

Dynamic Mechanical Properties of Photopolymerizable Poly(vinyl Alcohol)-Acrylate Monomer Blends

MITSUBU KOSHIBA,* TSUGUO YAMAOKA, and TAKAHIRO
TSUNODA, 1-33 Yayoicho, Chiba-shi, Chiba 260, Japan

Synopsis

Dynamic mechanical properties of photopolymerizable poly(vinyl alcohol) (PVA)-monoacrylate blends were investigated by measuring dynamic shear modulus G' and loss tangent, $\tan \delta$. The dynamic mechanical properties of the blends before being exposed to UV irradiation were governed by the weight percent of the monomers which act as plasticizers. On the other hand, the UV-irradiated blends seemed to be typical two-phase materials since they revealed two $\tan \delta$ maxima whose positions were independent of the monomer content. Those two maxima were assigned to PVA and photopolymerized acrylates with reference to the dynamic mechanical data of PVA and a PVA-polyacrylamide polyblend. Those dynamic mechanical data suggested that insolubilization of the blend type photopolymers should be caused by a decrease in solubility due to graft polymerization of acrylate monomers onto PVA.

INTRODUCTION

Blend-type photopolymers are widely used as plate-making materials for letterpress plates. In general, the photopolymers consist of binder polymer, photopolymerizable mono-, di-, and/or trifunctional monomers, and initiator. Typical binder polymers are water-soluble poly(vinyl alcohol) and alcohol-soluble nylon from the ecological point of view. UV irradiation initiates polymerization of the monomers contained, giving rise to a difference in solubility between irradiated and unirradiated parts. The letterpress plates are obtained by subsequent washing out of the unirradiated part with a suitable developer such as water and alcohol. Consequently, the mechanical properties of the irradiated part are important factors in terms of durability, processability, and printability of the letterpress plates. There have been, however, few studies¹ on these materials in terms of their mechanical properties, while several studies have been carried out on kinetic aspects because they involve reactions of photochemical interest. Moreover, any effective information has not been offered about molecular structures of the photopolymerized matrices, or we do not yet know what brings about the difference in solubility between the irradiated and unirradiated parts.

In the present paper, the main objective is to understand the relationships between mechanical properties and compositions of poly(vinyl alcohol)-monoacrylate blend photopolymers. The measurement of the dynamic mechanical

* Present address: Japan Synthetic Rubber Co., Ltd., 3-5-1 Higashi Yurigaoka, Asao-ku, Kawasaki 214, Japan.

TABLE I
 Sample Characterization

Sample code	PVA (g) ^a	nMAA (g) ^b	AA (g) ^c	2HEMA (g) ^d	Initiator (g) ^e	Irradiation time (min)
M-50-0	1.0	0.5			0.13	0
M-50-180	1.0	0.5			0.13	180
M-20-0	1.0	0.2			0.052	0
M-20-5	1.0	0.2			0.052	5
M-20-10	1.0	0.2			0.052	10
M-20-20	1.0	0.2			0.052	20
M-20-60	1.0	0.2			0.052	60
M-20-180	1.0	0.2			0.052	180
M-10-0	1.0	0.1			0.026	0
M-10-180	1.0	0.1			0.026	180
M-5-0	1.0	0.05			0.013	0
M-5-180	1.0	0.05			0.013	180
A-20-0	1.0		0.2		0.095	0
A-20-180	1.0		0.2		0.095	180
A-10-0	1.0		0.1		0.048	0
A-10-180	1.0		0.1		0.048	180
A-5-0	1.0		0.05		0.024	0
A-5-180	1.0		0.05		0.024	180
H-5-180	1.0			0.05	0.049	180

^a Poly(vinyl alcohol).

^b *N*-methylolacrylate.

^c Acrylamide.

^d 2-(Hydroxyethyl)methacrylate.

^e 2,2'-Azobis-(2-amidinopropane)-dihydrochloride.

properties should not only be of rheological interest, but will provide some information about the molecular structures and morphology of the materials.

EXPERIMENTAL

Preparation of Samples. Commercially available poly(vinyl alcohol) (PVA) (Nihon Gosei Gosenol NM-11, saponification value 98.5%) was dissolved in water to make 10% aq solution in weight and the prescribed amounts of monomer and initiator [2,2'-azobis-(2-amidino propane)dihydride] were added to the solution. Three kinds of monofunctional acrylate monomers were used; *N*-methylol acrylamide (nMAA), acrylamide (AA), and 2-(hydroxy ethyl)methacrylate. The sample code and composition are summarized in Table I. Although the sample codes are listed in Table I, let them be explained here; the first letters—A, M, and H—represent acrylamide, *N*-methylol acrylamide, and 2-(hydroxyethyl)-methacrylate, respectively. The numbers in the middle represent parts of the monomers to 100 g of PVA, and the last numbers denote the irradiation time (min).

The mixtures were cast on a ferrotype plate and dried under a constant condition (25°C for 48 h in air) to make the amount of residual water in the sample strips constant. Dimensions of the sample strips were approximately 120–150 $\mu\text{m} \times 0.8 \text{ cm} \times 4.5 \text{ cm}$.

Some of the sample strips were irradiated on both sides in an N₂ gas stream

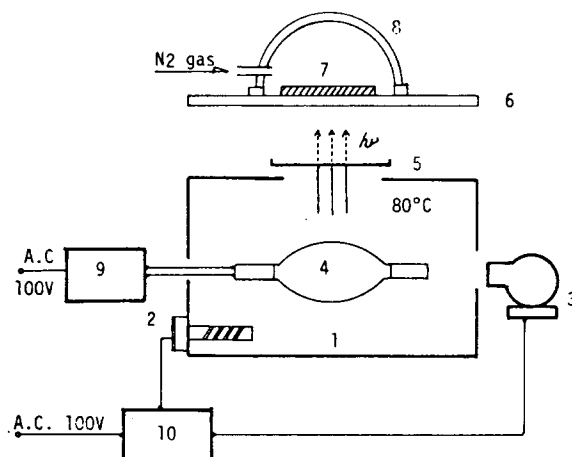


Fig. 1. A UV irradiation apparatus used in this study: (1) light source chamber; (2) thermostat; (3) blower; (4) high pressure mercury lamp; (5) shutter; (6) Pyrex glass plate; (7) sample; (8) sample chamber; (9) power source; (10) relay.

(1680 mL/min) by using a UV irradiation apparatus ($1.5 \text{ mJ/cm}^2\text{-s}$) illustrated in Figure 1. The irradiated samples were additionally dried under reduced pressure (10^{-2} mmHg) at 25°C for 10 h.

Dynamic Mechanical Measurement. Dynamic mechanical properties, dynamic shear modulus G' , and loss tangent, $\tan \delta$, of the sample strips were

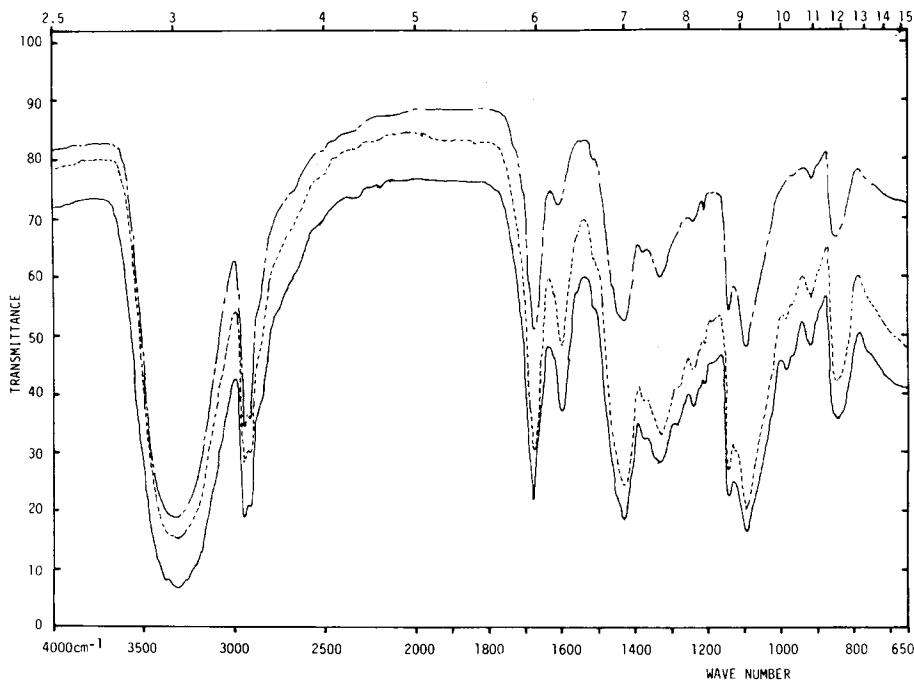


Fig. 2. Infrared spectra of a M-50 series (PVA/nMAA = 1.0/0.5) before and after UV irradiation (min): (---), 0; (- - -) 15; (—) 45.

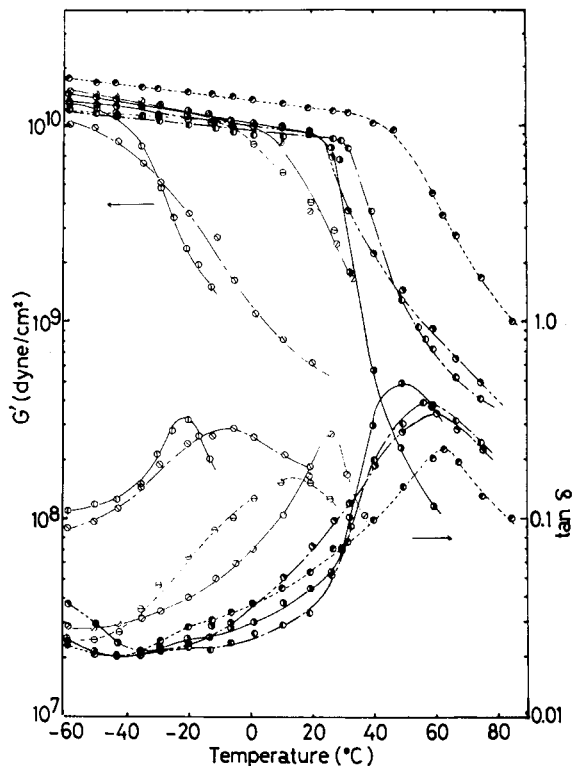


Fig. 3. Dynamic mechanical properties, shear modulus G' , and loss tangent, $\tan \delta$, of a PVA-nMAA series before and after UV irradiation: (\oplus) M-50-0; (\ominus) M-20-0; ($\omin�$) M-10-0; (\odot) M-5-0; (\bullet) M-50-180; (\circ) M-20-180; (\ominus) M-10-180; (\bullet) M-5-180.

measured by a recording torsion pendulum. The frequency of oscillation was not kept constant, but was in the range of 0.4–2.5 Hz. The heating rate of the sample chamber was about 1.5°C/min, and temperature was detected using a copper–constantan thermocouple.

Extraction of Water-Soluble Fractions of Irradiated Samples. Water-soluble fractions of the samples irradiated for 180 min were extracted in refluxing water for 24 h. The insoluble fractions were collected by filtration and weighed to calculate gel–sol ratios. Infrared spectra of the both fractions were measured at the same time.

RESULTS AND DISCUSSION

Photochemical Reactions. The main photochemical reaction of the PVA–acrylate monomer blends was followed by taking the infrared spectra of the samples at different irradiation time. The typical changes are shown in Figure 2. No appreciable change was observed except decreases in absorption peaks at 1600, 990, and 810 cm^{-1} associated with a C=C bond. This implies that the main photochemical reaction is photopolymerization of the acrylate monomers.

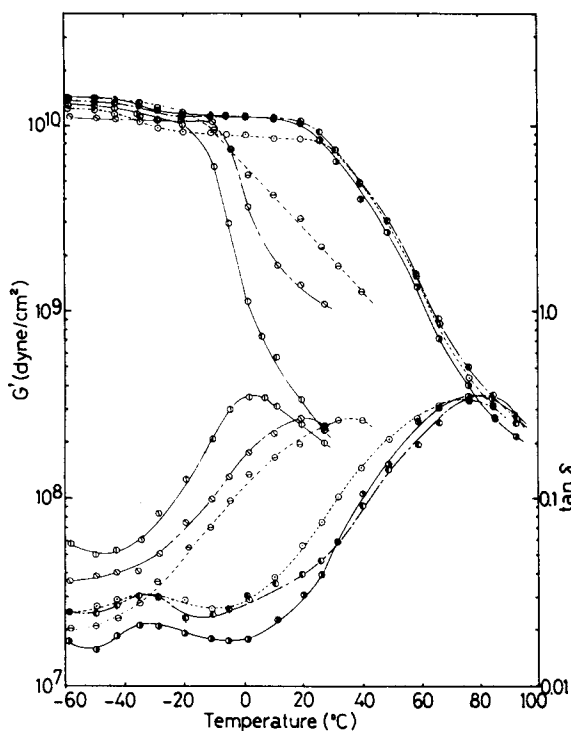


Fig. 4. Dynamic mechanical properties, shear modulus G' , and loss tangent, $\tan \delta$, of a PVA-AA series before and after UV irradiation: (○) A-20-0; (□) A-10-0; (△) A-5-0; (●) A-20-180; (■) A-10-180; (◇) A-5-180.

Dynamic Mechanical Properties. In Figures 3, 4, and 5 are plotted $\log G'$ and $\tan \delta$ obtained by a torsion pendulum experiment against temperature for unirradiated and 180-min irradiated PVA-nMAA, PVA-AA, and PVA-2HEMA (only for an irradiated sample) blends, respectively. Temperatures of $\tan \delta$ maxima are listed in Table II. In our measurement the frequency of oscillation was not kept constant but was in the range of 0.4–2.5 Hz. The temperatures of the $\tan \delta$ maxima could be different if the measurement had been done at exactly at 1 Hz. However, the deviation of the temperatures resulting from the frequency change should be within 2°C, based upon the relationship² between frequency and $\tan \delta$ maximum temperature proposed by Nielsen.

UV irradiation caused a shift of the transition zone to higher temperature, and two maxima, $T_{\max 1}$ and $T_{\max 2}$, became observable for the samples irradiated for 180 min. Hereafter $T_{\max 1}$ and $T_{\max 2}$ denote the lower and higher temperature maxima in $\tan \delta$ for irradiated samples, respectively.

Temperatures of $\tan \delta$ maxima for unirradiated samples, T_{\max} , greatly depend upon the monomer contents; Samples with lower monomer contents have higher T_{\max} , whereas $T_{\max 1}$ and $T_{\max 2}$ of the irradiated samples are less influenced by the monomer contents. A relationship³ between a glass transitions temperature of a plasticized polymer, T_g , and a weight fraction of the plasticizer, w , is expressed by the following equation (the whole equation is divided by $1-w$ for convenience):

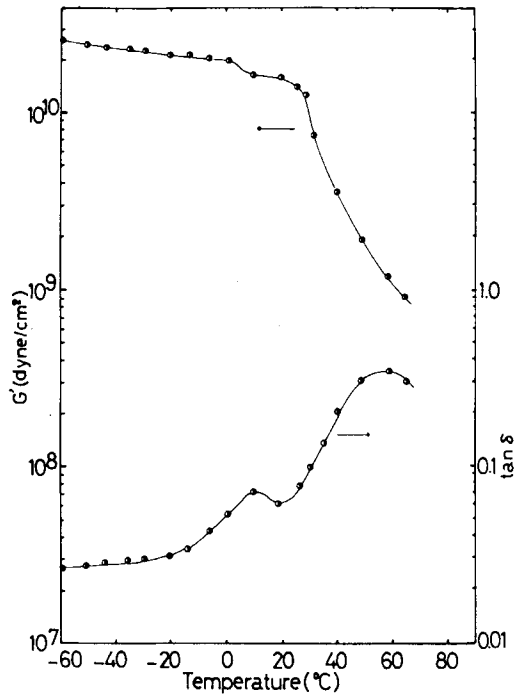


Fig. 5. Dynamic mechanical properties, shear modulus G' , and loss tangent, $\tan \delta$, of a PVA-2HEMA series after UV irradiation (H-5-180).

$$\frac{1}{T_g} \times \frac{1}{1-w} = \frac{1}{T_{ga}} + \frac{1}{T_{gb}} \times \frac{w}{1-w} \quad (1)$$

where T_{ga} and T_{gb} are glass transition temperatures of the unplasticized polymer and plasticiser ($^{\circ}\text{K}$), respectively.

TABLE II
Results of Dynamic Mechanical Measurements

Sample code	Before UV irradiation	After UV irradiation	
	T_{\max} ($^{\circ}\text{C}$)	$T_{\max 1}$ ($^{\circ}\text{C}$)	$T_{\max 2}$ ($^{\circ}\text{C}$)
M-50-0	-20		
M-50-180		-70 (approx.)	51
M-20-0	-4.8		
M-20-180		-70 (approx.)	58
M-10-0	14		
M-10-180		-70 (approx.)	60
M-5-0	28		
M-5-180		-70 (approx.)	63
A-20-0	4.6		
A-20-180		-34	78
A-10-0	20		
A-10-180		-31	81
A-5-0	28		
A-5-180		-28	75
H-5-180		10	58

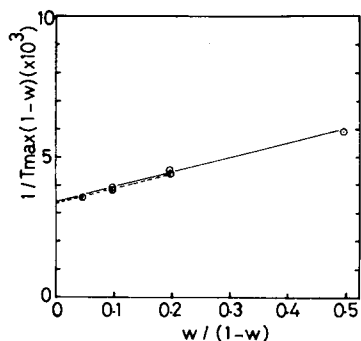


Fig. 6. Plots of $w/(1-w)$ vs. $1/[T_{\max}(1-w)]$ for PVA-nMAA and PVA-AA series.

Assuming that the temperature of a $\tan \delta$ maximum, T_{\max} , corresponds to a glass transition temperature of the sample, $1/[T_{\max}(1-w)]$ is plotted against $w/(1-w)$ for unirradiated samples in Figure 6, where w is a weight fraction of the monomer contained. It is obvious that a linear relation is applicable between $1/[T_{\max}(1-w)]$ and $w/(1-w)$. The extrapolated values to the ordinate, equal to the glass transition temperature of PVA according to eq. (1), is 35°C for PVA-AA blends and 29°C for PVA-nMAA blends. Figure 7 shows dynamic mechanical properties of PVA prepared under the same condition as for the unirradiated samples. The temperature of a $\tan \delta$ maximum for this PVA is 28°C and is in good agreement with the extrapolated values. Thus mechanical properties of the unirradiated PVA-monofunctional acrylate monomer blends are governed by weight fractions of the monomers, which act as plasticizer.

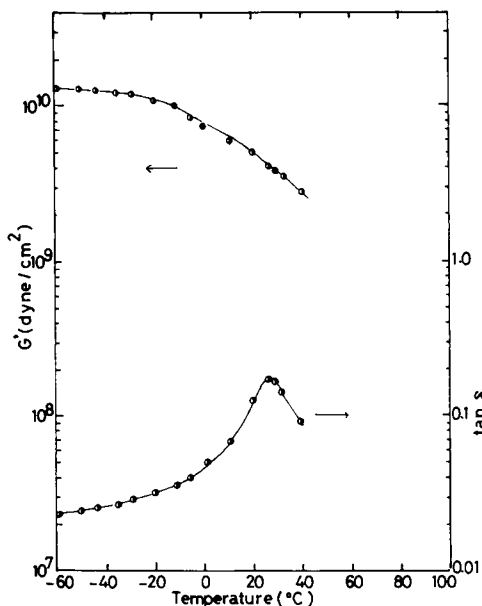


Fig. 7. Dynamic mechanical properties, shear modulus G' , and loss tangent, $\tan \delta$, of a PVA sample strip prepared under the same conditions as those for the sample strips before UV irradiation.

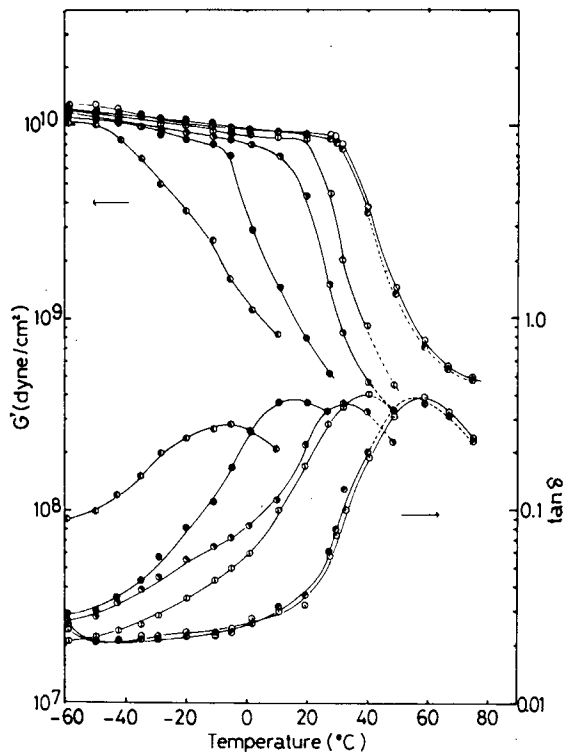


Fig. 8. Irradiation time dependence of dynamic mechanical properties of a PVA-nMAA series: (○) M-20-0; (●) M-20-5; (●) M-20-10; (⊙) M-20-20; (●) M-20-60; (○) M-20-180.

Morantz and Bilen¹ reported that, during photopolymerization of acrylamide in alcoholic medium, the specimen turned opaque with the coexistence of alcohol as was the case in the present study. He concluded that this phenomenon should be attributed to copolymerization between acrylamide and alcohol. In our case, it is more likely that this phenomenon should be attributed to phase separation⁴ between PVA and photopolymerized acrylate monomers since two $\tan \delta$ maxima are observed in the dynamic mechanical study.

In Figure 8 are shown dependence of $\log G'$ and $\tan \delta$ curves on the irradiation time for an M-20 series. It is seen that the transition zone and $\tan \delta$ curves shift to higher temperatures as the irradiation time increases. These shifts to higher temperatures should be ascribed to a decrease in the amount of the monomers acting as plasticizer, meaning that UV irradiation results in photopolymerization of the monomer.

In Figure 9 are shown dynamic mechanical properties of PVA and a PVA-polyacrylamide (PVA-polyAA) polyblend. The number average molecular weight of polyAA is $70-100 \times 10^4$. Both samples were prepared under the sample conditions as the irradiated samples. It is generally known⁵ that such composite materials as incompatible polyblends, grafted polymers, and block copolymers reveal two $\tan \delta$ maxima, and these two maxima are believed to be associated with glass transition of the two components. The dynamic mechanical data of a PVA-polyAA polyblend reveal two $\tan \delta$ maxima, which is suggestive of phase

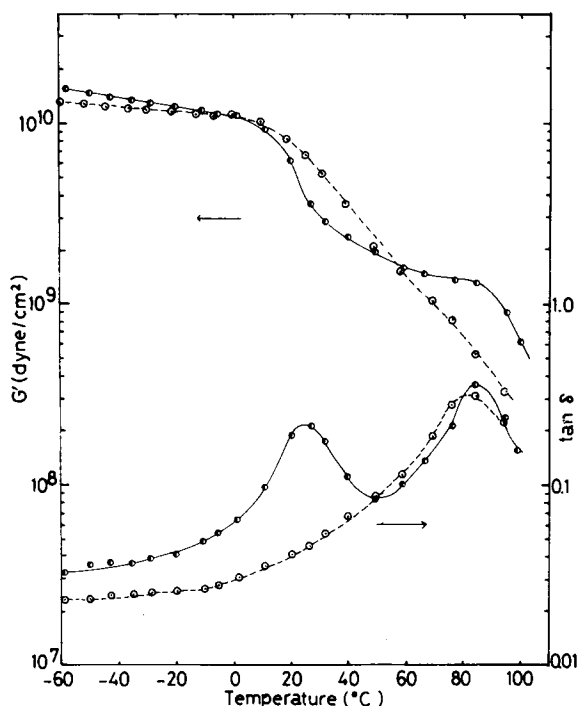


Fig. 9. Dynamic mechanical properties, shear modulus G' and loss tangent, $\tan \delta$, of PVA and a PVA-polyacrylamide polyblends: (\odot) PVA; (\bullet) PVA-polyAA.

separation.⁴ The higher and lower maxima are assigned to glass transition of PVA and polyAA, respectively, with reference to dynamic mechanical data of PVA. $T_{\max 2}$ of the samples irradiated for 180 min is located lower than that of polyAA in the PVA-polyAA polyblend by 45°C. The lower $T_{\max 2}$ may be explained by a fairly low degree of polymerization of AA in a PVA matrix since mobility of the AA monomer is limited during the solid state polymerization. It is conclusive that the two maxima of $\tan \delta$ of the samples irradiated for 180 min, $T_{\max 1}$ and $T_{\max 2}$, are assigned to the glass transition of PVA and photopolymerized monomer chains with a fairly low degree of polymerization.

Molecular Structure of Irradiated Samples. Table III shows the sol-gel fractions of the samples irradiated for 180 min, which were obtained by water

TABLE III
Sol-Gel fraction of Samples Irradiated for 180 min

Sample code	Monomer weight fraction w (%)	Sol fraction (%)	Gel fraction (%)
M-50-180	33.3	39.3	60.7
M-20-180	16.7	59.5	40.5
M-10-180	9.1	68.0	32.0
M-5-180	4.8	90.1	9.9
A-20-180	16.7	93.8	6.2
A-10-180	9.1	99.1	0.9
A-5-180	4.8	100.0	0.0

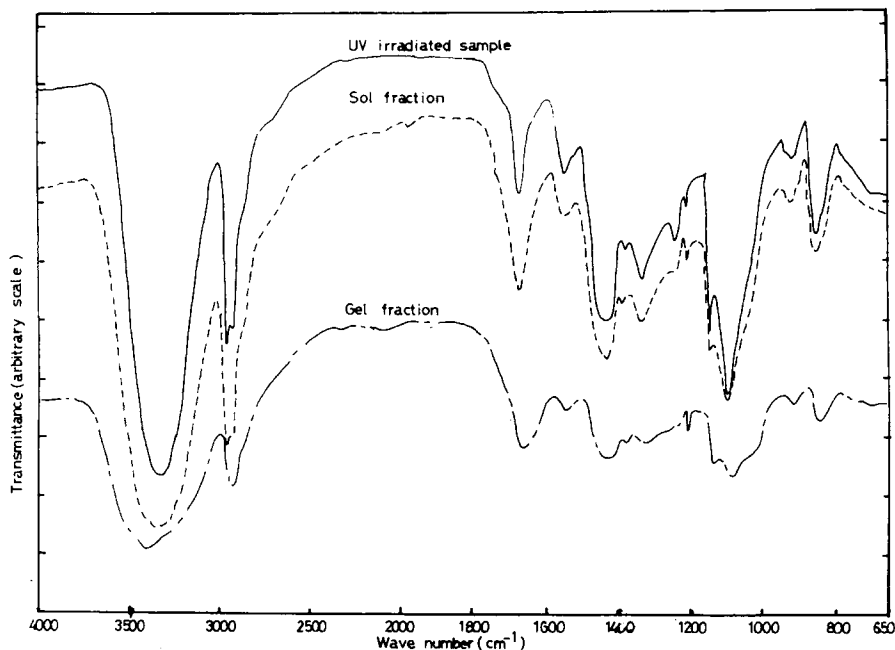


Fig. 10. Infrared spectra of a UV irradiated sample (M-20-180), and its sol and gel fractions.

extraction methods. Figure 10 shows an example of the infrared spectra of the sample irradiated for 180 min and its water soluble (sol) and insoluble (gel) fractions. The gel fraction increases in proportion to a weight fraction of the monomer contained. In addition, no distinct difference among those three spectra is observed. Those two observations suggest that both PVA and photopolymerized monomers are involved in sol and gel fractions, so that it is deduced that the irradiated samples are graft polymers of PVA and acrylate monomers. PVA may be grafted and/or crosslinked by photopolymerized monomer chains with a fairly low degree of polymerization.

CONCLUSIONS

The mechanical properties of PVA-monofunctional acrylate blend system before UV irradiation are governed by the weight fraction of monomers contained which act as a plasticizer. On the other hand, the UV-irradiated samples are typical heterogeneous composite materials which reveal two $\tan \delta$ maxima associated with PVA and photopolymerized acrylated monomer chains with a fairly low degree of polymerization.

It has been generally believed that insolubilization of the blend type photopolymers is attributed to entanglement between binder polymers and photopolymerized monomer chains. With reference to the results obtained in the present study, however, it is more reasonable to consider that the insolubilization is caused by a decrease in solubility due to graft polymerization and/or crosslinking of the systems.

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