid copolymers 1.00 g = [molecular weight of AAm–Ti(isoOC$_3$H$_7$)$_3$] × (ash weight)/(molecular weight of TiO$_2$) = 295.5 × ash weight/79.9 = 3.698 × ash weight. (2) Weight of MMA in the Ti hybrid copolymers 1.00 g = 1.00 − (3.698 × ash weight). (3) Molecular weight of AAm–Ti(isoOC$_3$H$_7$)$_3$ = (3.698 × ash weight)/295.5. (4) Molecular weight of MMA = 1.00 − (3.698 × ash weight)/molecular weight of MMA = [1.00 − (3.698 × ash weight)]/100. mol% of AAm–Ti(isoOC$_3$H$_7$)$_3$ = {(3)/[(3) + (4)]} × 100.

Table 3
Initial compositions, yields and characteristics of the Ti hybrid copolymers (AAm in the base copolymers and ClTi(isoOC$_3$H$_7$)$_3$, 1.0/1.1 mol ratio)

Experimental samples	Base copolymer weights[a] (g)	ClTi(isoOC$_3$H$_7$)$_3$ weights[a] (g)	Yields[b] (g/wt%)	Ash weights (g)	AAm−Ti(isoOC$_3$H$_7$)$_3$ calculated from ash weight[c] (mol%)	AAm−Ti(isoOC$_3$H$_7$)$_3$/ AAm (mol ratio)
Ti hybrid copolymer 10	40.0	10.4	38.1/76.4	0.068	10.2	1.27/1.00
Ti hybrid copolymer 15	40.0	14.3	43.9/81.8	0.080	12.5	1.14/1.00
Ti hybrid copolymer 20	40.0	20.0	49.0/83.1	0.090	14.4	0.96/1.00
Ti hybrid copolymer 25	40.0	27.1	56.9/86.6	0.120	21.3	1.07/1.00
Ti hybrid copolymer 30	40.0	35.8	61.9/83.6	0.130	23.9	0.92/1.00
Ti hybrid copolymer 35	40.0	39.5	65.7/88.4	0.137	25.8	0.86/1.00

[a] Initial compositions for syntheses of the Ti hybrid copolymers.
[b] Yields of nonvolatile matter.
[c] Calculated by the following equations: (1) weight of AAm−Ti(isoOC$_3$H$_7$)$_3$ in the Ti hybrid copolymers 1.00 g = [molecular weight of AAm−Ti(isoOC$_3$H$_7$)$_3$] × (ash weight)/(molecular weight of TiO$_2$) = 295.5 × ash weight/79.9 = 3.698 × ash weight. (2) Weight of MMA in the Ti hybrid copolymers 1.00 g = 1.00 − (3.698 × ash weight). (3) Molecular weight of AAm−Ti(isoOC$_3$H$_7$)$_3$ = (3.698 × ash weight)/295.5. (4) Molecular weight of MMA = 1.00 − (3.698 × ash weight)/molecular weight of MMA = [1.00 − (3.698 × ash weight)]/100. mol% of AAm−Ti(isoOC$_3$H$_7$)$_3$ = {(3)/ [(3) + (4)]} × 100.

Ti(isoOC$_3$H$_7$)$_3$ that reacted with the amide groups of the base copolymer 20 was confirmed by the following method. A part of the synthesized resin solution was dried in vacuo. A dried sample of the resin (1.00 g) was combusted at the base on the assumption that the incombustible matter in the hybrid copolymer 20 remained in a porcelain crucible at 800 °C for 30 min was TiO$_2$ (ash). The amount of the AAm−Ti(isoOC$_3$H$_7$)$_3$, which was the product of the reaction of ClTi(isoOC$_3$H$_7$)$_3$ with the AAm in the base copolymer 20, was determined using the obtained result by measuring the weight of the ash, and the result was 14.2 mol% as AAm−Ti(isoOC$_3$H$_7$)$_3$. The amounts of AAm−Ti(isoOC$_3$H$_7$)$_3$ for the other Ti hybrid copolymers are summarized in Table 2. It was confirmed that the AAm−Ti(isoOC$_3$H$_7$)$_3$ in the Ti hybrid copolymer 20 and AAm (15.0 mol%) in the base copolymer 20 was approximately 1:1 (mol ratio).

Although 1.1 mol of ClTi(isoOC$_3$H$_7$)$_3$ reacted with 1 mol of AAm in the base copolymers during the process of synthesizing the Ti hybrid copolymers, the amount of ClTi(isoOC$_3$H$_7$)$_3$ added to AAm was also controlled to 1 mol as shown in the last column of Table 3.

When a ClTi(isoOC$_3$H$_7$)$_3$ reacts with a hydrogen from the amide group of AAm in a solvent without an active hydrogen such as THF, acetone, DMF or xylene, the produced HCl attacks an oxygen in the amide group, and formed a resonating structure (salt). The salt has the chemical structure shown in Scheme 1(a). The formation of a salt is based on the same concept as Scheme A1.

Judging from the results in Tables 2 and 3, it is assumed that the formation of the salt hinders the addition reaction of more than 1 mol of ClTi(isoOC$_3$H$_7$)$_3$ with respect to the amide of AAm.

A DMF solution of the resonating salt has a pH of about 5. It is confirmed that when a liquid with an active hydrogen, such as an alcohol, water, amine or the like is mixed with the resonating salt solution, the salt is immediately decomposed and exhibits a strongly acidic pH. Therefore, the resonating

resin salt was treated with diethylamine to exclude HCl for the synthesis of the Ti hybrid copolymers. The Ti hybrid copolymers were dissolved in THF, acetone, DMF and xylene containing methanol.

To test the possibility of a reaction of ClTi(isoOC$_3$H$_7$)$_3$ with the ester groups, we tried the following experiment. The resonating salt in a DMF solution was decomposed with the addition of methanol, which was purified by dissolving in acetone and then separated it from methanol. The original structure of the base copolymer 20 was conformed by IR and ^{1}H NMR of the thus purified resin, and also a titer with 1N KOH indicated nearly zero (no acid). The combustion product of the resin was emptied in the crucible (no ash). As a result, the reaction of the mutual MMA unit and ClTi(isoOC$_3$H$_7$)$_3$ was not
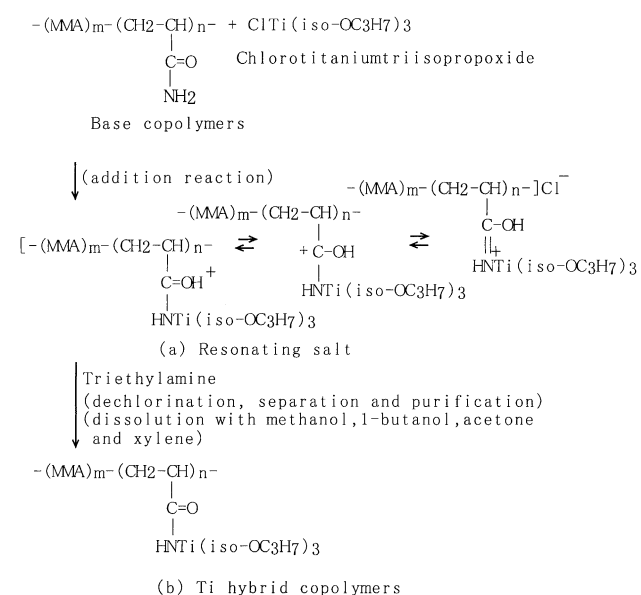
Scheme 1. Synthesis process of the Ti hybrid polymers.

confirmed to occur under the experimental conditions in this study.

2.4. Preparation of the reference thermosetting resin

The former type of thermosetting methacrylic resin (called R-copolymer) in which formaldehyde reacted with the amide groups of the base copolymers was used as the resin for evaluating the heat curing sensitivity and thermal stability of the Ti hybrid copolymers. The R-copolymers were prepared by the following method. The base copolymer 20 (10 g) and acetone (53 g) were simultaneously charged into a flask (500 ml). The former then dissolved in acetone. Methanol (53 g), 1-butanol (53 g), KOH (0.1 g), H_2O (10 g) and formalin (7.0 g) were added to the solution, and the mixture was maintained with agitation at 55 °C for 1 h. The pH of the reaction mixture was adjusted to about 5 using H_2SO_4, and the reaction mixture was then refluxed with agitation for 2 h. After xylene (25 g) was added to the reaction mixture, the mixture was concentrated to 30 wt%. According to the above preparation method, the R-copolymer 10 and R-copolymer 30 were prepared with the base copolymer 10 (10 g) and formalin (3.0 g), and base copolymer 30 (10 g) and formalin (12.0 g), respectively.

2.5. Polymer characterization

PMMA was used to obtain the IR difference spectra of the Ti hybrid copolymers using a Fourier transform infrared spectrophotometer (IR; FT/IR-550, JASCO). PMMA was prepared by the free radical copolymerization method. The mixture of MMA (100.0 g), BPO (0.30 g) and THF (233.3 g) was charged in a flask (1000 ml), and maintained at 75 °C for 24 h under a dry nitrogen gas. The reaction mixture was then poured into an excess amount of methanol to separate the resin. The separated resin was washed with methanol and then dried. The yield of the obtained PMMA was 99.8 wt%. M_w and M_n were 109,000 and 56,500, respectively.

The PMMA, the R-copolymers, the base copolymers and the Ti hybrid copolymers were dissolved in a mixed solution of methanol, 1-butanol, acetone and xylene (weight ratio = 1:1:1:1) to prepare a 15 wt% resin solution. The resin solutions were coated on a glass plate to prepare a film with a thickness of 25–30 μm, and then dried in vacuo. Samples for measuring the IR spectra included the films dried in vacuo and the film heat-cured with these resins that were heated at 100, 120, 140 and 180 °C for 10 min in the oven.

KBr tablets for measuring the IR spectra were prepared by the following method. The KBr (0.5 g) and the resin film (0.01 g) were weighed and then ground in an agate mortar to obtain the mixed powder. The mixed powder (0.06 g) was compressed at a pressure of 500 kg/cm^2 to prepare the tablet (diameter = 10 mm, thickness = 0.25 mm). The IR spectra of the KBr tablets were measured in the range of 400–4000 cm^{-1}.

The resin samples for the extraction test using a mixture of acetone and methanol were cured with the dried resin films in vacuo under the following conditions. The curing temperatures were 100, 120, 140 and 180 °C and the curing times were 10, 20 and 30 min for each temperature. The conditions for the extraction test was immersed in the mixed solvent of acetone and methanol for 240 h at room temperature, and the insoluble resin was weighed after drying for estimation of the curing sensitivity.

The elementary analysis (EA) of N, and Ti in the resins was determined using auto elementary analysis equipment (Vario; Elemental Co.) with helium gas as the carrier and inductively coupled plasma emission spectrometry (ICP) (Jalel Asch Japan Co.). The purified resin samples for EA were dried in vacuo, and then used.

The T_x of the resins was determined by TGA and differential thermal analysis (DTA) (TGA/DSC-6200; Seiko Instruments). The TGA and DTA were measured using the resin films dried in vacuo and the cured films which were heated at 140 °C for 10 min on the Ti hybrid copolymers and at 170 °C for 10 min on the former type resins. The T_x and DTA were measured under the conditions stated in Section 2.2. The thermal stability of the various polymers were evaluated by both the weight loss when heated to the T_x and IR spectra results of the thermal degradation test using the cured resins, which were held in an oven at 130 °C for 720 h. The temperature in the oven was determined by the resin soft temperature (T_s) from the double differential scanning calorimeter (DDSC) when the resin samples were heated at 50–200 °C under nitrogen gas.

3. Results and discussion

3.1. Characterization of the Ti hybrid copolymers

Fig. 1(a)–(c) shows the IR spectra of the PMMA, base copolymer 20 and Ti hybrid copolymer 20, respectively. To confirm the chemical structure of the copolymers shown in Scheme 1(b), the IR difference spectra of the base copolymer 20 (Fig. 2(a)) and the Ti hybrid copolymer 20 (Fig. 2(b)) were obtained by subtracting the IR spectrum of Fig. 1(a) from Fig. 1(b) and (c).

The characteristics of the IR spectra bands in Fig. 2 were identified only by comparing its IR spectra with those of the analog reference standardized data.

Fig. 2(b), which is the AAm–Ti(isoOC$_3$H$_7$)$_3$ component of the Ti hybrid copolymer 20, has a mono-substitution amide group bonded with a triisopropoxytitanium [–CO–NH–Ti(isoOC$_3$H$_7$)$_3$]. From the analysis of the IR spectra peaks in Fig. 2(a), which are due to –CO–NH$_2$, these peaks were checked by superposing each reference absorption band of –CO–NH– and –CO–N< in order to gain confidence in the –CO–NH$_2$ peak assignment, and were only selected based on the absorption bands without mutually overlapping peaks. Moreover, the absorption
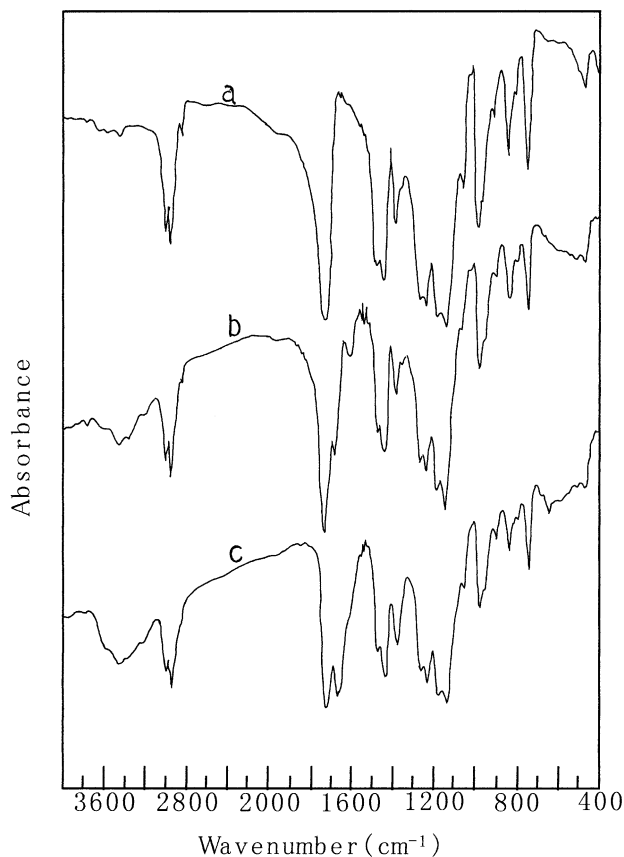
Fig. 1. IR spectrum of (a) poly(methyl methacrylate), (b) base copolymer 20, and (c) Ti hybrid copolymer 20.
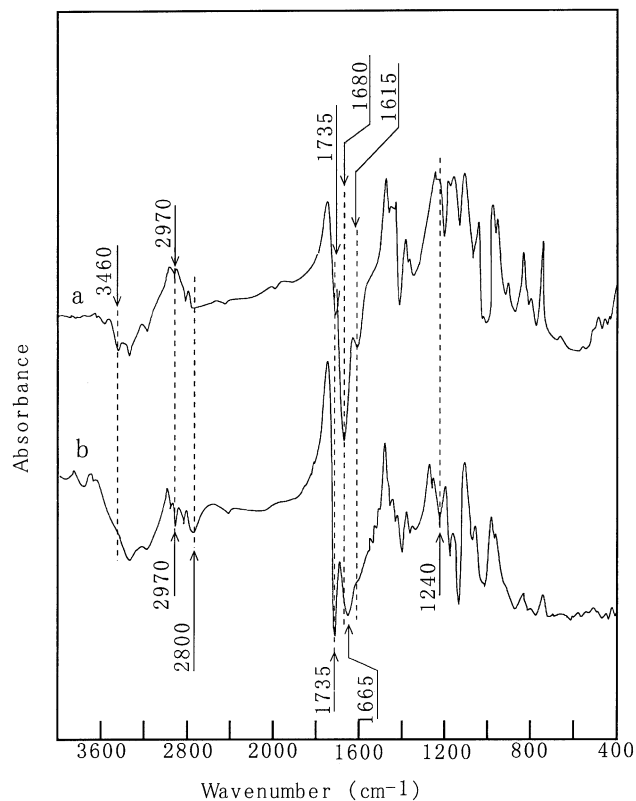

Fig. 2. IR difference spectrum between (a) poly(methyl methacrylate) and base copolymer 20, (b) poly(methyl methacrylate) and Ti hybrid copolymer 20.

bands of CH and CO in AAm were determined using the reference data. The absorption bands at 1615, 1680 and 3460 cm^{-1} in Fig. 2(a) are attributable to the amide groups (–CO–NH$_2$) of the AAm. The absorption bands at 1735 and 2970 cm^{-1} in Fig. 2(a) are attributable to the CO and CH of the AAm, respectively. The IR absorption bands attributable to the –CO–NH$_2$ disappeared in Fig. 2(b) and the IR spectra peaks that newly appeared in Fig. 2(b) were checked. The absorption bands of CO and CH still remained in Fig. 2(b), and the absorption band at 1665 cm^{-1} is attributable to the –CO–NH– component, moreover, the absorption band at 1240 cm^{-1} is attributable to a component of –Ti(isoOC$_3$H$_7$)$_3$ observed in Fig. 2(b). The bond of triiso-propoxytitanium and AAm in the Ti hybrid copolymer 20 could be determined by the presence of these peaks.

The elemental molar ratio of N and Ti in the Ti hybrid copolymer 20 was 0.11 (1.6 wt%) and 0.12 (5.6 wt%), respectively. The same ratio of Ti hybrid copolymer 10 was 0.06 and 0.08, and those of the Ti hybrid copolymer 30 were 0.17 and 0.18. From these results, the ratios of N and Ti showed approximately 1:1. The chemical structure for the side group of the Ti hybrid copolymer 20 is shown in Scheme 1(b). The NMR data were not obtained because the purified Ti hybrid copolymers was insoluble in the NMR solvent.

3.2. Curing temperature of the Ti hybrid copolymers

When the Ti hybrid copolymer 20 film sample dried in vacuo was heated at temperatures higher than 140 °C with a heating time of still 10 min, the peak strength of the IR absorption band at 1665 cm^{-1} in Fig. 2(b) only decreased. This result is shown in Fig. 3.

This phenomenon changed to a decreased state of IR spectrum strength at 1655 cm^{-1} in Fig. 3 by heating which was indicated to be shifted during the curing stage of the resins, and the heated resins were already insoluble in the mixture solvent of acetone and methanol.

This phenomenon was presumed to be a result of the condensation reaction of a hydrogen in the amide group with an isopropoxide in the –CO–NH–Ti(isoOC$_3$H$_7$)$_3$ group by heating as shown in Scheme 2.

Thus, in order to understand the relationship between the decreased state of the IR spectrum strength at 1655 cm^{-1} in Fig. 3 and the lower limit of the heat curing temperature and time which occurred with the cured stage resins, the Ti hybrid copolymer samples were examined based on the measured weight of the insoluble resins by the extraction with a mixed solvent of acetone and methanol using the following resin samples and R-copolymers for reference, and thus their curing temperature and time were determined.
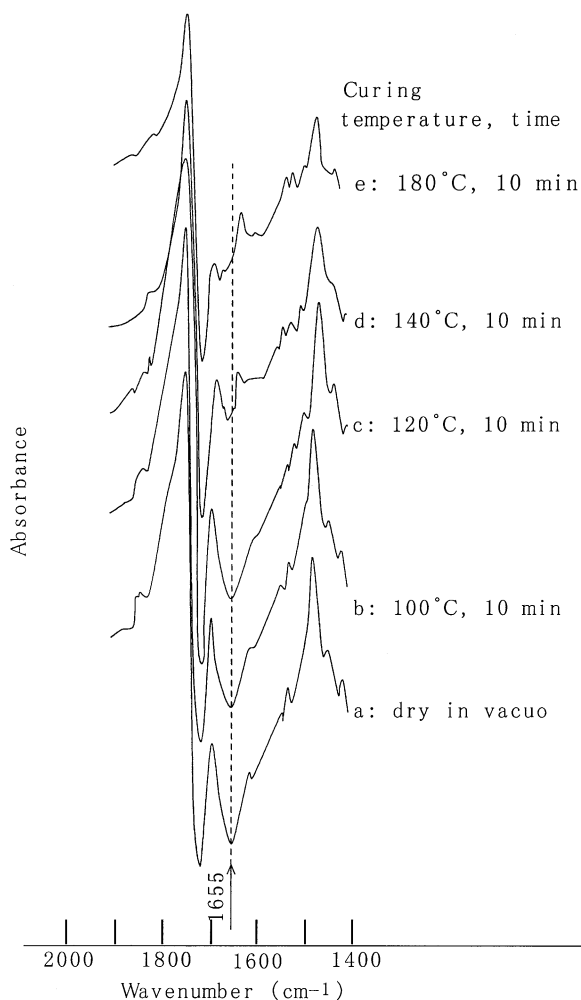
Fig. 3. IR difference spectra strength at 1655 cm^{-1} of the Ti hybrid copolymer 20 as the curing temperature changed.

The resin samples of the Ti hybrid copolymers 10, 15, 20, 25 and 30, and the R-copolymers 10, 20 and 30 were dried in vacuo at room temperature, and the curing treatments and the extraction test were done using the conditions stated in Section 2.3.

The amounts of the resin represented by a weight percent based on the weight of the samples before immersion were plotted versus the –CO–NH–Ti(isoOC$_3$H$_7$)$_3$ mol% in the Ti hybrid copolymers (see the AAm–Ti(isoOC$_3$H$_7$)$_3$ column in Table 2). These results are shown in Fig. 4.

In Fig. 4, the insoluble resins weight percent in the mixture of acetone and methanol definitely increased to over 40 wt% with the curing conditions higher than 140 °C for 10 min for all the Ti hybrid copolymers. Plots of 40 wt% or more are regarded as cured resins.

Fig. 5, which selectively compared the samples at the cure time of 10 min in Fig. 4 with the insoluble resins weight percent of the R-copolymers, were plotted as the insoluble resins weight percent in the mixed solvent of acetone and methanol versus the curing temperature (°C) for the Ti hybrid copolymer 10 (Fig. 5(a)), Ti hybrid copolymer 15

Scheme 2. Curing mechanism
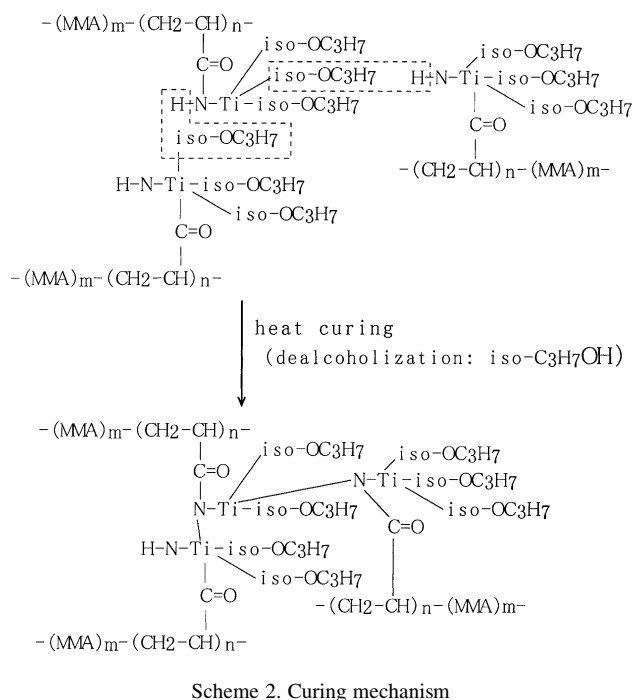
(Fig. 5(b)), Ti hybrid copolymer 20 (Fig. 5(c)), Ti hybrid copolymer 25 (Fig. 5(d)), Ti hybrid copolymer 30 (Fig. 5(e)), Ti hybrid copolymer 35 (Fig. 5(f)), the R-copolymer 10 (Fig. 5(g)), the R-copolymer 20 (Fig. 5(h)) and the R-copolymer 30 (Fig. 5(i)).

In Fig. 5, the amounts of the insoluble resin became nearly constant when the curing temperature of the Ti hybrid copolymers was higher than 140 °C. The decreased change in the IR spectra peak strength (area) at 1655 cm^{-1} in Fig. 3 was in agreement with this result. It is presumed that the curing temperatures of the R-copolymer 20 (Fig. 5(h)) and the R-copolymer 30 (Fig. 5(i)) were found to be higher than 170 °C without the R-copolymer 10 (Fig. 5(g)). These results indicate that the curing temperature of the Ti
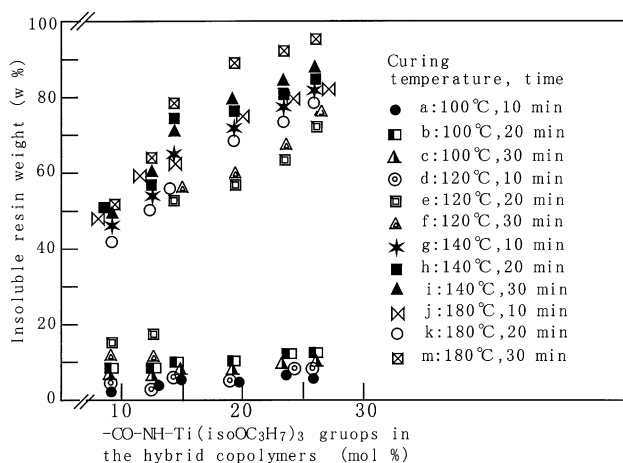

Fig. 4. Plots of insoluble resin weight (%) versus –CO–NH–Ti(isoOC$_3$H$_7$)$_3$ groups in the hybrid copolymers (mol%) as the curing temperature (°C) and time (min) changed.
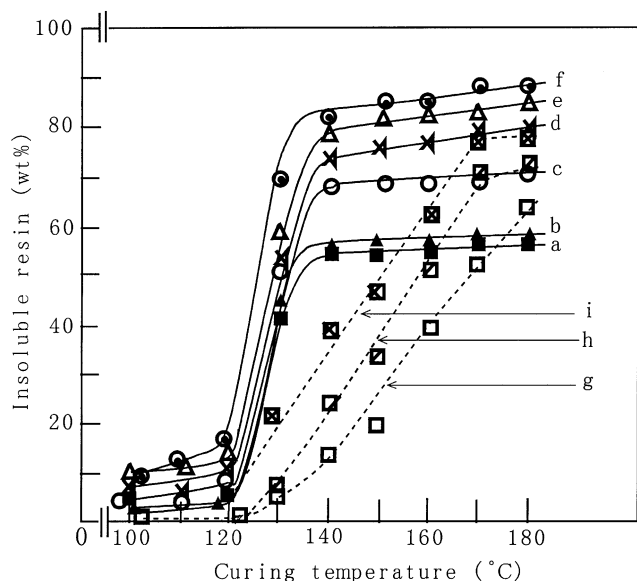
Fig. 5. Plots of insoluble resin weight (%) versus curing temperature (°C). (a) Ti hybrid copolymer 10, (b) Ti hybrid copolymer 15, (c) Ti hybrid copolymer 20, (d) Ti hybrid copolymer 25, (e) Ti hybrid copolymer 30, (f) Ti hybrid copolymer 35, (g) R-copolymer 10, (h) R-copolymer 20, and (i) R-copolymer 30.
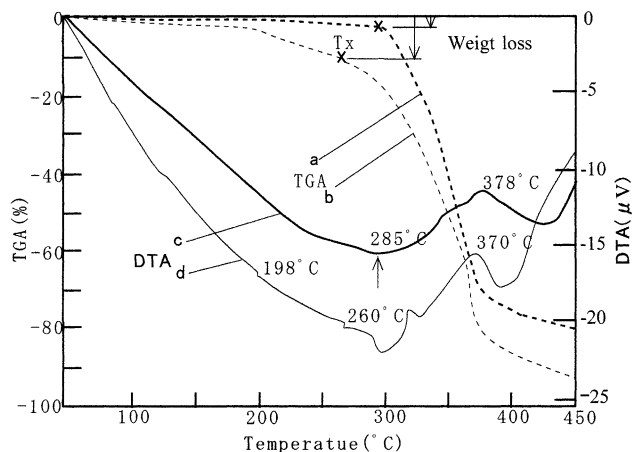

Fig. 6. Thermogravimetric analysis (TGA) of (a) Ti hybrid copolymer 20, (b) R-copolymer 20, and differential thermal analysis (DTA) of (c) Ti hybrid copolymer 20 and (d) R-copolymer 20.

hybrid copolymers can definitely be decreased by 30 °C when compared to the R-copolymers.

As can be seen in Fig. 5, the extent of the change in the insoluble resin weight in the solvents quickly increased between 130 and 140 °C when the curing temperature becomes high, because the curing process proceeds faster than that of the R-copolymers. It is possible that this phenomenon is caused by the condensation reaction of an isopropoxy group in the $-CO-NH-Ti(isoOC_3H_7)_3$ group with a hydrogen atom bonded on the nitrogen atom in the other $-CO-NH-Ti(isoOC_3H_7)_3$ group. The curing reaction of the Ti hybrid copolymers progresses with the elimination of isopropyl alcohol from the reactor by the condensation reaction, which is described in Scheme 2.

The insoluble resin weight only slightly increased and became almost constant when the curing temperature became higher than 140 °C. The viscosity of the resin matrix under such conditions is increased and produced a glass state, thus the curing reaction could hardly proceed. The samples, which were subjected to the curing treatment at 140 °C or more, showed a moderate decrease in the IR spectra absorption strength (Fig. 3). This phenomenon is brought about by the fact that the reaction of the hydrogen atom attached to the nitrogen atom of the side groups with isopropoxide becomes difficult, because the segment movement of the polymer was restricted by the progress of the crosslinking reaction. Therefore, it was possible that this phenomenon involves a substantial termination of the resin's curing reaction. For the R-copolymers, which were prepared as a comparative example, this phenomenon was observed at curing temperatures of 170 °C or more.

3.3. Thermal analysis of Ti hybrid copolymers

To evaluate the thermal stability of the Ti hybrid copolymers and the R-copolymers, the TGA, DTA, DDSC and IR spectra were measured using the curing treatment samples. The curing treatment was done for the hybrid copolymers cured at 140 °C for 10 min and the R-copolymers cured at 170 °C for 10 min, which were regarded as the polymers wherein the curing reaction had been completed based on the results in Fig. 5. The TGA results are shown in Fig. 6 for the Ti hybrid copolymer 20 (Fig. 6(a)) and R-copolymer 20 (Fig. 6(b)). The DTA results were compared with the TGA in Fig. 6 for the Ti hybrid copolymer 20 (Fig. 6(c)) and R-copolymer 20 (Fig. 6(d)). The TGA and DTA results for the Ti hybrid copolymer 10, Ti hybrid copolymer 30, R-copolymer 10 and R-copolymer 30 are shown in Table 4.

On the basis of TGA results in Fig. 6, the T_x value and weight loss of these copolymers at the T_x were determined based on the TGA and DTA. The Ti hybrid copolymer 20 exhibited a T_x of 285 °C, which was higher by 25 °C than the T_x of the R-copolymer 20. The T_x of the Ti hybrid copolymer 20 had the highest T_x of all the other hybrid copolymers. It is possible that the Ti hybrid copolymer 20 has the optimum amount of functional groups, which produces a dense matrix composition with a high T_x. The weight loss at the T_x of the Ti hybrid copolymer 20 was 5 wt%. This was 1/3 the weight loss (15 wt%) at the T_x of the R-copolymer 20.

When Fig. 6(a) was compared with Fig. 6(c), it was confirmed that the Ti hybrid copolymer 20 had no thermal decomposition until the temperature reached the T_x. On the other hand, Fig. 6(d) shows the first stage of decomposition at 198 °C and the endothermic peak of this stage indicated that formaldehyde had begun to decompose from the cured resin by heating. This removal of formaldehyde from the resin continued from 198 to 260 °C, which indicated that the

Table 4
Decomposition temperature and softening temperature of the resins by the curing films

Experimental samples	Weight loss, T_x (°C)	DTA		DDSC, T_s (°C)
		At T_x (wt%)	First peak (°C)	
Ti hybrid copolymer 10[a]	260	3	–	141
Ti hybrid copolymer 20[a]	285	5	–	133
Ti hybrid copolymer 30[a]	270	5	–	130
R-copolymer 10[b]	250	11	194	138
R-copolymer 20[b]	260	15	198	132
R-copolymer 30[b]	261	17	196	130

[a] Curing temperature and time: 140 °C, 10 min.
[b] References, curing temperature and time: 170 °C, 10 min.

R-copolymer 20 gradually began to decompose without leading to the T_x.

Fig. 7 shows the IR spectra results of a thermal degradation test using the Ti hybrid copolymer 20 by the curing treatment carried out at 140 °C for 10 min, which had been held in an oven at 130 °C for 0 h (original; Fig. 7(a)), 96 h (Fig. 7(b)) and 720 h (Fig. 7(c)). Fig. 8 shows the IR spectra results of the R-copolymer 20 by curing treatment at 170 °C for 10 min for samples that were treated the same as in Fig. 7. The hold temperature in the oven for the samples (130 °C) was based on the softening point (T_s) of the resin samples by the DDSC results, which are summarized in Table 4.

The evaluation of the IR absorption bands in Figs. 7 and 8 was done on the basis of Figs. 1 and 2. The square numbers in Figs. 7 and 8 are the specificity absorption of the MMA components in the resin. In Fig. 7, the absorption bands at 1665 and 3370 cm^{-1} are attributable to the –CO–NH– of the AAm in the Ti hybrid copolymer 20. The absorption band at 1240 cm^{-1} is attributable to the alkoxy

group, which is isoOC$_3$H$_7$ in –CO–NH–Ti(isoOC$_3$H$_7$)$_3$. The absorption of Fig. 7(b) overlapped Fig. 7(a) absorption without the band at 1665 cm^{-1}. The absorption of that treated by aging in Fig. 7(c) generally overlapped both the original absorption and the 96 h absorption without the bands at 1665 and 3370 cm^{-1}. The reduction of the absorption bands at 1665 and 3370 cm^{-1} was due to the presence of a reaction between the functional groups of –CO–NH– and the alkoxy groups. The Ti hybrid copolymer 20 has consequently been endowed with an excellent thermal stability.

In Fig. 8 which was the IR spectra absorption bands of the R-copolymer 20, Fig. 8(b) decreased at 1240, 1665 and 3370 cm^{-1} when compared with Fig. 8(a) absorption. The reduction of the absorption band at 1240 cm^{-1} was attributable to the alkoxy groups which was –OC$_4$H$_9$ in –CO–NH–CH$_2$OC$_4$H$_9$. Fig. 8(c) had the decrease in the absorption bands at 1240, 1665 and 3370 cm^{-1}, and it became progressively greater than the absorption for 96 h (Fig. 8(b)), moreover, it appeared that the newly decreased bands at 753, 1150, 1735 and 2970 cm^{-1} are attributable to C–C,
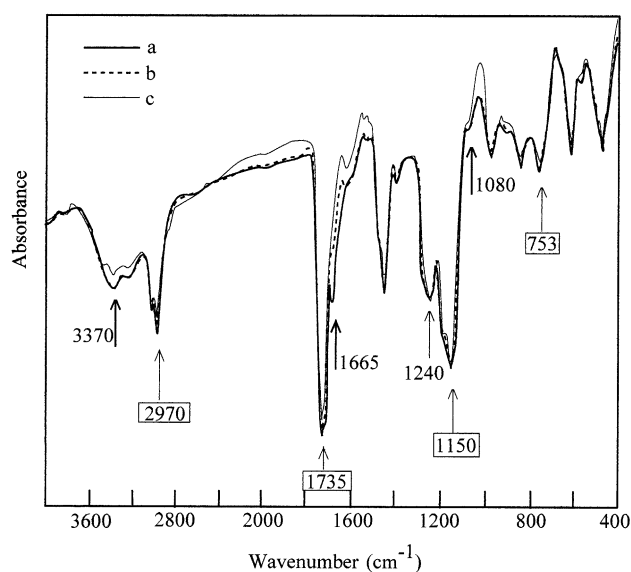

Fig. 7. IR spectrum of the Ti hybrid copolymer 20 while in an oven at 130 °C for (a) 0 h (original), (b) 96 h and (c) 720 h.
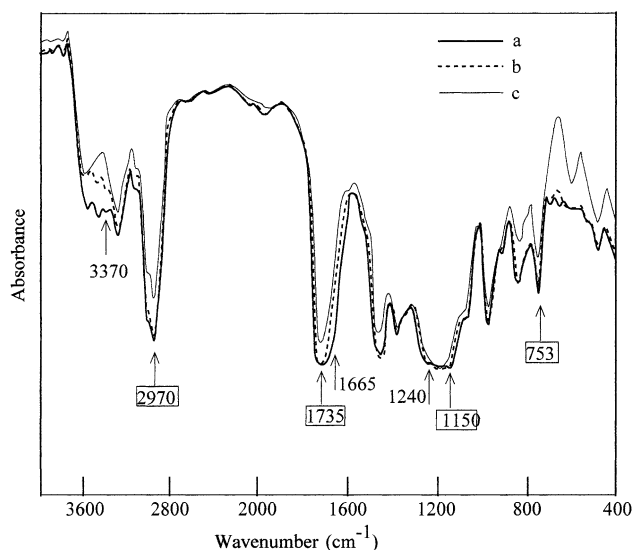

Fig. 8. IR spectrum of the R-copolymer 20 while in an oven at 130 °C for (a) 0 h (original), (b) 96 h and (c) 720 h.

C–O–C, C=O and C–H, respectively. From these results, the R-copolymer 20 was presumed to undergo both a thermal degradation of the functional groups during the aging of the resin and a thermal degradation of the main chain in the resin.

4. Conclusions

The self-thermosetting Ti hybrid copolymers synthesized according to the present study were cured at 140 °C for 10 min in the absence of a curing accelerator. The curing temperature of the Ti hybrid copolymers is 30 °C lower than that of the typically former type of self-thermosetting methacrylic resins which are prepared by the addition reaction of formaldehyde with the copolymers of methyl methacrylate and the acrylamide monomer. When the thermal stability was evaluated using both the T_x and weight loss at the T_x by thermogravimetry and the IR spectra result of the resins, which were held in an oven at 130 °C for 720 h. The Ti hybrid copolymers realized an increased T_x and improvement in the weight loss at the T_x, and was maintained at approximately the same state as the original sample during thermal degradation. The Ti hybrid copolymer 20 was the best among the synthesized copolymers.
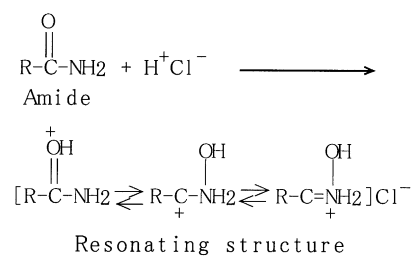
Scheme A1.

Appendix A

Gasparro [11] and Yamaguchi [12] have described the following reaction for the amide group. When a R–CO–NH$_2$ (expression with general constitutional formula) produces a protolytic reaction with H$^+$ in a solvent including some water, the R–CO–NH$_2$ changes to R–COOH and NH$_3$, that is, this reaction produced R–CO–N$^+$H$_3$ as an intermediate compound, and decomposed at the part between N and CO bonds. In dehydrated solvent, H$^+$ has a protolytic reaction with O of CO in the R–CO–NH$_2$; this reaction has the suitable form of a resonating salt such as in Scheme A1.

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