

Effect of surface treatment agents on bond strength of auto-polymerized acrylic resin to poly(ethylene terephthalate)

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Purpose: This study evaluated the adhesive strength between a thermoplastic poly(ethylene terephthalate) (PET) sheet and an auto-polymerized acrylic resin (Unifast III).

Materials and Methods: The shear bond strength of auto-polymerized acrylic resin to PET with or without surface treatment was measured. Four surface treatment agents, Unifast III Liquid, Resin Primer, Adhesive, and GP Solvent, were used.

Results: The shear bond strengths were 28.8 MPa for GP Solvent, 26.5 MPa for Resin Primer, 24.6 MPa for Adhesive, 24.4 MPa for the untreated control, and 23.4 for Unifast III Liquid. Significant differences were found between the control and GP Solvent, between Unifast III Liquid and GP Solvent, and between Adhesive and GP Solvent ($p < 0.05$). SEM observation showed that the surfaces of the thermoplastic sheets had dissolved due to the application of Unifast III Liquid, Adhesive, and Resin Primer.

Conclusion: Specimens treated with GP Solvent, Resin Primer, and Adhesive exhibited higher bond strength value compared to the control specimens. GP Solvent had the highest adhesive strength. SEM observation indicated that the surface changes of the PET treated with Resin Primer were the most remarkable.

(Int Chin J Dent 2010; 10: 57-62.)

Key Words: auto-polymerized acrylic resin, poly(ethylene terephthalate), shear bond strength, surface treatment agent, thermoplastic sheet

Introduction

Dental processing of thermoplastic resins is broadly classified into two fabrication methods: injection molding with thermoplastic resin pellets and fabrication under pressure or suction of the heated sheet-type thermoplastic resin. The use of thermoplastic sheets has recently increased¹⁻⁷ for splints for temporomandibular disorders, nightguards, obturator prostheses, splint-type temporary dentures, treatment or diagnostic dentures, and oral appliances for obstructive sleep apnea (OSA).^{4,5} The fabrication procedure of prosthetic devices using thermoplastic sheets is very simple and can be accomplished in a short time. Four types of sheets, namely, polycarbonate,¹ poly(ethylene terephthalate) (PET),⁴ cellulose acetate butyrate,⁷ and ethylene vinyl acetate (EVA)^{2,5} are available for clinical use. One of these kinds of thermoplastic sheets can be selected for each situation, depending on the case and purpose as well as the hardness needed.

In prosthodontic practice, the combination of thermoplastic resin sheets and auto-polymerized acrylic resin is necessary in some situations. For instance, splint-type dentures or OSA appliances are easy to produce using these materials, resulting in an effective treatment.^{3,4,7} To use these devices clinically over a long period of time, the bonding of thermoplastic resin sheets and auto-polymerized acrylic resin becomes an important factor. Thus far, such bonding has not been totally successful since debonding of the acrylic resin from the thermoplastic sheets has frequently occurred during short-term clinical observations. One reason for the debonding may be due to the stress concentration at the bonding interface since thermoplastic resin is very flexible. The methods for increasing the adhesive strength between a denture base acrylic resin and auto-polymerized acrylic resin include roughening the bonding surface of an acrylic resin using a carbide bur,⁸ abrading with alumina particles,⁹ and using surface treating agents.¹⁰⁻¹³ Thus far, the influence of the surface treatment agents on the bonding between the thermoplastic resin sheets and the auto-polymerized acrylic resin has not been investigated.

The purpose of this study was to evaluate the influence of surface treatment agents on the bonding strengths between thermoplastic sheets and auto-polymerized acrylic resin. Using PET as the thermoplastic resin, the shear bond strengths of auto-polymerized acrylic resin treated with one of four types of surface treatment agents were measured.

Materials and Methods

Specimen fabrication

The materials used in this study and their chemical compositions are presented in Table 1. Figure 1 shows a diagram of the specimen fabrication process based on the laboratory situation. The thermoforming of PET (3 mm thick) on the plasterboard was performed using a pressurized thermoforming device (Mini-star S, Morita, Tokyo, Japan) (Heating temperature: 220°C for 80 s; pressurized power: 0.3 MPa). The thermoformed PET was cut into 10×10 mm pieces using a supersonic wave cutter (Labo Sonic Cutter NE87 Nakanishi, Kanuma, Japan) and then fixed to an auto-polymerized acrylic resin block (30 mm diameter, 20 mm high; Unifast III) with cyanoacrylate adhesive (Aron Alpha; Toagosei, Tokyo, Japan). The surface of the PET was cleaned using a steam cleaner for 5 s.

Table 1. Materials used in this study

Materials	Code	Composition	Lot number	Manufacturer
Thermoplastic poly (ethylene terephthalate) sheet				
Duran	PET	poly(ethylene terephthalate)	071016	Sheu-Dental GmbH, Iserlohn, Germany
Auto-polymerized acrylic resin				
Unifast III		Powder: poly(methyl methacrylate) Liquid: methyl methacrylate (MMA)	P: 0711012 L: 0712121	GC Corp., Tokyo, Japan
Surface treatment agent				
Unifast III Liquid		MMA	0712121	GC Corp.
Resin Primer	RP	dichloromethane, MMA	0712111	GC Corp.
Adhesive	AH	ethyl acetate	782	Tokuyama Dental Corp., Tokyo, Japan
GP Solvent	GP	n-hexane, d-limonene	UB5	Nippon Shika Yakuhin Co. Ltd., Shimonoseki, Japan

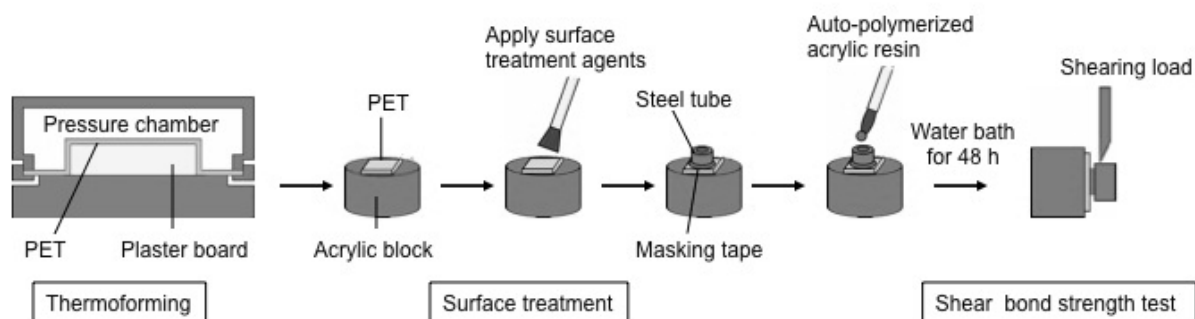


Fig. 1. Schematic illustrating the study design

Four surface treatment agents, Unifast III Liquid, Resin Primer (RP), Adhesive (AH), and GP Solvent (GP), were used in this study. They were applied only once on the PET surface using a new writing brush (GC Corp., Tokyo, Japan). The agents on the PET surface volatilized immediately and did not remain. Specimens without surface treatment were also prepared as a control. After the surface treatment, a piece of masking tape with a

3-mm diameter hole was adhered to the treated PET surface to indicate a prescribed area. A stainless steel tube (4 mm inner diameter, 4 mm high) was placed on the masking tape, and auto-polymerized acrylic resin (Unifast III) was applied within the tube using the brush-on technique. The resins were polymerized at room temperature (25°C) and ambient atmospheric pressure, and the polymerized specimens were stored in distilled water for 48 hours. Ten specimens for each agent (total of 50 specimens) were fabricated. Only one dental technician with 30 years' experience made the specimens since operator dexterity has been found to significantly influence the specimen quality.

Shear bond strength and Knoop hardness

The specimens were mounted on a universal testing machine (Instron 5565; Instron Corp., Canton, MA, USA), and shear testing was performed at a 0.5 mm/minute crosshead speed. The shear bond strengths (MPa) were calculated by dividing the peak load at fracture by the surface area.

In addition, to examine the influence of the surface treatment agents on the PET surface, the Knoop hardness of the treated surfaces was measured (MVK-E hardness tester, Akashi, Tokyo, Japan) with an applied load of 10 g for 30 s. The Knoop hardness of the control and the specimen without thermoforming were similarly measured. The hardness was measured at five points on the surface of each specimen, and the mean hardness values were calculated.

The data collected on the shear bond strengths and Knoop hardness were statistically analyzed using a one-way analysis of variance (ANOVA) and Bonferroni multiple comparisons test at a significance level of $\alpha=0.05$. SPSS for Windows Ver.12.0 (SPSS Japan Inc., Tokyo, Japan) was used for both statistical analyses.

Observation of treated surfaces and fractured surfaces

The treated surfaces were observed using a scanning electron microscope (SEM; JSM-5600LV, JEOL, Akishima, Japan). After shear testing, the fractured surfaces of the PET were examined using a stereomicroscope (SZH-10 Olympus, Tokyo, Japan) and SEM.

Results

The results of the shear bond strength and hardness testing are shown in Table 2. The mean shear bond strength of the agents ranged from 23.4 MPa to 28.8 MPa. GP had the highest strength (28.8 MPa) among the products tested, followed by RP and AH. There were significant differences between GP and the control, between GP and Unifast III Liquid, and between GP and AH ($p<0.05$).

Table 2. Shear bond testing and Knoop hardness testing results

Surface treatment agent	Shear bond strength (MPa)			Knoop hardness number (KHN)		
	Mean	Category	SD	Mean	Category	SD
Without thermoforming	NA	NA	NA	10.70	a, b, c	0.19
Control	24.4	a	1.8	10.23	d, e	0.24
Unifast III Liquid	23.4	b	4.3	5.23	a, d, f	1.77
RP	26.5		2.2	≤ 3.00		
AH	24.6	c	2.8	7.39	b, e, g	0.44
GP	28.8	a, b, c	2.0	9.99	c, f, g	0.15

NA, Not available; Identical letters indicate significant difference ($p<0.05$).

Knoop hardness testing results of the treated surfaces on the PET sheet are also summarized in Table 2. There was no significant difference between the conditions before and after thermoforming. After applying the surface

treatment agents, the hardness significantly decreased compared to the control, except for GP. In particular, RP became so soft that it exceeded the measurement range.

Each treated surface observed by SEM is shown in Fig. 2. The surfaces of Unifast III Liquid, RP, and AH had dissolved after treatment. RP looked especially rough, and there were micro scratches on GP. The images seen with the microscope and the SEM of the fractured surfaces after testing are found in Fig. 3. All specimens exhibited mixed failures interfacial failure between PET and the auto-polymerized acrylic resin and cohesive failure within PET. However, in the SEM images, the control and Unifast III Liquid looked like threads, while RP, AH, and GP had flakes on the stratum.

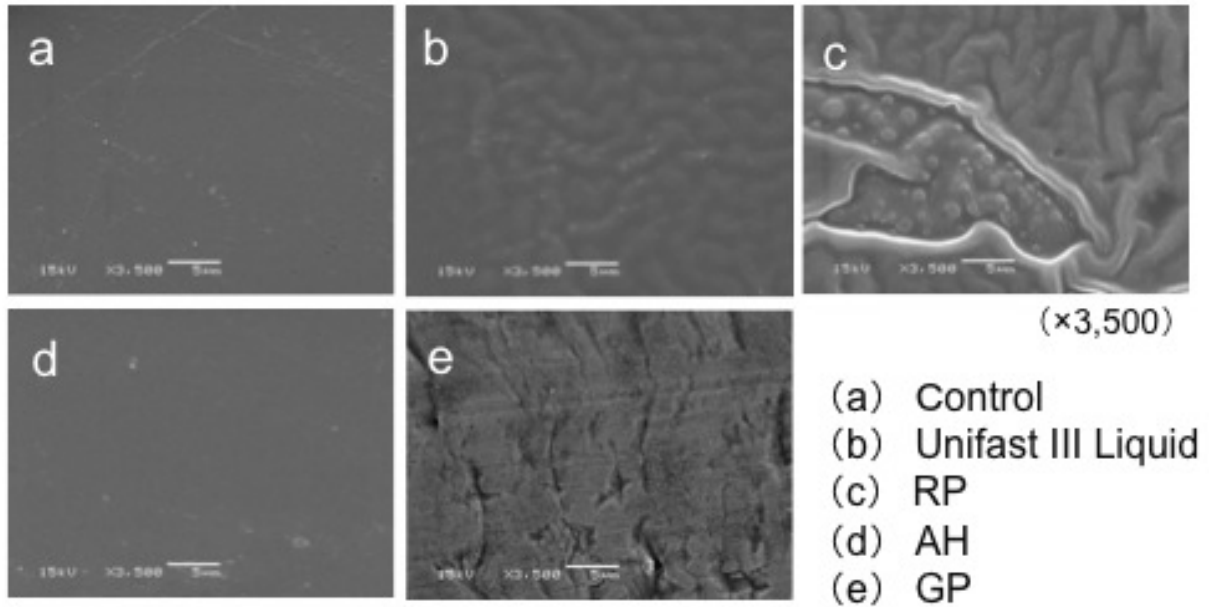


Fig. 2. SEM images of treatment surfaces

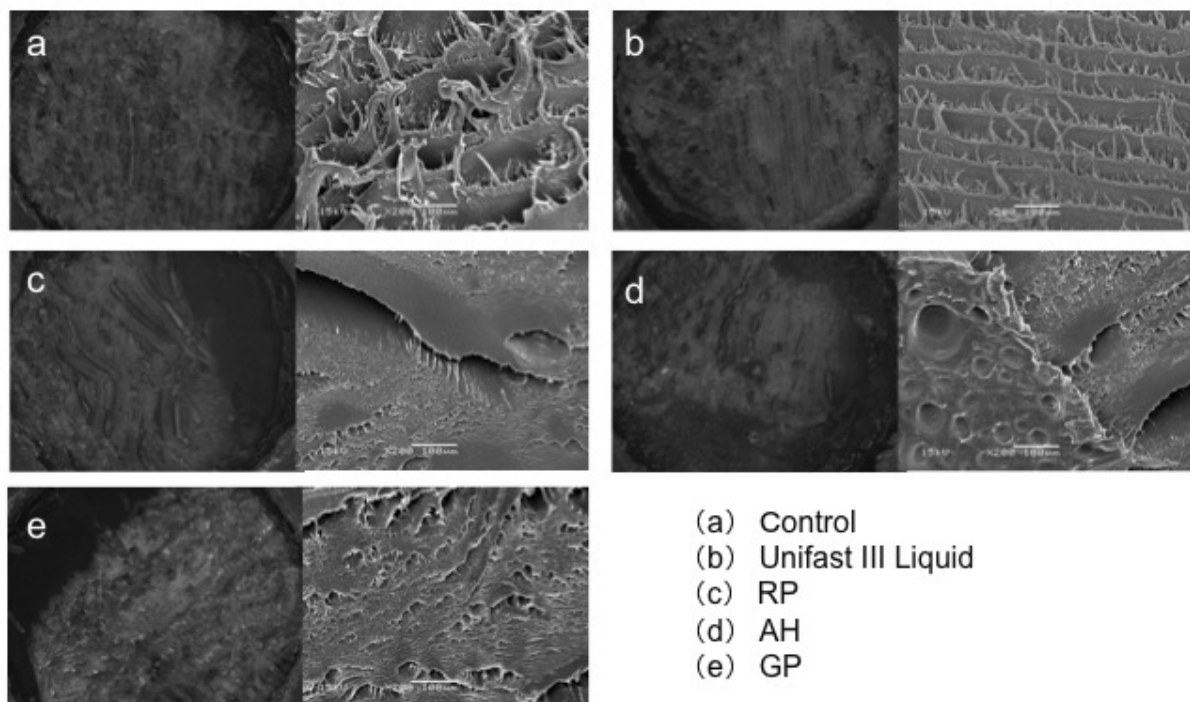


Fig. 3. Fracture surfaces of PET side: left, microscope image (x40); right, SEM image (x200)

Discussion

The adhesive strength between acrylic resin and PET greatly affects the durability of a prosthetic device. The bonding surface of the denture base acrylic resin is usually roughened using a carbide bur or by abrading with alumina particles to enhance the adhesive strength to the auto-polymerized resin. In addition, it is beneficial to treat the surface with agents such as an organic solvent or primer.⁹⁻¹³ Methyl methacrylate (Unifast III Liquid), dichloromethane (RP), and ethyl acetate (AH) are frequently used as surface treatment agents. Since the effectiveness of dichloromethane was reported,^{10,11,13} the present study examined these four agents including monomer and dichloromethane as surface treatments. GP, which is widely used for softening or dissolving the gutta-percha in endodontic therapy,^{14,15} showed the highest shear bond strength (28.8 MPa). The d-limonene (GP) has been used for many years and is considered to be a reliable and safe chemical. Although RP produced high strengths, dichloromethane is specified as a dangerous chemical. In contrast, ethyl acetate exhibited a lower bonding strength than that of RP and GP. Many studies reported that the ethyl acetate had little effect on the adhesion to acrylic resin.^{11,12} It is reported that it is necessary to apply the monomer for a relatively long time (180 s) to increase the adhesive strength of the denture base acrylic resin.^{10,16} In this study, Unifast III Liquid did not apply to RET surface such a long time. However, the Knoop hardness deteriorated remarkably.

The shear bond strengths between the auto-polymerized acrylic resin and denture base acrylic resin were reported to be 9-17 MPa by Sarac et al.,¹⁶ 20.2 MPa by Shimizu et al.,¹⁷ and approximately 35 MPa by Minami et al.⁹ Takahashi et al. demonstrated that the shear bond strength between auto-polymerized acrylic resin and injection-type PET had a constant value of 27-28 MPa.¹⁸ Moreover, the shear bond strengths between the auto-polymerized acrylic resin and other injection-type thermoplastic resin, nylon and polycarbonate were approximately 5 MPa and 15-25 MPa, respectively.^{18,19} PET has higher bonding strengths to auto-polymerized acrylic resin compared to the other thermoplastic resins. In the present study, the shear bond strength of the auto-polymerized acrylic resin to the thermoplastic resins was about 23-28 MPa, similar to the value found by Takahashi.¹⁸ Because PET is more flexible than acrylic resin, it was easy to bend under occlusal force, and it seems that the bonded resin peels off easily. Therefore, the effect of the surface treatment agents was important.

Many small pores are commonly observed on the denture base acrylic resin surfaces treated by dichloromethane or ethyl acetate,^{10,11,16,17,20,21} However, there was no porosity on the surfaces treated with RP and AH; only swollen and dissolved surfaces were seen in this study. The adhesive strength of RP and GP appeared to have increased because of the dissolubility, which caused the cracks and undercuts on the surface of PET. However, the Knoop hardness of GP was similar to that of the control, Unifast III Liquid was 5.23, and RP could not be measured. From this result, the influence of each surface treatment agent seemed to be different. The PET surface was more severely dissolved by RP as evidenced by the Knoop hardness results. Because the PET surface has changed greatly after only one application using the brush, it is surmised that the PET surface might have deteriorated because of the long treatment time with RP.

The results of the present study showed that the use of surface treatment agents tended to increase the adhesive strength of the auto-polymerized acrylic resin to the thermoplastic resin. However, further evaluation of the adhesive strengths after bending fatigue testing based on simulated clinical situations is necessary due to the great difference between the flexure of thermoplastic sheets and acrylic resins.

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Accepted November 29, 2010.

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