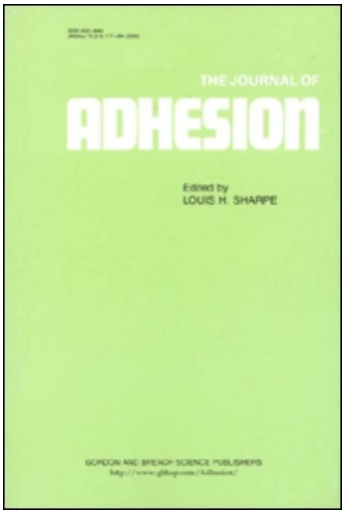

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Terpolymers Composed of Ethyl Acrylate, Methoxypolyethyleneglycol Methacrylate and Methoxypolypropyleneglycol Methacrylate as Pressure Sensitive Adhesives and their Blood Compatibility

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Terpolymers Composed of Ethyl Acrylate, Methoxypolyethyleneglycol Methacrylate and Methoxypoly-propyleneglycol Methacrylate as Pressure Sensitive Adhesives and their Blood Compatibility

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Terpolymers composed of ethyl acrylate (EA), methoxypolyethyleneglycol methacrylate (MPEGMA) and methoxypolypropyleneglycol methacrylate (MPPGMA) were synthesized by the photopolymerization technique. The high molecular mobilities for these terpolymers were shown by dynamic contact angle and adhesion tension measurement. The 180-degree peel strength and probe tack for pressure sensitive adhesives (PSA) made of these terpolymers were good but the holding power was not enough to apply them as PSAs. It was found that these terpolymers should be modified to obtain high holding power. The blood compatibility of these terpolymers was also investigated. It was found that they had a significant blood compatibility. Thrombi were not observed on the terpolymer surface after immersion in blood while, on a polystyrene (PSt) surface, many blood clusters were observed. After immersion in platelet-rich plasma (PRP), a few adhered platelets were observed on terpolymer surface but they did not deform and maintained their spherical form, while many platelets were observed on polystyrene.

* Corresponding author.

Keywords: Terpolymer; molecular mobility; dynamic contact angle; adhesion tension relaxation; pressure sensitive adhesive; peel strength; holding power; probe tack; blood compatibility; platelet

1. INTRODUCTION

We [1 – 5] have reported on the surface molecular mobility for multicomponent polymeric systems, having hydrophilic (polyethyleneglycol) and/or hydrophobic (polydimethylsiloxane or polypropyleneglycol) side chains, *via* X-ray photoelectron spectroscopy (XPS), dynamic contact angle (DCA), adhesion tension relaxation (ATR) and so on. It was shown that methacrylic polymers having these side chains showed a large contact angle hysteresis and adhesion tension relaxation due to their high molecular mobility. In addition, it was found that these systems had a significant blood compatibility. It was expected that these systems were also good adhesives, since these amphiphilic materials could adhere two materials which had different philicity. Therefore, we tried to apply these systems to pressure sensitive adhesives (PSAs).

Recently, much effort has been made to develop adhesives for medical use. Many PSAs have also been used for medical applications such as plasters, drug delivery systems, surgical tapes and so on. In medical applications, it is necessary for adhesives to have bio-compatibility. If PSAs have bio-compatibility, they may be more extensively used in medical applications. We [5] have already reported that some methacrylic terpolymers, having both hydrophobic and hydrophilic side chains, showed a significant blood compatibility. Therefore, we tried to develop blood compatible PSAs.

We synthesized terpolymers composed of ethyl acrylate (EA), methoxypolyethyleneglycol methacrylate (MPEGMA) and methoxypolypropyleneglycol methacrylate (MPPGMA) by the photopolymerization technique. The molecular mobility for these terpolymers was investigated *via* DCA and ATR. Three PSA properties for these terpolymers were determined. In addition, a blood compatibility for these terpolymers was also investigated.

2. EXPERIMENTAL

2.1. Materials

Synthesis of Terpolymers

Terpolymers composed of ethyl acrylate (EA), methoxypolyethyleneglycol methacrylate (MPEGMA) and methoxypolypropyleneglycol methacrylate (MPPGMA) were synthesized by the photopolymerization technique. The molecular structures of these monomers is shown in Scheme 1.

$CH_2 = CHCOOCH_2CH_3$ EA

$CH_2 = C(CH_3)COO(CH_2CH_2O)_nCH_3$ MPEGMA

$CH_2 = C(CH_3)COO(CH(CH_3)CH_2O)_nCH_3$ MPPGMA

SCHEME 1

EA was commercially available grade. MPEGMA and MPPGMA were supplied by Sinnakamura Chemicals Co. They were polymerized in benzene at 30°C for 3.5 h with a sealed bottle using *p*-xylylene-bis-(N,N-diethyl dithiocarbamate) (XDC) as photoinitiator. The molecular structure of the photoinitiator is shown in Scheme 2.

$C_6H_4(CH_2S_2CN(C_2H_5)_2)_2$

SCHEME 2

EA/MPPGMA/MPEGMA terpolymers had equivalent weight fractions of MPPGMA and MPEGMA but different EA contents, varying from 70 to 95 wt%. In addition, MPEGMA, whose degree of polymerization of PEG was 23 and MPPGMA, whose degree of polymerization of PPG was 20, were used for the polymerization of these terpolymers. Polystyrene (PSt, Mw = 45,000), polymethylmethacrylate (PMMA, Mw = 75,000) and uncoated glass plates were used as references surfaces.

Preparation of Sample Plates

Aluminum plates were used to prepare sample plates for dynamic contact angle measurement. Glass plates were used to prepare sample plates for blood compatibility measurement, since their transparency made it convenient to observe blood clusters adsorbed on the terpolymer surface. The specimens were prepared as follows: The glass and aluminum plates were dipped in an MEK solution of terpolymer or of PMMA, or in a toluene solution of PSt (each 10 wt%). The coated specimens were then dried in a vacuum oven at 65°C for 36 hours. We confirmed by SEM that the plates coated with the polymers had a flat surface.

Preparation of Pressure Sensitive Adhesive Tape

The adhesive tapes of the terpolymers used for the measurement of pressure-sensitive adhesive properties were prepared by solution casting from 20 wt% toluene solution onto a poly(ethylene terephthalate) (PET) film base using a hand coating bar. After coating, the films were dried at 90°C for 10 min and kept at 20°C for more than a week. The terpolymers were 30 μm thick in their dry state. PSA tapes generally consist of adhesive, backing film and release liner. Film surfaces were covered with the release liner.

2.2. Measurements

Dynamic Contact Angle

We carried out dynamic contact angle measurement (DCA) to obtain the fundamental data of surface characteristics of the samples, using the Wilhelmy plate method [6]. A sample plate hanging onto a load cell was dipped into and out of water. In principle, adhesion tension ($F = \gamma_L \cos\theta = \gamma_S - \gamma_{SL}$) was measured and θ was calculated using F and the surface tension of water (γ_L) by this method. We measured DCA at a dipping velocity of 20 mm/min. The principle of the method has been described in detail elsewhere [3].

Adhesion Tension Relaxation

We also measured adhesion tension relaxation using the same sample plate and instrument as for the DCA. The principle of this method was described elsewhere [3]. The measurement was performed as follows: first, the sample plate was mounted so that the bottom was just in contact with the liquid surface; then it was lowered 20 mm at a velocity of 100 mm/min and stopped. At this position, the force ($F_A(t)$) applied to the sample plate in the advancing process was measured as a function of elapsed time (t) for 30 min. Then it was retracted 10 mm and $F_R(t)$ in the receding process was similarly measured for 30 min. Here $F_A(t)$ and $F_R(t)$ could be described, respectively, as follows:

$$F_A(t) + F_b = P\,\gamma_L\,\cos\theta_A(t) = P(\gamma_S - \gamma_{SL,A}(t)) \tag{1}$$

$$F_R(t) + F_b = P\,\gamma_L\,\cos\theta_R(t) = P(\gamma_{S,R}(t) - \gamma_{SL,aq}) \tag{2}$$

where F_b is the buoyancy, a constant value that does not depend on time. P is the perimeter of the sample plate. γ_S and γ_{SL} were the surface tension of the sample plate and the interfacial tension between the sample plate and water, respectively. Suffix A and R indicate advancing and receding processes, respectively.

The variation of $F_R(t)$ was due only to that of $\gamma_{S,R}(t)$ which depended on the rate of reorientation of the PPG segment in the part of the plate which was retracted from the water into the air. We can discuss molecular mobility of polymer *via* $F_A(t)$ and $F_R(t)$.

Gel Permeation Chromatography (GPC)

The molecular weight of the synthesized terpolymers was determined using GPC (SCL-6B, Shimadzu Manufacturing Ltd.) with the PSt standard.

Dynamic Mechanical Properties

The dynamic mechanical properties of the terpolymers were measured by a shearing method using a Rheometrics Co. Ltd. Dynamic

Mechanical Analyzer, type RDA-2. The temperature dependence of dynamic mechanical properties such as storage moduli, G', and loss moduli, G'', and dynamic loss tangent, $\tan\delta$, were measured at an angular velocity, ω, of 6.28 rad/s = 1 Hz.

PSA Properties

Peel adhesion of the terpolymers to stainless steel was measured at 180 degree peel angle using a Toyo Seiki Co. type E-L machine, according to ASTM D1000-79. The peel rate was 300 mm/min. Probe tack of the terpolymers was measured at 23°C, using a Toyo Seiki Co. probe tack tester, type Tmi Series 400 Tester according to ASTM D-2979-71. The probe used in probe tack testing was made of stainless steel. These measurements were carried out at 23°C and 65% RH. Holding power was also measured with stainless steel using a Teraoka Seisakusho Co. Ltd. Creep tester at 40°C and under load of 300 gf, according to PSCT-7. The contact area of the terpolymers and stainless steel was 4.0 cm^2.

Immersion in Whole Blood

Glass plates coated with the sample polymers, glass plates coated with PSt and PMMA, and uncoated glass plates were dipped in 2 ml of whole blood (collected from an adult man) at 37°C for 25 min under static conditions, then rinsed with phosphate buffer solution (PBS). We then observed the adhered blood.

Platelet Adhesion Experiment

A blood sample (90 ml) collected from an adult man was added to sodium citric acid (10 ml), and then centrifuged at 1000 rpm for 10 min. We skimmed platelet-rich plasma (PRP) from this separated blood. A glass plate coated with the sample polymers was dipped in PRP at 37°C for 2 h under static conditions, then rinsed with phosphate buffer solution (PBS). The adsorbed platelets were fixed in 2% glutaraldehyde PBS at 4°C for 24 h. They were dehydrated step by step in ethanol–water solutions of from 50 to 100% ethanol

concentration, and then were dried with a critical point dryer (HCP-2, Hitachi Manufacturing Ltd). After gold vacuum evaporation, we observed the platelet form and the number of adsorbed platelets using SEM.

RESULTS AND DISCUSSION

Characteristics of Synthesized Terpolymers

Table I shows the characteristics of synthesized EA/MPPGMA/MPEGMA terpolymers. Molecular weight of terpolymers were more than 15,000 and the distribution were less than 3.6. Glass transition temperatures (Tg) were from −28.4 to −57.3°C.

Dynamic Contact Angle

The composition dependence of dynamic contact angle (DCA) for EA/MPPGMA/MPEGMA terpolymers is shown in Figure 1. Both advancing contact angles (θ_A) and receding contact angles (θ_R) did not depend on the composition in the region of the measured EA content. However, θ_Rs showed very much lower values than θ_A. Johnson and Dettre [8] showed that, at a heterogeneous surface, a hydrophobic component predominately contributed to the θ_A angle and a hydrophilic one to θ_R. The large values of θ_A for these terpolymers were due to low surface tension segments such as PPG and to the methoxy terminal groups of MPEGMA and MPPGMA. Since the hydrophilic PEG segment could be re-oriented to the polymer/water interface so as to minimize interfacial tension when they were immersed in the water, θ_Rs showed low values.

TABLE I Characterization of terpolymers used

Terpolymer	*Composition (wt%) EA/MPEGMA/MPPGMA*	*Mn*	*Mw*	*Mw/Mn*	*Tg/°C*
EA95	95/2.5/2.5	36900	85600	2.3	−28.4
EA90	90/5/5	19100	68500	3.6	−35.8
EA70	70/15/15	16500	38300	2.3	−57.3

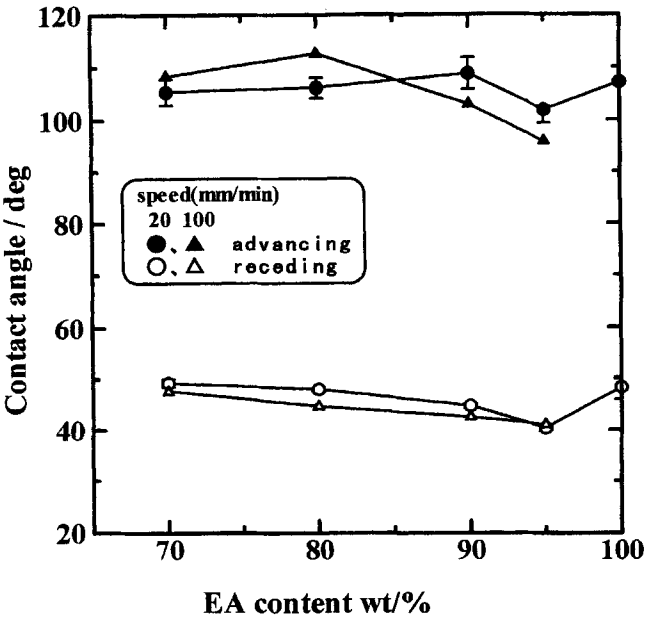


FIGURE 1 Composition dependence of dynamic contact angle (DCA) for EA/MPPGMA/MPEGMA terpolymers.

Adhesion Tension Relaxation

Figures 2 and 3 shows the adhesion tensions $F_A(t)$ and $F_R(t)$, respectively, for EA/MPPGMA/MPEGMA as a function of the elapsed time. $F_A(t)$s for the terpolymers increased with elapsed time but for PEA it did not vary. The increase in $F_A(t)$ was due to the re-orientation of the polyethyleneglycol side chain to the water/polymer interface to decrease the interfacial tension ($\gamma_{SL,A}(t)$ in Eq. (1)). $F_R(t)$ of all samples decreased with elapsed time. The decrease in $F_R(t)$ was due to the re-orientation of the polypropyleneglycol side chain to the surface that retracted from water to air to decrease the surface tension ($\gamma_{S,R}(t)$ in Eq. (2)). This fact showed that these terpolymers had very high molecular mobility.

PSA Properties

Figure 4 shows reversible heat flow curves (DSC) of the terpolymers. Since the Tg of the terpolymers monotonically increases with EA

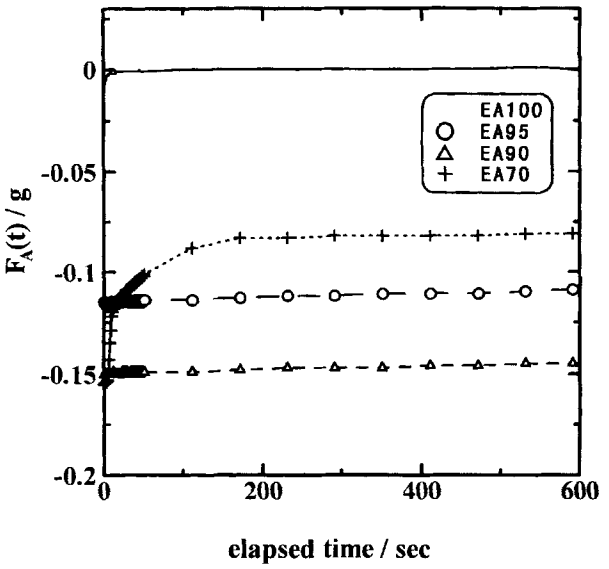


FIGURE 2 Adhesion tension, $F_A(t)$, in advancing process for EA/MPPGMA/MPEGMA as a function of the elapsed time.

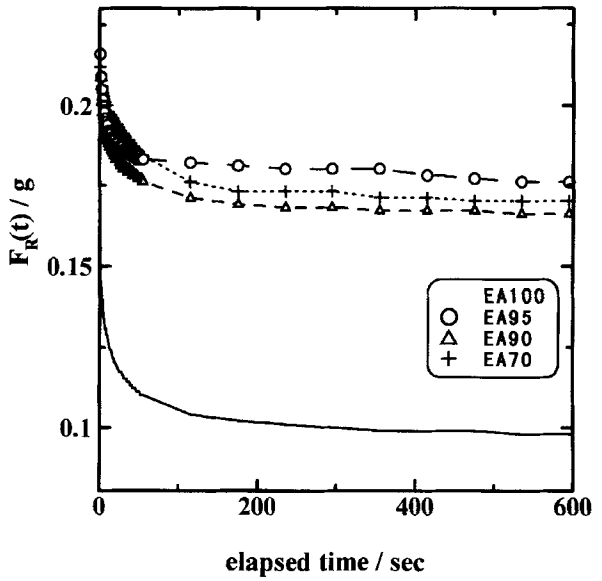


FIGURE 3 Adhesion tension, $F_R(t)$, in receding process for EA/MPPGMA/MPEGMA as a function of the elapsed time.

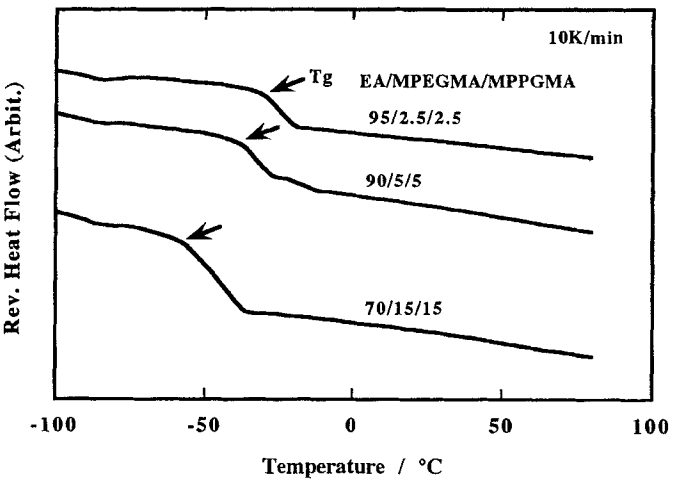


FIGURE 4 Reversible heat flow curves (DSC) for EA/MPPGMA/MPEGMA.

content, we judged that the terpolymers were completely copolymerized.

The PSA properties for the terpolymers are given in Table II. The 180-degree peel strength decreases with decreasing EA content and all samples showed cohesive failure of the adhesive (terpolymer) layer. The maximum value of probe tack was obtained for EA90. In the probe tack measurement, EA70 exhibited cohesive failure of the adhesive layer. The values of holding power decreased with a decrease in EA content. These values of holding power, however, were too low to apply these polymers as PSA. We presumed that the PSA properties of the terpolymers were correlated with dynamic mechanial properties. Therefore, the temperature dependence of dynamic mechanical properties, such as storage moduli, G', loss moduli, G'', and dynamic loss tangent, $\tan\delta$, were measured for the terpolymers and are shown in Figure 5. The G' decreased with rising temperature and increased with increasing EA content. The curves of the G'' *versus* temperature plots were similar to those of the G' *versus* temperature plots for the terpolymers. The maximum temperature of $\tan\delta$ (T_{Dmax}) shifted toward the higher temperature side with increasing EA content. For all terpolymers, G' values at room temperature were lower than 10^5 Pa and a rubbery plateau region could not be observed. Presumably, the

TABLE II PSA properties for terpolymers

Terpolymers	180° *Peel strength/g gf/25 mm*	*Probe tack g/5 mmϕ*	*Holding power (s)*
EA95	1180	640	1000
EA90	720	1030	380
EA70	780	590	60

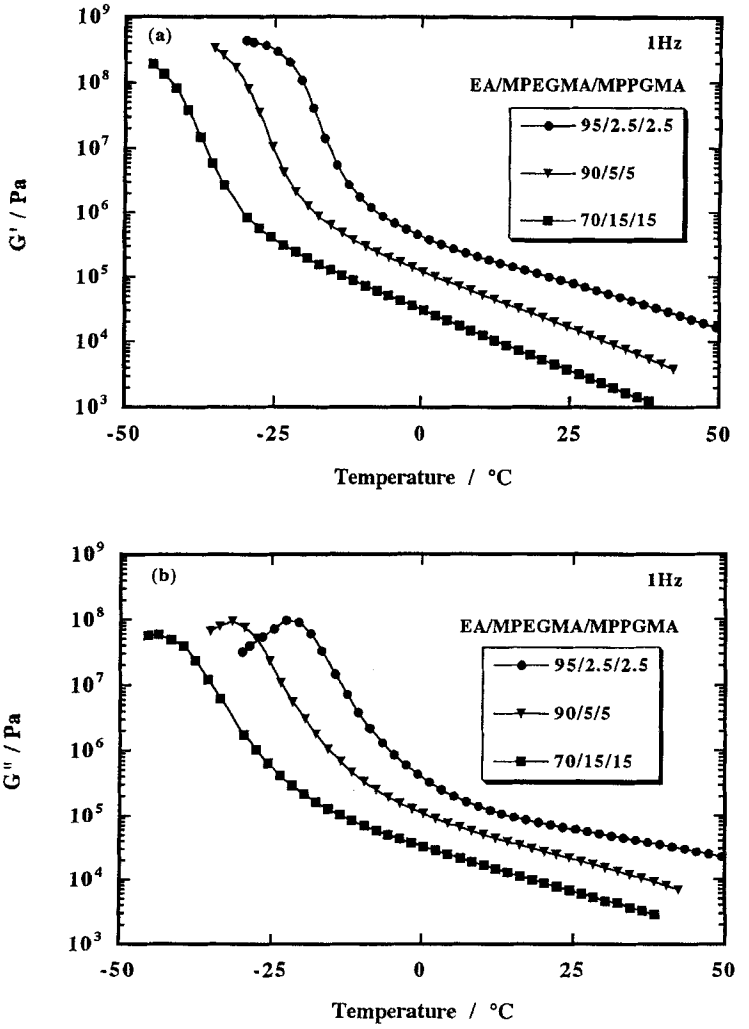


FIGURE 5 Temperature dependence of (a) storage moduli, G', (b) loss moduli, G'', and (c) dynamic loss tangent, $\tan\delta$, for EA/MPPGMA/MPEGMA.

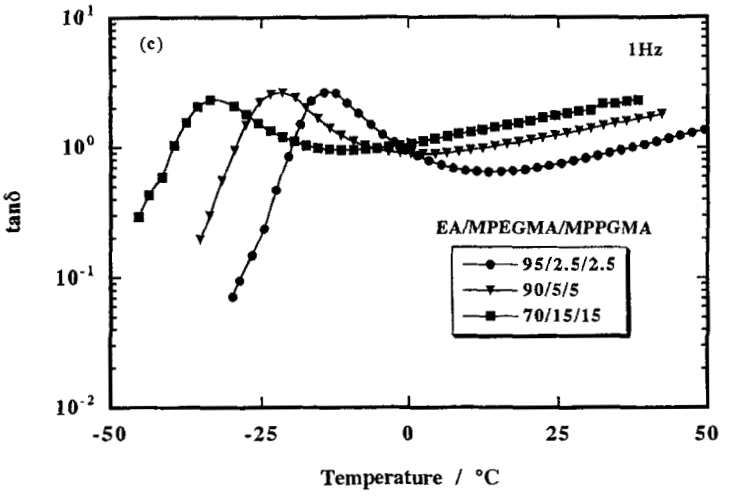
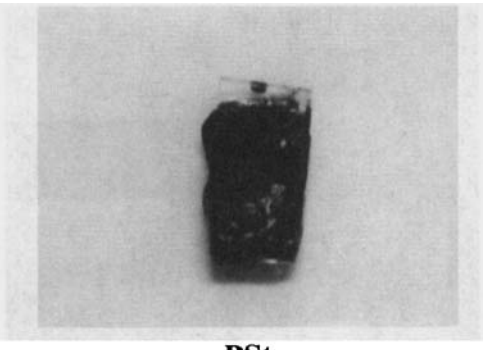


FIGURE 5 (Continued).

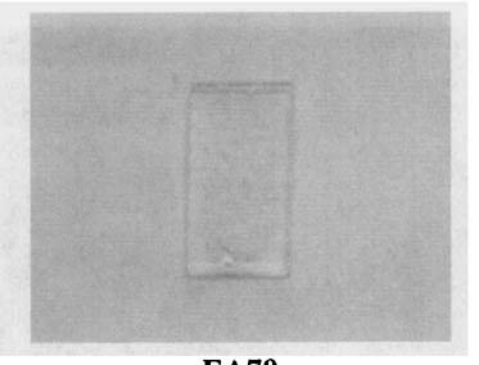
G' behaviors for the terpolymers caused cohesive failure of the adhesive layer. In general, poly(ethyl acrylate) (PEA), poly(butyl acrylate) (PBA) and poly(2-ethylhexyl acrylate) (P2EHA) have been utilized as the main components of acrylic PSAs because these polymers had low $Tg \leq 20°C$ and were very flexible at room temperature. On the other hand, to prevent cohesive failure, acrylic acid (AA) was copolymerized with the above main components and the synthesized copolymer could be crosslinked by a curing agent. In our future studies, we will investigate PSA properties and dynamic mechanical properties of copolymers (EA/MPEGMA/MPPGMA/AA).

Evaluation of Blood Compatibility

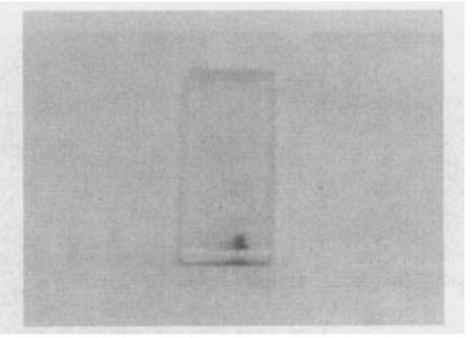
Figure 6 shows photographs of PSt and terpolymers after immersion in whole blood for 25 min under static conditions. PSt was covered with blood clusters over the entire surface. It was clear that the samples had no blood compatibility. On the other hand, on the terpolymers, no blood clusters were observed. These results suggested that these terpolymers had a significant blood compatibility.



PSt

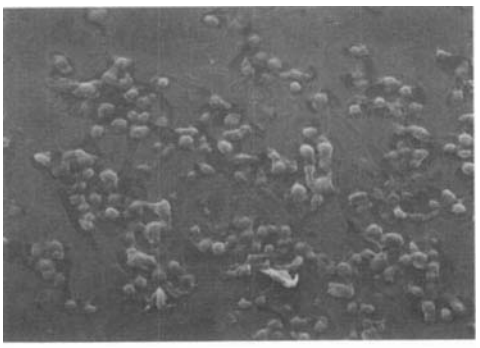


EA70

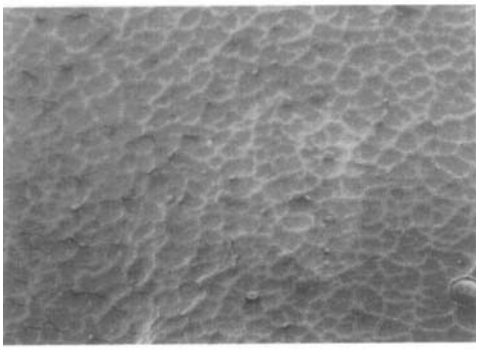


EA90

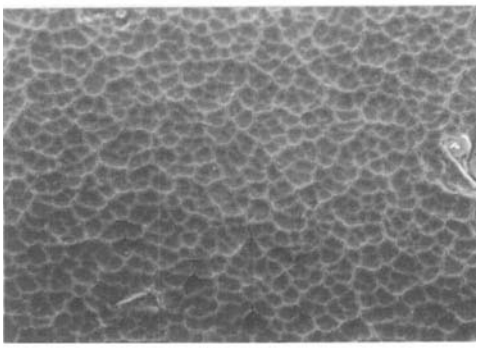
FIGURE 6 Photographs of PSt and EA/MPPGMA/MPEGMA surfaces after immersion in whole blood for 25 minutes under static conditions.



PSt



EA70



EA90

FIGURE 7 SEM photographs for the PSt and EA/MPPGMA/MPEGMA surfaces after immersion in PRP for 2 hours under static conditions.

It is known that thrombus formation is induced by surface activated platelets. Therefore, we investigated the adsorption behavior of the platelets.

Evaluation of Platelet Adhesion

Figure 7 shows SEM photographs for the PSt and terpolymers after immersion in PRP for 2 h under static conditions. On PSt surfaces, many adhered platelets and thrombus formation could be observed. On the terpolymer surfaces, a few adhered platelets were observed but they were not deformed and maintained their native spherical shape. These behaviors correspond to the results of the experiments of immersion in whole blood as shown above.

CONCLUSION

EA/MPPGMA/MPEGMA terpolymers were synthesized. The high molecular mobility for these terpolymers was shown by dynamic contact angle and adhesion tension measurement. The 180-degree peel strength and probe tack for PSAs made of these terpolymers were good but the holding power was not enough to apply them as PSAs. It was found that these terpolymers should be modified to obtain high holding power. The blood compatibility of these terpolymers was also investigated. Terpolymers had a significant blood compatibility. Thrombus formation was not observed on the terpolymer surfaces after immersion in blood, while on the PSt surface many blood clusters were observed. After immersion in PRP, a few adhered platelets were observed on the terpolymer surfaces but they did not deform and maintained their spherical form, while many platelets were observed on PSt.

It was found that a blood compatible PSA could be developed using these terpolymers. Although we have not any idea on practical application of blood compatible PSA in medical use, we expected that it may be able to apply in this field.

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