

Preparation of an Acrylics-Grafted Polyester and Its Aqueous Dispersion—Mechanical Properties of Acrylics-Grafted Polyesters

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ABSTRACT: Mechanical properties of grafted polyesters were discussed. In the case of grafting of acrylics of more than 25% in the grafting product, mechanical properties of the grafting products decreased greatly compared with the raw polyester. The influence of the molecular structure of the grafted polyester was not observed. The effect of composition of the grafted polymers was discussed. Mechanical properties varied with the composition of the side chain. In the case of grafting onto aromatic polyesters, grafting of an aromatic unsaturated monomer improved the mechanical properties of the grafted polymer. On the other hand, in the case of grafting onto an aliphatic polyester, grafting of an aliphatic unsaturated monomer improved mechanical properties of the grafting polymer. We found that the grafting of the polymer having a high compatibility with the polyester improved the mechanical properties of the grafting products, from the determination of the compatibility of each polymer and the mechanical properties of the grafting products. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1149–1157, 2000

Key words: grafted polyester; grafting reaction; mechanical property; tensile strength; elongation to break

INTRODUCTION

The reduction of volatile organic compounds and CO₂ has been acquiring intensive attention and the reduction of the solvent emission from organic coatings such as paints and adhesives has been considered for about 20 years.¹ High-solids coatings, powder coatings, and water-borne coatings have been developed to replace conventional solvent-borne coatings; however, these coatings involved several problems,² for example, high-solids coatings still contain some solvents, powder coating systems need a breakthrough in the control of the film thickness, and even water-borne coating

systems have some problems. Among these coatings, water-borne coatings are most preferable because of the compatibility of conventional coating systems.

As conventional water-borne coatings, acrylic emulsions, produced by emulsion polymerization, are widely used. However, for high demands, high-performance water-borne coatings, like epoxy emulsions,^{3,4} polyester dispersions,^{5,6} and polyurethane dispersions,⁷ are intensively developed.

The methods to disperse these resins in aqueous media are: (1) emulsifying mechanically using emulsifiers, and (2) self-emulsifying by introduction of hydrophilic groups into the molecules of resins. By the former method, the water-resistance and adhesion of the coatings obtained from the dispersion are reduced because emulsifiers

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Table I Composition of Polyesters

	(Unit)	1	2	3	4	5	6
DMT	(g)	460.8	460.8	485.0	460.8	—	460.8
DMI	(g)	460.8	460.8	155.2	460.8	—	460.8
SA	(g)	—	—	292.9	—	—	—
1,4-CHDA	(g)	—	—	—	—	1121.0	—
FA	(g)	29.0	—	29.0	29.0	29.0	29.0
MAnh	(g)	—	24.5	—	—	—	—
EG	(g)	443.3	443.3	443.3	130.2	443.3	465.0
NPG	(g)	400.4	400.4	400.4	—	400.4	—
3-MPD	(g)	—	—	—	531.0	—	—
1,4-CHDM	(g)	—	—	—	—	—	528.0
M_n	(—)	6400	5200	7800	6800	7500	6900
M_w	(—)	37,500	24,000	35,500	34,000	35,000	32,000

migrate to the surfaces and interfaces. To avoid the use of emulsifiers, polyesters are copolymerized with the hydrophilic monomers. In the case of linear high molecular weight polyesters, often sodium 5-sulfoisophthalic acid⁸ or polyethylene glycol⁹ or hydrophilic monomers are copolymerized. However, the copolymerization increases the melt viscosity, and decreases water resistance and adhesion.

We developed a new class of water-borne polyesters that are excellently dispersible without using additional emulsifiers. These water-borne polyesters that are of the acrylics-grafted type, form stable aqueous dispersions. They consist of “core-shell” particles with a core of high molecular weight polyester. In previous articles, we discussed the preparation and the characterization of an acrylics-grafted polyester and its dispersions, i.e., the effect of grafting conditions, reac-

tivities of grafting monomers, grafting solvents,¹⁰ grafting methods¹¹ on the molecular structures of grafted polyesters, the particle structures,¹³ the particle diameters of their dispersions,¹⁰ and the dispersion viscosity and the dispersion rheology.¹²

In recent studies, the microstructures of block polymers and graft polymers are discussed vigorously. However, mechanical properties of these polymers are not sufficiently discussed. In this article, we discuss the mechanical properties of acrylics-grafted polyesters to make the factor affecting the mechanical properties clear.

EXPERIMENTAL

Materials

Dimethyl terephthalate (DMT), dimethyl isophthalate (DMI), 1,4-cyclohexane dicarboxylic acids

Table II Composition of Grafting Products

	(Unit)	1	2	3	4	5	6	7
Polyester 1	(g)	60.0	60.0	60.0	72.0	52.0	40.0	—
Polyester 2	(g)	—	—	—	—	—	—	60.0
EA	(g)	8.0	8.0	8.0	3.2	12.8	16.0	8.0
AA	(g)	12.0	12.0	12.0	4.8	19.2	24.0	12.0
MEK	(g)	60.0	60.0	96.0	60.0	96.0	96.0	60.0
IPA	(g)	20.0	20.0	24.0	20.0	24.0	24.0	20.0
AIBN	(g)	1.2	1.2	1.2	1.2	1.9	2.4	1.2
OcM	(g)	1.0	0.2	1.0	1.0	1.6	2.0	1.0
Polyester/acrylics	(—)	75/25	75/25	75/25	90/10	65/35	50/50	75/25
M_w of side chain*	(—)	15,000	25,000	10,000	12,000	15,000	16,000	15,000

AIBN; azobisisobutyronitrile. OcM; octyl mercaptane.

* The side chains of the grafting products were separated by hydrolysis of the polyester segments of the grafting products. See ref. 11.

(CHDA), sebacic acid (SA), ethylene glycol (EG), neopentyl glycol (NPG), 3-methyl-1,5-pentane diol (MPD), and 1,4-cyclohexane dimethylol (CHDM) were of commercial grade. Other reagents were of reagent grade. All reagents were used without further purification.

Preparation of Polyester

DMT (460.8 g), DMI (460.8 g), EG (443.3 g), NPG (400.4 g), and *t-n*-butyl titanate (0.52 g) were charged in a stainless steel autoclave equipped with a stirrer, a thermometer and a refluxing condenser. Transesterification was carried out between 160 and 220°C for 4 h. After the reaction, mixture was cooled to 200°C, and fumaric acid (FA, 29.0 g) was added to this reaction mixture. Temperature was elevated from 200 to 220°C over 1 h for esterification. Finally, the temperature was raised to 255°C, and the pressure was gradually released over 1.5 h to 0.2 mmHg. In case of the polyester having unsaturated bonds at the terminal of the molecules, maleic anhydride was added to the polyester and the mixture was stirred under nitrogen at 220°C for 30 min. The polyester obtained was pale yellow and transparent. It was used without further purification. Other polyesters were prepared by the same procedure. The results are shown in Table I.

Preparation of Grafted Polyester by Use of the Conventional Grafting and Its Aqueous Dispersion

A polyester (60.0 g), methyl ethyl ketone (MEK, 45.0 g), isopropyl alcohol (IPA, 15.0 g) were charged in a reaction vessel equipped with a stirrer, a thermometer, a refluxing device, and an inlet device. The mixture was stirred under reflux (at 75°C) to dissolve the polyester. After complete dissolution of the polyester, a mixture of acrylic acid (AA, 12.0 g), ethyl acrylate (EA, 8.0 g), azobisisobutyronitrile (1.2 g), octyl mercaptane (1.0 g) in MEK (15.0 g), and IPA (5.0 g) were dropwise added over 1.5 h. The reaction mixture was further reacted for 3 h to obtain a solution of the grafted reaction product. To the solution of the grafted reaction product, triethylamine (33.6 g) was added to neutralize to it. Deionized water (160.0 g) was added to the neutralized mixture and stirred for 30 min. Then the remaining solvents and the excess of triethylamine removed by distillation to obtain an aqueous dispersion.

Preparation of Grafted Polyester by Use of the Alternating Copolymerization and Its Aqueous Dispersion

A polyester (60.0 g), methyl ethyl ketone (MEK, 72.0 g), isopropyl alcohol (IPA, 18.0 g), and maleic anhydride (MANh, 12.0 g) were charged in a reaction vessel equipped with a stirrer, a thermometer, a refluxing device, and an inlet device. The mixture was stirred under reflux (at 75°C) to dissolve the polyester. After complete dissolution of the polyester, a mixture of styrene (St, 8.0 g), azobisisobutyronitrile (1.2 g), and octyl mercaptane (1.0 g) in MEK (24.0 g) and IPA (6.0 g) were dropwise added over 1.5 h. The reaction mixture was further reacted for 3 h to obtain a solution of the reaction product. To the solution of the reaction product, ethanol (20.0 g) was added to react with MANh for 0.5 h under reflux, and cooled to room temperature. After the polymerization, the polymer was obtained by drying. Other polymers were prepared by the same procedure. These polymers were used in order to evaluate the compatibility to the various polyesters.

Preparation of Acrylics

Methyl ethyl ketone (MEK, 45.0 g), isopropyl alcohol (IPA, 15.0 g) were charged in a reaction vessel equipped with a stirrer, a thermometer, a refluxing device, and an inlet device. A mixture of

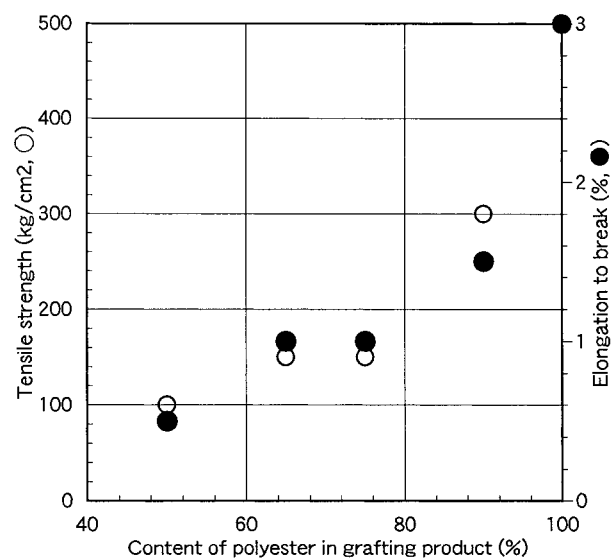


Figure 1 Relationship of the content between the polyester in the grafting product and the mechanical properties of the grafting product (○, tensile strength; ● elongation to break).

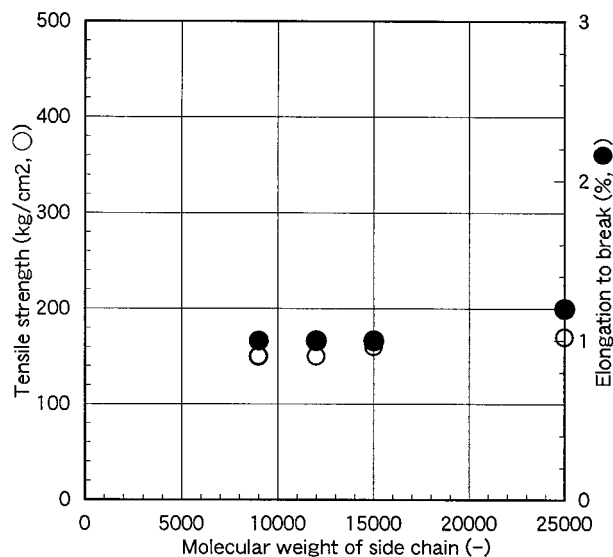


Figure 2 Relationship of the molecular weight between the grafted side chain and the mechanical properties of the grafting product (○, tensile strength; ●, elongation to break).

acrylic acid (AA, 12.0 g), ethyl acrylate (EA, 8.0 g), azobisisobutyronitrile (1.2 g), and octyl mercaptane (1.0 g) in MEK (15.0 g) and IPA (5.0 g) were dropwise added over 1.5 h under reflux. The reaction mixture was further reacted for 3 h. After the polymerization, the polymer was obtained by drying. Other polymers were prepared by the same procedure. These polymers were used in order to evaluate the compatibility to the various polyesters.

Molecular Weight

The number average molecular weight (M_n) and weight average molecular weight (M_w) of polymers was determined by GPC apparatus (Shimadzu Seisakusho. Inc., 6A series) using the column (Showa Denko Inc., KF80M 8 mm i.d. \times 30 cm \times 1, KF801 8 mm i.d. \times 30 cm \times 1, KF802 8 mm i.d. \times 30 cm \times 1). Measurement was carried

Table III Mechanical Property of Grafting Products

	Tensile Strength (kg/cm ²)	Tensile Elongation to Break (%)
Graft type	150	1.0
Block type	200	1.0
Raw polyester	500	3.0

Table IV Mechanical Property of Grafting Products

	Tensile Strength (kg/cm ²)	Elongation to Break (%)	T_g (°C)
Before centrifuge	150	1.0	45
After centrifuge	300	1.2	65
Raw polyester	500	3.0	65

out using a refractive index detector and tetrahydrofuran as a solvent. The column was calibrated using polystyrene standard samples of defined molecular weights.

Glass Transition Temperature (T_g)

T_g s were determined by the use of differential scanning calorimetry (Seiko Instruments Inc., DSC 220). The samples were scanned at a heating rate of 20°C/min in a nitrogen environment.

Mechanical Property

The mechanical property was measured by the use of tensile tester (Orientec Corporation, RTM-100). The condition is following; sample, 10.0 \times 40.0 \times 0.05 mm; crosshead speed, 100 mm/min.

Compatibility

The polymers forming the main chain and side chain of the grafting products were separately synthesized. Each polymer was dissolved in tetrahydrofuran to form transparent solutions hav-

Table V Composition of Grafting Products

	(Unit)	1	2	3
Polyester	(g)	60.0	60.0	60.0
EA	(g)	8.0	—	—
AA	(g)	12.0	12.0	—
MMA	(g)	—	6.0	—
St	(g)	—	2.0	8.0
MANh	(g)	—	—	12.0
MEK	(g)	96.0	96.0	96.0
IPA	(g)	24.0	24.0	24.0
AIBN	(g)	1.2	1.2	1.2
OcM	(g)	1.0	1.0	1.0
Polyester/acrylics	(—)	75/25	75/25	75/25
M_w of side chain*	(—)	10,000	12,000	9,000

MMA; methyl methacrylate.

* See Tab. II.

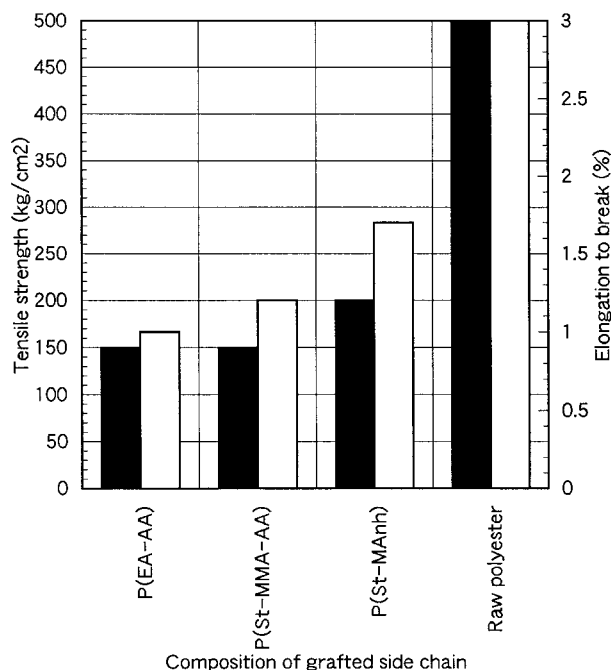


Figure 3 Mechanical properties of the grafting product having various grafted side chains (○, tensile strength; ● elongation to break).

ing a solid concentration of 5%. The polymer solutions were mixed together at a solid ratio by mass of 50/50. The mixture was applied to a glass plate so that the dried coating film had a thick-

ness of 0.1 mm, and was dried at 120°C for 10 min to obtain a coating film. The transparency of the coating film was visually observed. When the coating film had high transparency, compatibility rating was 5. When the coating film was turbid, compatibility rating was 3. When the coating film was white, compatibility rating was 1.

RESULTS AND DISCUSSION

In this study, we define the term “a grafting product” as a mixture of acrylics-grafted polyesters, ungrafted polyesters, and ungrafted acrylics. In addition, the films obtained from the grafting products in this study were all transparent, without removal of the ungrafted acrylics. Therefore, no macrophase separation that the existence of the grafted polymer caused was observed, and the structure of the macrophase separation had no effect on the mechanical properties. We discussed the mechanical property of films where an acrylics-grafted polyester, an ungrafted polyester, and an ungrafted acrylics were homogeneously mixed at the dimension of less than the 100-nm level.

Effect of Molecular Structure of Grafted Polyester

The effect of the molecular structure of the grafted polyester, i.e., the mass ratio of the main

Table VI Mechanical Property of Grafting Products

		Polyester			
		1 TPA/IPA/FA// EG/NPG	3 TPA/IPA/SA/FA// EG/NPG	4 TPA/IPA/FA// EG/3-MPD	5 CHDA/FA// EG/NPG
Raw Polyester					
σ	(kgf/cm ²)	500	40	1	14
ε	(%)	3.0	800	2000	630
Grafting product					
Grafting of P(EA-AA)					
σ	(kgf/cm ²)	150	140	110	10
ε	(%)	1.0	255	340	370
Grafting of P(St-MMA-AA)					
σ	(kgf/cm ²)	150	180	140	15
ε	(%)	1.2	280	340	350
Grafting of P(St-MAnh)					
σ	(kgf/cm ²)	200	350	205	250
ε	(%)	1.7	365	360	150

TPA; terephthalic acid. IPA; isophthalic acid. CHDA; 1,4-cyclohexane dicarboxylic acid. SA; sebacic acid. EG; ethylene glycol. NPG; neopentyl glycol. MPD; 3-methyl-1,5-pentane diol. CHDM; 1,4-cyclohexane dimethylol.

Table VII Compatibility Rating between Raw Polyesters and Grafted Side Chains

		TPA/IPA/FA// EG/NPG	TPA/IPA/SA/FA// EG/NPG	TPA/IPA/FA// EG/3-MPD	CHDA/FA// EG/NPG
P(EA-AA)	(40/60)	1	2	2	5
P(EA-AA)	(80/20)	1	1	2	5
P(<i>St</i> -MMA-AA)	(10/30/60)	2	2	3	4
P(<i>St</i> -MAnh)	(40/60)	4	4	3	2

TPA; terephthalic acid. IPA; isophthalic acid. CHDA; 1,4-cyclohexane dicarboxylic acid. SA; sebacic acid. EG; ethylene glycol. NPG; neopentyl glycol. MPD; 3-methyl-1,5-pentane diol. CHDM; 1,4-cyclohexane dimethylol.

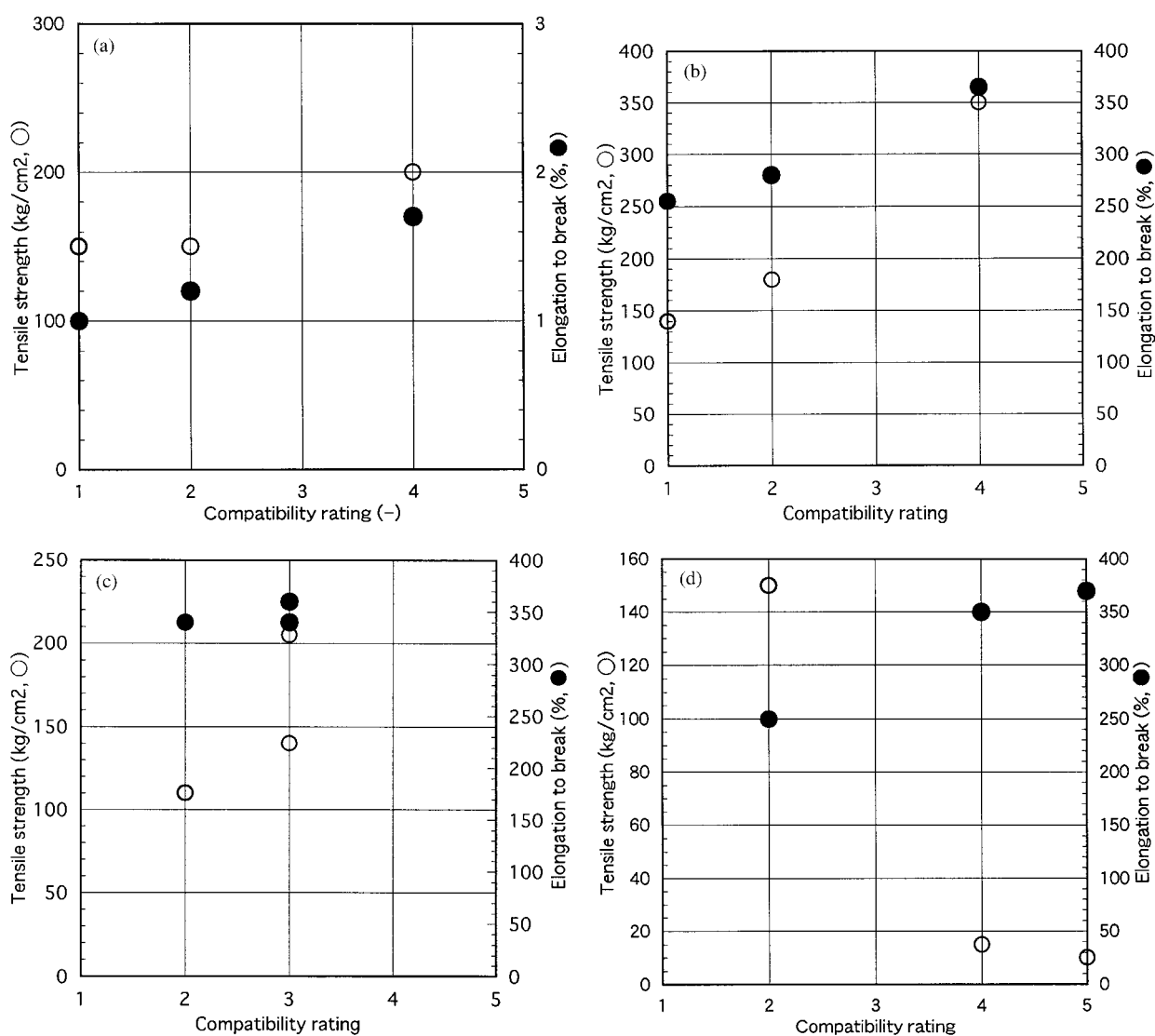


Figure 4 Relationship of the compatibility rating between the main chain and the side chain and the mechanical properties of the grafting products (○, tensile strength; ●, elongation to break). The main chains are (a) polyester-1; (b) polyester-3; (c) polyester-4; (d) polyester-5. See Tab. VI.

Table VIII Compatibility Rating between Various Polymers and Raw Polyester

	P(<i>St</i> -MAnh) 40/60	P(<i>St</i> -MAnh) 60/40	P(<i>St</i> -MMA-MAnh) 30/30/40	P(<i>St</i> -DEF-MAnh) 40/20/40
Compatibility rating	4	4	4	5

chain to the side chain, the molecular weight of the side chain, and the attached position of the side chain, on the mechanical properties was discussed. Preparation of grafted polyesters having various mass ratios and various molecular weights of side chains was carried out in a similar procedure described in previous article.¹² The attached position of the side chain was changed by the position of the introduced unsaturated bond in polyester. Table II shows the compositions of the grafted polyesters. Results are shown in Figures 1, 2, and Table III. Tensile strength (σ) and elongation to break (ϵ) of each grafted polyester was almost same. However, compared with the raw polyester, α and ϵ of the grafted polyesters were largely reduced. Grafting of the side chain largely affects mechanical properties. The influence of molecular structure of grafted polyester was not observed in this case.

Effect of the ungrafted acrylic polymer (that is, the polymer that did not react with polyester) on mechanical properties was discussed. Ungrafted acrylics after neutralization are soluble in water; therefore, they can be removed by ultracentrifuge described in a previous article.¹³ Results are shown in Table IV. It shows doubled tensile strength and increased T_g by 20°C after removal of the ungrafted acrylics. About the T_g s, we found that a lowering of T_g after grafting occurred due to the residue acrylics oligomers in the grafting product, described in a previous article.¹³ However, the polyesters changed from ductile to brittle by grafting from the data of elongation to break.

From the results, grafting of the side chain largely affects mechanical properties. The influence of the molecular structure of the grafted polyester was not observed. The ungrafted acrylics do not decrease the elongation to break of the grafted polyester. However, it seemed strange that grafting of small amounts of acrylics (ca. 25%) in the grafting product largely decreased the mechanical property of the grafted polyester.

Effect of Composition of Grafted Polymer

The effect of composition of the grafted polymer was discussed. First, the mechanical properties of

the grafted polymers having various side chains, prepared by a similar procedure described in previous article,^{10,11} were determined. The composition of the grafted polymers are listed in Table V. Results are shown in Figure 3. σ and ϵ varied with the the composition of the side chain. In the case of the grafting of styrene and maleic anhydride, σ and ϵ were largely improved, compared with other grafted polyesters. From the results, the copolymerization of styrene in the side chain increased the mechanical property of grafting products.

The effect of the composition of the main chain was discussed. Mechanical properties of the grafted polymers prepared using various polyesters were determined. Results are shown in Table VI. From the results, the tensile strength changed according to the composition of the grafted side chain. However, in the case of grafting onto aromatic polyesters, grafting of an aromatic unsaturated monomer increased the elongation to break of the grafted polymer. On the other hand, in the case of grafting onto an aliphatic polyester, grafting of an aliphatic unsaturated monomer increased the elongation to break of the grafting polymer.

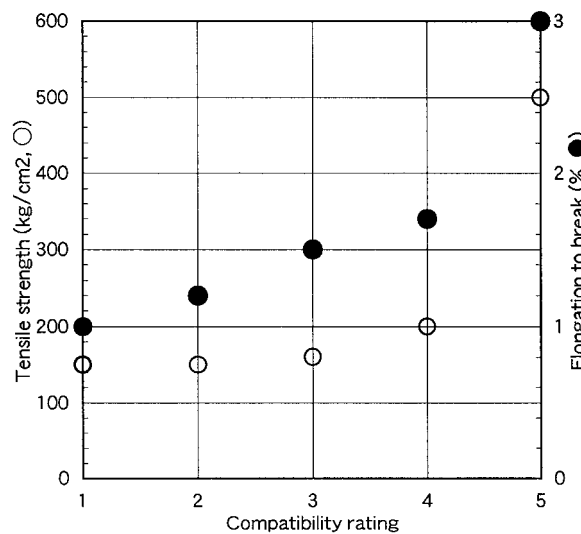


Figure 5 Relationship of the compatibility ratings between the main chain and side chain and the mechanical properties of the grafting products (○, tensile strength; ●, elongation to break).

Table IX Compatibility Rating between Various Polyesters and P(*St*-MANh)

	TPA/IPA/FA// EG/NPG (47.5/47.5/5//50/50)	TPA/IPA/FA// EG/NPG/3-MPD (47.5/47.5/5//40/30/30)	TPA/IPA/FA// EG/CHDM (47.5/47.5/5//50/50)	TPA/IPA/FA// EG/DEG (47.5/47.5/5//50/50)
Compatibility	4	5	4	4

Factor That Affects the Mechanical Properties

From the above results, compatibility between the main chain and the side chain of the grafted polymer seemed to affect the mechanical property of the grafted polyester. We discussed the relationship between the compatibility and the mechanical properties. Table VII shows the result of compatibility between the main chain polymer (raw polyester) and the side chain polymer (which was polymerized in the absence of the polyester). As we thought, the film obtained from the blend of the aromatic polyesters and the polymers that copolymerized with styrene had high transparency. Formation of a transparent film means that the compatibility between the mixed polymers is good. On the other hand, the aliphatic polyester and the polymer that copolymerized with acrylates formed transparent films. According to the above results, the relationship between the mechanical properties and the compatibility were plotted. This was shown in Figure 4. The compatibility of the main chain and the side chain correlates closely with the mechanical property of the grafted polyester.

Next, we studied the improvement of the mechanical property of the grafted polymer. From the above results, it seemed that the mechanical property, especially ductility, of the grafted polymer could be increased by grafting of the polymer having higher compatibility with raw polyester. Compatibility between various polymers and raw polyesters was determined. The results are shown in Table VIII. The P(*St*-DEF-MANh) polymer had the highest compatibility with the raw polyester. Figure 5 shows the relationships between the compatibility and the mechanical property of the grafted polymers. By the grafting of P(*St*-DEF-MANh), the mechanical property was improved to that equal to the raw polyester.

Moreover, compatibility between various polyesters and P(*St*-MANh) were determined. The results are shown in Table IX. The polyester (TPA/IPA/FA//EG/NPG/MPD) had the highest compatibility with P(*St*-MANh). Figure 6 shows the

relationships between the compatibility and the mechanical property of the grafted polymer. In this figure, a clear tendency was not observed because various polyesters were used. Therefore, the relationship between the compatibility and retention of elongation to break were plotted (Fig. 7). As well in this case, by the grafting to the polyester (TPA/IPA/FA//EG/NPG/MPD) that had the highest compatibility with P(*St*-MANh), the mechanical property was increased to that equal to the raw polyester.

From above results, it is valid that the grafting of the polymer having high compatibility with the polyester improved the mechanical property of the grafting products.

CONCLUSION

Mechanical properties of grafted polyesters were discussed. In the case of grafting of small

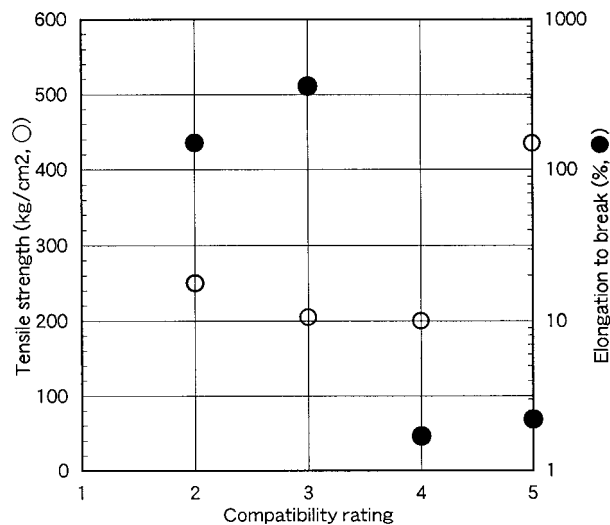


Figure 6 Relationship of the compatibility rating between the main chain and the side chain and the mechanical properties of grafting products (O, tensile strength; ●, elongation to break).

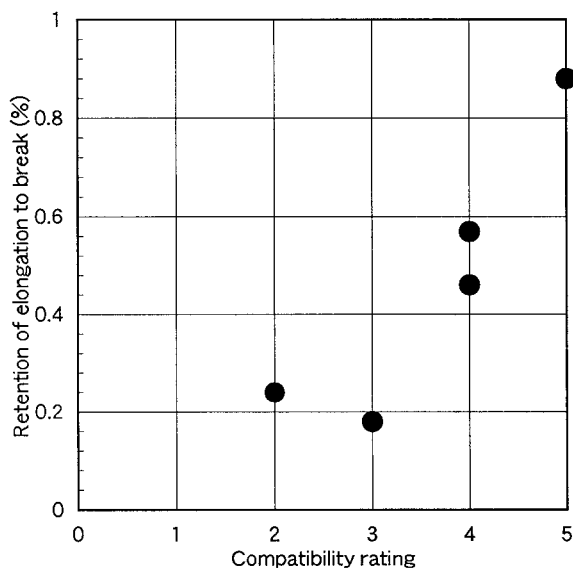


Figure 7 Relationship of the compatibility rating between the main chain and the side chain and the retention of elongation to break of the grafting products.

amounts of acrylics (ca. 25%) in the grafting product, mechanical properties of the grafting product largely decreased compared with raw polyester. The influence of the molecular structure of the grafted polyester was not observed. Removal of the ungrafted acrylics did not increase the ductility of the grafted polyester.

The effect of the composition of the grafted polymer was discussed. Mechanical property varied with the composition of the grafted side chain. In the case of grafting onto aromatic polyesters, grafting of an aromatic unsaturated monomer improved the elongation to break of the grafted polymer. On the other hand, in the case of grafting onto an aliphatic polyester, grafting of an ali-

phatic unsaturated monomer improved the elongation to break of the grafting polymer. We found that the grafting of the polymer having high compatibility with the polyester improved the mechanical property (ductility) of the grafting products from the determination of the compatibility of each polymer and the mechanical properties of the grafting products.

In following articles, the micorphase structure of the grafting product will be determined, and the relationships between the micorphase structure and the mechanical property will be discussed.

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