Surface Free Energy Analysis of Vinyl Triethoxy Silane-Methyl Methacrylate Copolymers and Their Homopolymer Blends

TUNCER ÇAYKARA,[1] MEHMET S. EROĞLU,[2] OLGUN GÜVEN[3]

[1] Gazi Univetsity, Faculty of Art and Science, Department of Chemistry, 06500, Besevler, Ankara, Turkey

[2] TUBİTAK-Marmara Research Centre, Department of Chemistry, P.O. Box 21, 41470, Gebze, Kocaeli, Turkey

[3] Hacettepe University, Department of Chemistry, 06532, Beytepe, Ankara, Turkey

ABSTRACT: Methyl methacrylate (MMA) was copolymerized with vinyl triethoxy silane (VTES) using ^{60}Co γ-radiation at varying mol fractions of VTES from 0.02 to 0.11. The homopolymers of MMA and VTES were also synthesized by the same method. Homopolymer blends having different VTES mol fractions varying from 0.03 to 0.15 were prepared. The mol fractions of VTES units in the synthesized copolymers were determined by elemental analysis of Si using inductive coupling plasma spectroscopy (ICP). The thin copolymer and homopolymer blend films were prepared by casting from tetrahydrofurane (THF) on a mercury surface. Contact angles of paraffin, water, ethylene glycol, dimethyl formamide, and glycerol drops were measured on these copolymer and homopolymer blend films. Contact angle data were evaluated for the determination of surface free energy components of the copolymer and homopolymer blend films by using Van Oss-Good methodology. It was observed that the Lifshitz-Van der Waals component (γ_s^{LW}) and the electron donor component (γ_s^-) of the surface free energy of copolymer and homopolymer blend films were changed to a considerable extent with the change in the VTES mol fraction of both copolymers and homopolymer blends. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1551–1556, 1998

Key words: surface free energy analysis; vinyl triethoxy silane-methyl methacrylate copolymers; homopolymer blends

INTRODUCTION

Silicon-containing monomers and their formed polymers have attracted special interests because they incorporate the beneficial properties of organic and silane groups into the same molecule. The common spot-lighted properties of these materials are extremely low glass transition temperature, high chain flexibility, UV stability, biocompatibility, surface activity, and high oxygen permeability.[1] Because of these exceptional properties, silicon-containing polymers and their copolymers with different vinyl monomers have found application in many areas such as surface modification, enzyme immobilization, gas separation, biomedical applications, etc. Therefore, a lot of work has been done to observe the improving effect of organosilicon materials on the aforementioned properties of different copolymers and homopolymer blends.[2–10]

For many years, organofunctional silanes have been widely used as coupling agents with an aim to improving the total adhesive strength and
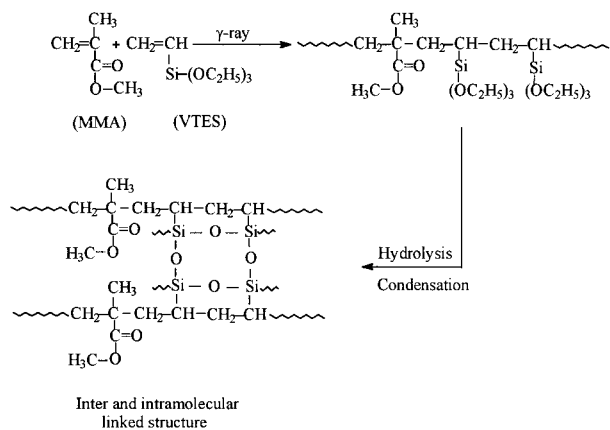
Scheme 1

aging resistance of organic and inorganic substrates.[4,7,9,10] One of the most known organofunctional silane is vinyl triethoxy silane (VTES), which has three hydrolyzable ethoxy groups attached to silicon, and this imparts additional chain flexibility and improves the adhesive properties against substrates containing Si such as glass and stone. Bonds are made by energetic interaction by forming siloxane bonds between silane groups of the substrate and the organic phase. The hydrolysis of ethoxy groups of VTES in both the copolymer and blend takes place through the elimination of alcohol and water accompanied by the formation of Si—O—Si bonds. The result is a inter- and intramolecular-linked structure, as depicted in Scheme 1.[7,8,11] This coupling phenomenon imparts an additional mechanical resistivity into copolymers and blends carrying VTES and vinyl monomers such as vinyl esters, vinyl chloride, styrene, and methyl methacrylate.

The copolymers carrying (VTES) and methyl metacrylate (MMA) units and their homopolymer blends are strongly expected to have promising applications on the simultaneous preservation and consolidation of archaeological artifacts made of stone or glass. Therefore, the primary objective of this study is to conduct radiation-induced copolymerization and homopolymerization of VTES and MMA monomers, and secondly, to prepare their homopolymer blends and also to analyze the surface free energy properties of copolymers and homopolymer blends using contact angle measurements. For this purpose, contact angle measurements was employed for the data to calculate the surface free energy components of copolymers and homopolymer blends carrying different

amounts of VTES moieties, and these were evaluated by Van Oss-Good methodology with a comparison of their surface free energy properties.

EXPERIMENTAL

Materials

Methyl methacrylate was purchased from Merck and purified by passing through a column filled with adsorption alumina (Al_2O_3). Vinyl triethoxy silane was purchased from Merck and distilled under reduced pressure, with care being taken to avoid contact of monomer with air and moisture. Tetrahydrofurane and methanol were used as solvents and nonsolvent for copolymers, respectively. They were purchased from Merck, dried over anhydrous calcium chloride for a day, and then distilled prior to use.

Synthesis of VTES and MMA Copolymers and Homopolymers

To synthesize the copolymers of vinyl triethoxy silane (VTES) and methyl methacrylate (MMA), various monomer mixtures having different VTES/MMA mol ratios were placed in glass tubes and evacuated to 10^{-7} mmHg. Before sealing the glass tubes, the dissolved gas (air) in the reaction mixture were removed by freezing and thawing cycles. After the glass tubes were flame sealed, monomer mixtures were irradiated with a γ-ray to a dose of 8.5 kGy at room temperature. The dose rate was determined as 0.60 kGy h^{-1} by using a standard Fricke dosimeter. After irradiation, copolymers were dissolved in 5 mL tetrahydrofurane and precipitated with 100 mL dry methanol. The precipitated copolymers were filtered and dried under 650 mmHg vacuum at 50°C. The copolymer compositions and reaction yield were calculated from their carbon, hydrogen, and silicon content. To obtain the homopolymers of VTES or MMA, pure monomers were placed in a reaction tube and polymerized by the same procedure mentioned above. MMA was completely polymerized at 8.5 kGy dose. However, homo-PVTES could be synthesized at relatively a high irradiation dose, namely 290 kGy. This is due to the difference between reactivity ratios of MMA and VTES (reactivity ratios of MMA and VTES are 1.04 and 0.2, respectively).[12,13] This homopolymer was a viscose liquid and showed poor physical properties.

As shown in Scheme 1, The hydrolyzation of

Table I   Contact Angle Results of VTES/MMA Copolymer Films

VTES Mol Fraction	Contact Angle, θ				
	Paraffin	Water	Glycerol	Dimethyl Formamide	Ethylene Glycol
0.00	23	67	60	45	40
0.02	42	78	76	64	53
0.06	40	88	86	83	79
0.07	38	93	89	88	87
0.08	37	95	90	90	89
0.11	32	97	91	91	90

copolymer containing MMA and VTES units yields intra- as well as intermolecular linked network structures.[8,12] This property has been exploited to determine the conversion of the monomer mixture to copolymers. For this purpose, copolymer samples were hydrolyzed in the presence of water at 85°C for 24 h[2,8] and the homo-PMMA portion of the resultant network was extracted in THF for 24 h at room temperature. After extracted samples were dried under 650 mmHg vacuum at 50°C, they were weighed. It was observed that the weight of the copolymer samples after hydrolysis did not change considerably.[8,13]

Instrumentation

Irradiation of the reaction mixture was carried out in a Gammacell 220 type ^{60}Co-γ irradiator. Carbon and hydrogen content of copolymers were determined by using a Carlo Erba 1106 model elemental analyzer. For the determination of Si content of copolymers, an Atom Scan 25 model Inductive Coupling Plasma Spectroscopy (ICP) was used. The contact angle measurements were carried out by using a model G-III Contact Angle Meter (Kernco Instrument Co. Inc., El Paso, TX).

Preparation of Copolymer and Homopolymer Blend Films

Copolymer and homopolymer blend films of VTES and MMA were prepared by solution casting from THF. To obtain the copolymer films having the uniform thickness, samples were dissolved in THF and the solutions were cast on the mercury surface. Evaporation of the THF was done slowly at room temperature, and the copolymer films were dried in a vacuum oven at 40°C.

For the preparation of blend films of PVTES and PMMA, stock solution of each homopolymer (4% by weight) were prepared in THF and the predetermined amounts of solution were mixed and poured on the mercury surface. The solvent was slowly evaporated at room temperature and the films were dried in a vacuum oven at 40°C.

Contact Angle Measurements

The surface free energy components of VTES and MMA block copolymer and their homopolymer

Table II   Contact Angle Results of PVTES/PMMA Homopolymer Blend Films

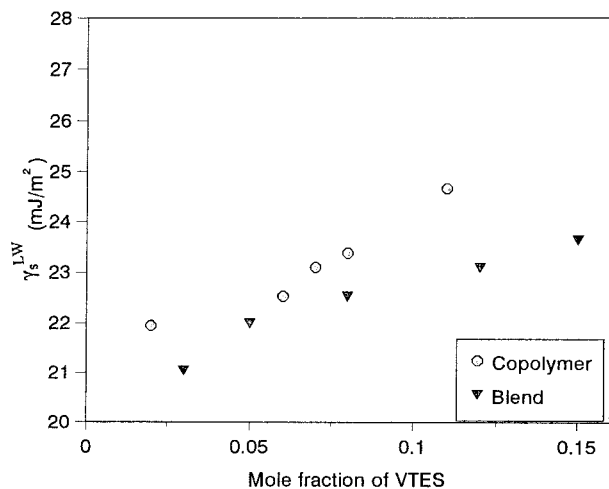| VTES Mol Fraction	Contact Angle, θ				
	Paraffin	Water	Glycerol	Dimethyl Formamide	Ethylene Glycol
0.00	23	67	60	45	40
0.03	45	88	85	84	82
0.06	41	90	88	85	84
0.08	40	91	90	87	85
0.12	38	93	92	89	88
0.15	36	97	95	93	91

Figure 1 Change of γ_S^{LW} with the mol fraction of VTES in copolymers and blends.

blend films cast from THF were determined by measuring the contact angles of water, glycerol, ethylene glycol, dimethyl formamide, and paraffin oil drops on the copolymer and blend surfaces. Drops of each liquid of 5 μm in size were deposited onto the polymer surface with a hypodermic syringe. The readings on the drop were directly taken using a cathetometer fitted with a gonimeter eyepiece at 20°C. The one-liquid method (air–liquid drop-polymer system) was used. All measured contact angle values were an average of three measurements within ±2° deviation.

RESULTS AND DISCUSSION

The surface free energy components of the copolymers and blend films containing various mol fraction of VTES units were calculated from the contact angle data of various liquids by using Van Oss-Good methodology. The free energy components of the solid in contact with a liquid can be represented by the following complete Young equation comprising both the apolar and polar interactions.[14,15]

$$\gamma_L(1 + \text{Cos } \theta)$$
$$= 2(\sqrt{\gamma_s^{LW}\gamma_L^{LW}} + \sqrt{\gamma_s^-\gamma_L^+} + \sqrt{\gamma_s^+\gamma_L^-}) \quad (1)$$

In the above equation, the superscript LW represents the apolar Lifshitz-Van der Waals forces. Subscripts L and S refer to liquid and solid. respectively. γ_L is the total surface free energy of liquid, θ is the contact angle of liquid drop on the

solid surface, and γ_L^{LW} and γ_S^{LW} are the apolar Lifshitz-Van der Waals components of liquid and solid, respectively. γ_S^+ and γ_L^+ are the electron–acceptor surface free energy components of solid and liquid, respectively. γ_S^- and γ_L^- are the electron donor components of the surface free energy of solid and liquid, respectively. For an apolar liquid, $\gamma_L^+ = \gamma_L^- = 0$ and $\gamma_L^{LW} = \gamma_L$; hence, the last two terms of the right hand side of eq. (1) become zero, and therefore, this equation can be written as follows,

$$\gamma_L(1 + \text{Cos } \theta) = 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} \quad (2)$$

By using eq. (2) and the data obtained from contact angle measurements for an apolar liquid, γ_S^{LW} of the solid can be calculated. The remaining electron donor and acceptor components of the surface free energy of the solid (γ_S^+ and γ_S^-) can be calculated by simultaneously solving the two different forms of eq. (1) obtained for the two different polar liquids whose γ_L^{LW}, γ_L^+ and γ_L^- parameters are known. In this study, the surface free energy component values of the used solvents are taken from Van Oss et al.[16]

The contact-angle values of water, glycerol, ethylene glycol, dimethyl formamide, and paraffin oil drops on copolymers and blends are listed in Tables I and II. These data were evaluated to determine the surface free energy component of copolymer and blend films by using Van Oss-Good methodology thorough eqs. (1) and (2). Because VTES has a relatively low reactivity ratio compared to MMA, the copolymer samples containing
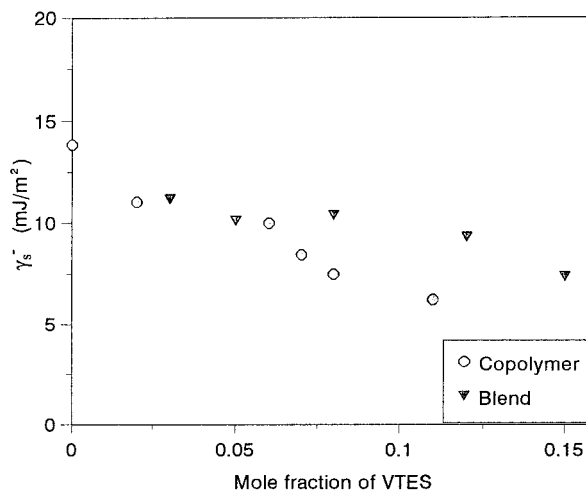

Figure 2 Change of γ_S^- with the mol fraction VTES in copolymers and blends.

Table III Surface Free Energy Measurements of VTES/MMA Copolymer Films

VTES Mol Fraction	γ_S^{LW} mJ/m^2	γ_S^- mJ/m^2	γ_S^+ mJ/m^2	γ_S^{AB} mJ/m^2	γ_S^{TOT} mJ/m^2
0.00	26.65	13.85	2.47	11.29	37.94
0.02	21.95	11.03	1.22	6.91	28.86
0.06	22.53	10.76	0.03	1.01	23.54
0.07	23.10	8.45	0.36	3.12	26.22
0.08	23.38	7.49	0.51	3.56	26.94
0.11	24.67	6.23	0.71	3.96	28.63

more than 0.11 VTES mol fraction could not be obtained.[12,13] Besides, the blend films carrying more than 0.15 VTES mol fraction showed poor physical properties. Therefore, the VTES content of the copolymer and blend films obtained for the contact angle measurements were in the ranges of 0 to 0.11 and 0 to 0.15 VTES mol fraction, respectively.

Figure 1 illustrates the change in the apolar Lifshitz-Van der Waals components (γ_S^{LW}) of copolymers and blends as a function of VTES mol fraction. It is seen from this figure that as the VTES mol fraction increases, the γ_S^{LW} values of copolymers and blends increase appreciably, while γ_S^{LW} values of copolymers are higher than that of blends at each composition. This can be explained on the basis that VTES containing chains have a lower dispersion force than MMA containing chains. It is well known that there is an inverse relationship between the intermolecular distance and the dispersion forces present. As seen from Figure 1, the γ_S^{LW} values of copolymer and homopolymer blends were found between $21.95-24.67$ mJ/m^2 and $21.05-23.64$ mJ/m^2, respectively. These values deviated only $\pm 8\%$ from the mean.

The changes in the electron donor component of surface free energy (γ_S^-) with a VTES content of copolymers and blends are shown in Figure 2. These data are determined from the bulk properties of copolymers and blends. A linear decrease in values was observed with the increase of VTES content in the bulk. Because PMMA has —COO groups (Lewis base), the decreasing surface basicity (γ_S^-) with the increase of the VTES content of the copolymer and blend was observed. This result shows that the surface of the copolymers and blends enriched with VTES units (Lewis acid) by increasing the VTES concentration in bulk. In contrast to γ_S^{LW} values, the γ_S^- values of blends were found to be higher than those of the copolymers at each composition (Fig. 2). This result is reasonable because the VTES units in blends have higher chain mobility than the VTES units in the copolymers. The γ_S^- values of the copolymers and the blends were between $13.85-6.23$ mJ/m^2 and $11.18-7.39$ mJ/m^2, respectively. γ_S^- values were deviated within $\pm 47\%$ from the mean. These values were changed to a considerable extent compared to apolar γ_S^{LW} components of the copolymer and the blends (this is nearly six times greater than those of deviation obtained for γ_S^{LW}). This considerable decrease in values with increasing amount of their VTES content is probably due to the decrease in the interaction between ethoxysilyl ($CH_3CH_2OSi—$) groups of VTES and carbonyl groups of MMA and

Table IV Surface Free Energy Measurements of PVTES/PMMA Blend Films

VTES Mol Fraction	γ_S^{LW} mJ/m^2	γ_S^- mJ/m^2	γ_S^+ mJ/m^2	γ_S^{AB} mJ/m^2	γ_S^{TOT} mJ/m^2
0.03	21.05	11.18	0.10	2.09	23.14
0.05	22.25	10.13	0.16	2.19	24.44
0.08	22.53	10.40	0.34	3.49	26.02
0.12	23.10	9.34	0.50	4.15	27.25
0.15	23.64	7.39	0.84	4.87	28.51

lower polarity of VTES compared to MMA monomer.[2]

CONCLUSION

The stone-based monumental artifacts are usually exhibited outdoors, and they suffer from frost, acid rains, and salts carried by air movements. The preservation and consolidation at the same time of such materials has been of interests of scientists, and is possible by coating them with some polymeric materials without changing their structure. Due to the coupling ability of organofunctional silanes, the copolymers carrying VTES units may have a promising application in due course. For this purpose, the copolymers of MMA with VTES and their homopolymer blends were prepared and their characteristic surface energy components were determined by the one liquid contact angle measurements. It was observed that for the copolymer and blend films, the apolar Lifshitz-Van der Waals component (γ_S^{LW}) increased while the electron donor component of their surface free energy (γ_S^-) decreased with increasing their VTES content.

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