

Oxygen Permeability and Surface Free Energy Properties of Silicone-Containing Copolymers of Methyl Methacrylate

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Synopsis

Novel organofunctional siloxanes from γ -methacryloxypropyltrimethoxysilane (MPTMS) were synthesized by transesterification reactions with high monohydric alcohols, branched alcohols, ether alcohols, phenol, and mandelic acid. The factors effecting the substitution ratios were determined. Copolymers of these siloxanes with methyl methacrylate (MMA) were prepared by bulk copolymerization in glass molds and their swelling, thermal, oxygen permeability, and surface free energy characteristics were investigated in order to determine the effect of the substituted group on the produced copolymer. The changes in these properties by the cross-linking of the copolymer with ethylene glycol dimethacrylate (EGDM) were also investigated. The copolymers containing branched, nonpolar, and lengthy pendant groups were found to be highly oxygen permeable possibly due to the introduction of larger free volume by these groups. The surface energy analysis showed that the main variation was found to be in γ_{SV}^P values rather than γ_{SV}^d values and only ether alcohol substitution increased γ_{SV}^P values to a greater extent.

INTRODUCTION

Organofunctional siloxanes are the compounds that contain unsaturated or other functional groups in the organic substituents attached to silicone.¹ The applications of organofunctional siloxanes are numerous and widespread (e.g., adhesion promotion, improved dispersion, enzyme immobilization, free-ion recovery, gas separation membranes). The copolymers obtained by reacting the methacryloxy or acryloxy group containing organofunctional siloxanes with other acrylate methacrylate esters are mostly glassy, possess high oxygen permeability, and are used in biomedical applications, especially as hard gas-permeable contact lens materials.²⁻⁷ The physical, thermodynamic, morphological, and oxygen transport characteristics of some of the copolymers of methyl methacrylate with disiloxanes and other silicone-containing monomers have been discussed and the effect of increasing silicone content upon the oxygen diffusion coefficient and steady-state oxygen permeation rate has been analyzed.⁸⁻¹⁰

γ -Methacryloxypropyltrimethoxysilane (MPTMS) is an organofunctional siloxane monomer containing three methoxy groups attached to silicone that contribute to flexibility of the formed homopolymer and copolymers. The transesterification of the methoxy groups by high alcohols, phenols, and some other organic molecules is possible¹ and the transesterification process can be accelerated by catalysts such as sodium alkoxides,¹¹ titanate acid esters,¹² sulfuric acid,¹³ trifluoroacetic acid,¹⁴ and tetramethyl ammonium hydroxide.¹⁵

The purpose of the present study is to derive novel organofunctional siloxanes from MPTMS by transesterification process and examine the effect of the nature and the amount of the introduced organic group on the oxygen permeability and surface free energy properties of the copolymers formed from methyl methacrylate and these novel monomers. The effect of the crosslinking with ethylene glycol dimethacrylate is also investigated.

EXPERIMENTAL

Monomer Preparation

MPTMS monomer (A174 of Union Carbide) was placed in a round-bottomed flask equipped with a magnetic stirrer and connected with a short distillation column filled with glass beads, and a condenser was placed on the top of the column to remove formed methanol. Oil bath was used when heating was required. The organic compound used in transesterification was first mixed with the catalyst, then added to siloxane monomer in stoichiometric ratio. The reaction continued until the methanol formation ceased.

Monomer Characterization

Transesterification reactions were followed by gas chromatography (PYE Unicam Ltd.) with a column of Chromosorb W-AW, DMCS (with 5% OV-1) and infrared (IR) (Perkin-Elmer, Model 599 B). Reaction products were analyzed by elemental analysis (Carlo Erba Model 1106) and silicone content was determined gravimetrically.¹⁶ The substitution ratios were calculated from the elemental analysis results and confirmed by the weight increase of the produced siloxane in the flask after the reaction completed since all the organic groups introduced had higher molecular weights than removed methoxy group.

Copolymer Preparation

The initiator 2,2'-azo-*bis*-*iso*-butyronitrile was from BDH Chemicals Ltd., England, and was recrystallized from methanol and dried prior to use. Proper mixtures of freshly distilled methyl methacrylate, novel siloxane monomer, and the cross-linking agent ethylene glycol dimethacrylate were placed in glass tubes and 0.2%wt initiator was dissolved. Then, N₂ gas was allowed to pass for 5 minutes to remove the O₂ present in monomer mixture. Two glass plates were covered with Melinex sheets (a heat-resistant polyester sheet, Boyden Data Papers Ltd., England) and a polyethylene gasket was placed between them to form a mold of 50 × 50 × 0.2–0.4 mm in dimension, which was held by metal clips. The prepared comonomer mixture was injected by means of a syringe and a needle inside the mold. The mold was kept in an oven for two days at 60 ± 0.5°C and for one day at 90 ± 0.5°C to complete the membrane formation.

Copolymer Characterization

The bulk copolymerized products were obtained as hard and transparent sheets of thickness 0.2–0.4 mm. The mole fraction of siloxane monomer in the final copolymer (F_1) was determined from silicone content estimated gravimetrically.¹⁷

Thermal analysis was performed using a DSC equipment (DuPont 910 DSC). The sample chamber was purged with N_2 and glass transition temperature (T_g) was determined between -60°C – $+280^\circ\text{C}$ at a scanning speed of $5^\circ\text{C}/\text{min}$ and at loading of 6 mg.

Swelling studies were performed in methylene chloride, chlorobenzene, and ethyl acetate solvents.

The surface free energy components were determined by measuring the contact angles of the water and methylene iodide drops on the copolymer surfaces. Prior to contact angle measurements, the polymer surfaces were cleaned by washing with a detergent solution followed by a thorough rinsing with distilled water, and finally drying in a vacuum desiccator at room temperature. Drops of each liquid $5\ \mu\text{L}$ 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 goniometer eyepiece at 20°C . Variation in the contact angle measurement was not greater than ± 2 degrees and the average of at least four measurements was reported.

The "dissolved" oxygen permeability coefficient measurements of the copolymer membranes were carried out by using an oxygen fluxmeter containing a polarographic electrode cell (Schema Versatae Oxygen Fluxmeter S/V-920a). This instrument consisted of a control chassis containing power supply, amplifiers, meter, and the plexiglass two-piece cell. $0.9\ N$ NaCl saline solution was placed in the cell, the copolymer was placed between the pieces of the cell, and dry nitrogen gas was passed to stabilize the system until the attainment of equilibrium was shown on the chart recorder. The meter was then zeroed, after which oxygen was passed through for the measurement of oxygen permeability coefficient. The meter reading was taken when equilibrium had been attained with oxygen gas. Calibration was performed by using reference poly-4-methyl pent-1-ene and polystyrene films having 22 and $2 \times 10^{-11}\ \text{cm}^3\ (\text{STP})\ \text{cm} / \text{cm}^2\ \text{s}\ \text{mmHg}$ oxygen permeability coefficients, respectively.

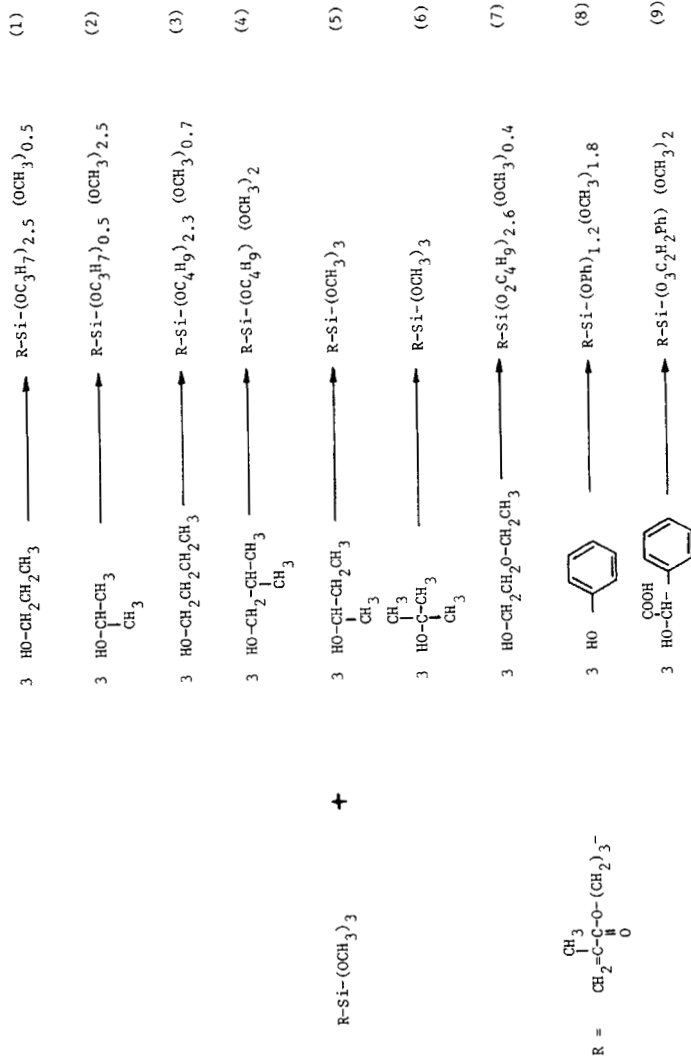
Protein deposition tests were carried out in a solution that contained 2% starch, 3% vegetable oil, and 95% $0.9\ N$ NaCl solution by weight.¹⁸

RESULTS AND DISCUSSION

Monomer Properties

Since the noncatalyzed, high temperature transesterification of MPTMS usually resulted in polymerized products due to thermal polymerizability of the methacryloxy group present, several catalysts were tried to carry out the reactions at room temperature. Ethyl sulfuric acid was used as catalyst;¹³ however, it gave low yields, and the required neutralization and salting-out steps in this process produced contaminated monomers that were difficult to purify. Tetrabutyl titanate catalyst was tried,¹² which produced high yields with the application of heat. This catalyst, however, introduced a yellow color to the product and undesired thermally polymerized products were obtained, especially above 60°C .

Metallic sodium catalyzed reactions were carried out at room temperature under a vacuum that was sufficient to remove the formed methanol and was found to be the most controllable method for the transesterification of



Scheme 1. Results of transesterification reactions.

TABLE I
The Results of Elemental Analysis and Silicone Content Determination

Reaction number in Scheme 1	1	2	3	4	5	6	7	8	9
C (%)	57.2	51.1	59.4	54.6	49.0	48.2	45.3	59.9	55.8
H (%)	9.5	8.5	9.9	9.1	8.2	8.2	10.8	7.1	6.1
Si (%)	8.7	10.8	8.2	9.6	11.3	11.2	8.3	8.6	7.5
Estimated formula Substitution (%)	$C_{15}H_{30}O_6Si$ 83	$C_{11}H_{22}O_5Si$ 17	$C_{17}H_{34}O_5Si$ 74	$C_{13}H_{26}O_5Si$ 34	$C_{10}H_{20}O_5Si$ 0	$C_{10}H_{20}O_5Si$ 0	$C_{12.5}H_{35}O_{7.5}Si$ 87	$C_{16}H_{22.5}O_5Si$ 40	$C_{17}H_{24}O_7Si$ 34

MPTMS. The use of excessive amounts of metallic Na should be avoided in order to prevent the decomposition of MPTMS. Favorably, 0.1–0.3 wt% metallic sodium was dissolved in the organic compound first and then added to MPTMS. The applied vacuum was selected so that it would allow the removal of formed methanol but would prevent the vaporization of the high boiling alcohols present. A range of 200–5 mmHg pressure was applied at room temperature (20–23°C). The transesterification reactions took a period of 50–80 h to obtain the maximum substitution ratio.

The summary of the results of the applied transesterifications is given in Scheme 1. Reactions (1)–(7) were carried out by using metallic sodium catalyst and reactions (8) and (9) were performed by heating the reaction mixture to 90°C without using catalyst.

The results of the elemental analysis and the silicone content analysis is shown in Table I. The substitution ratios in Scheme 1 were calculated from Table I. Transesterifications were followed by GC and IR and sample GC results of reaction (3) of Scheme 1 are presented in Figure 1. As seen from this figure, the substitution reaction is a stepwise process. At the beginning, mostly the monosubstituted siloxane molecules form, then after the completion of monosubstitution, di- and trisubstituted siloxane molecule formation continues at the expense of monosubstituted molecules. Later, the number of trisubstituted molecules increase at the expense of disubstituted molecules.

The comparison of the IR spectra of the reaction mixtures before the reaction and the products obtained after the reaction confirmed the substitution. The strongest infrared absorption of Si—OCH₃ was at 1100–1080 cm⁻¹ due to the asymmetric Si—O—C stretch. The other alkoxy groups showed two bands different from methoxy group, one in the 1170 to 1140 cm⁻¹ region and another in the 980 to 940 cm⁻¹ region. The Si—O—Ph showed a band in 925 cm⁻¹ region due to a Si—O—C stretching mode.

As seen in Scheme 1, the substitution ratios of the branched alcohols were found to be low due to the steric hinderance. No substitution was obtained with *sec* and *tert*butanol. Only monosubstitution was obtained with isobutanol. Substitution ratio was further lower with isopropanol than isobutanol showing the effect of the chain length of the organic molecule on the steric hinderance. High substitution ratios obtained for linear alcohols, *n*-propanol, *n*-butanol, and 2-ethoxyethanol. The steric hinderance of the bulky phenyl group allowed only 34–40% substitution of phenol and mandelic acid in transesterification reactions.

Copolymer Structure

The mole fraction of the siloxane monomer in the feed (f_1) and in the copolymer structure (F_1) and the EGDM mole fraction in the feed (f_3) of all the prepared copolymers are tabulated in Table II. Calculation of the reactivity ratios for this system was not undertaken, since the reactions were carried out to high extent of reaction.

The increase in mole fraction of siloxane in monomer feed (f_1) resulted in a corresponding increase in mole fraction of siloxane in copolymer (F_1), indicating thereby the formation of random copolymers.

Glass transition temperatures (T_g) were measured for all the produced copolymers using differential scanning calorimetry (DSC); however, broad and

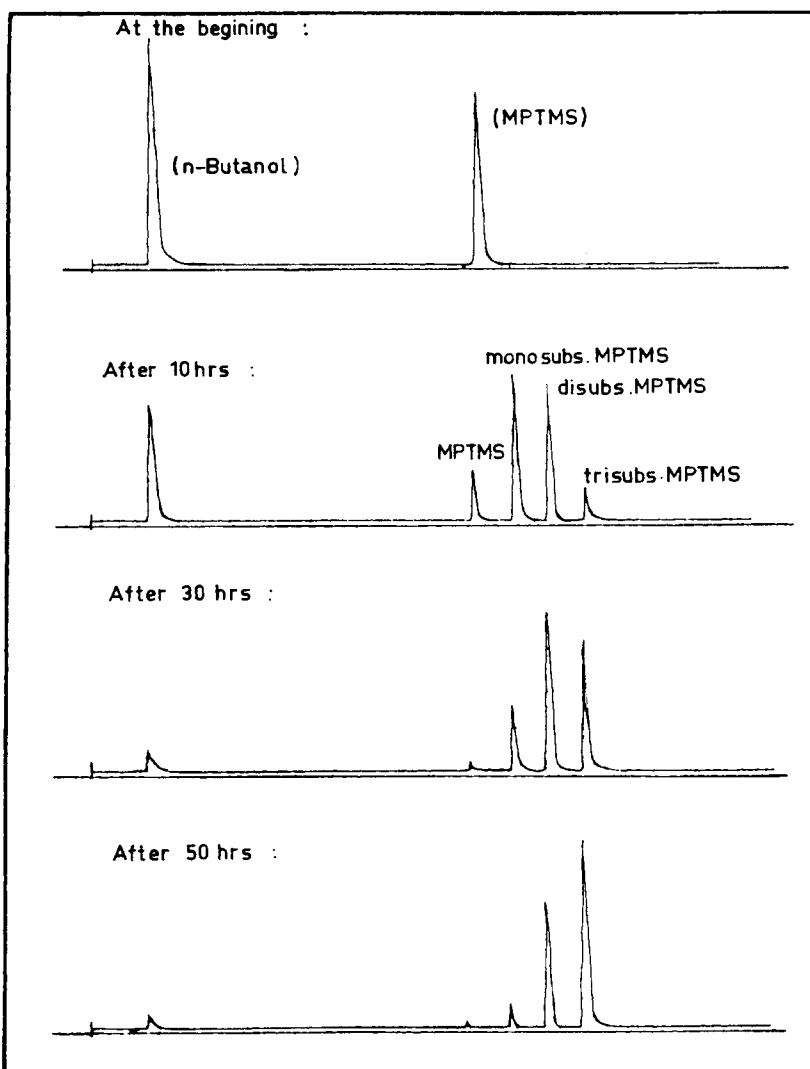


Fig. 1. The change of the reaction mixture composition with time: GC results of reaction (3) in Scheme 1.

ill-defined T_g values between 115 and 140°C were determined. It was recognized that the measured T_g values did not depend on the type of the siloxane and the increase of the siloxane content in the copolymer composition. Since, the flexibility of the polymer chain is the most important factor influencing T_g and decrease of T_g is expected when more flexibility is introduced, such results are not well understood. It was thought that the siloxane groups in the copolymer structure might be crosslinked in the presence of atmospheric moisture at high temperatures. Consequently, the formation of new cross-links restricted the molecular motion of the chains; thus high T_g values were measured. It was reported earlier that such a moisture-curing mechanism was possible for MPTMS by the hydrolysis of methoxy groups bounded to Si atom.¹⁹

TABLE II
The Analysis Results and Swelling Behavior of Siloxane-Methyl Methacrylate Copolymers

Type of siloxane	Feed mole fraction of EGD ₃ f_3	Feed mole fraction of siloxane f_1	Copolymer mole fraction of siloxane F_1 ($\pm 0-0.03$)	Swelling ratio at 25°C q		
				Methylene chloride	Chloro-benzene	Ethyl acetate
MPTMS	0	0.25	0.22	Soluble	Soluble	2.05
	0	0.45	0.41	Soluble	2.18	1.74
	0	0.70	0.62	1.17	1.11	1.00
	0.06	0.60	0.59	Crazing	Crazing	Crazing
	0.11	0.70	0.68	Crazing	Crazing	2.62
	0.22	0.78	0.78	2.02	1.87	1.46
	0.33	0.67	0.67	1.08	1.09	1.06
	0	0.20	0.21	Soluble	Soluble	2.10
	0	0.45	0.43	Soluble	2.21	1.87
	0	0.70	0.68	Crazing	1.17	1.05
Product of reaction (1) in Scheme 1	0.06	0.60	0.57	Crazing	Crazing	Crazing
	0.11	0.70	0.67	Crazing	Crazing	2.27
	0	0.20	0.16	Soluble	Soluble	2.41
	0	0.25	0.24	Soluble	2.38	1.97

ENERGY PROPERTIES OF COPOLYMERS

Product of reaction (3) in Scheme 1	0	0.45	0.42	2.17	1.70	1.41
	0	0.70	0.66	2.05	1.24	1.10
	0.06	0.60	0.57	Crazing	Crazing	Crazing
	0.12	0.70	0.63	Crazing	Crazing	2.37
Product of reaction (4) in Scheme 1	0	0.30	0.27	Soluble	Soluble	1.83
	0	0.45	0.44	Soluble	2.02	1.71
	0	0.70	0.62	1.29	1.17	1.05
	0.06	0.60	0.58	Crazing	Crazing	Crazing
Monosubstituted product of reaction (3) in Scheme 1	0.11	0.70	0.65	2.08	1.77	2.58
	0	0.20	0.20	Soluble	Soluble	2.28
	0	0.45	0.39	Soluble	1.92	1.56
	0	0.78	0.72	Crazing	1.17	1.07
Product of reaction (7) in Scheme 1	0	0.10	0.10	Soluble	Soluble	Soluble
	0	0.20	0.18	Soluble	Soluble	1.25
	0	0.45	0.32	Soluble	1.32	1.17
	0	0.60	0.52	Soluble	1.22	1.02
Product of reaction (8) in Scheme 1	0	0.30	0.26	Soluble	Soluble	1.24
	0	0.60	0.52	Soluble	Soluble	1.07
Product of reaction (9) in Scheme 1	0	0.20	0.11	Soluble	Soluble	1.21
	0	0.45	0.29	Soluble	1.30	1.07
	0	0.60	0.47	Crazing	1.07	1.02

Table II presents the swelling characteristics of the copolymers in three solvents studied. The swelling ratio, q , was determined at 25°C. Determination of the molecular weight between crosslinks for the crosslinked samples with EGDM via equilibrium swelling was not possible due to the lack of Flory interaction parameter χ values. Some samples were soluble in the solvents used; however, in many cases, complete solubilization took approximately two weeks. Some samples developed crazes during swelling, leading to fragments of swollen copolymer. The increase of F_1 decreased the craze formation tendency and the swelling ratio. The increase of the EGDM content in the feed (f_3), decreased the swelling ratio as expected. These swelling characteristics showed that EGDM-containing copolymers were highly crosslinked structures and the crazing was due to the non-Fickian transport of the swelling agent in amorphous copolymers. The effect of the type of the siloxane used (i.e., the effect of the substituted groups) was not clearly exhibited in the swelling behavior of the copolymers having no EGDM content. This was due to the similar q values obtained in ethyl acetate, which was a poor solvent for the siloxane copolymer. Only the effect of the substitution of the phenoxy group is distinguishable in Table II, leading to less swelling than other siloxanes. Complete solubility was obtained for good solvents, such as methylene chloride up to $F_1 = 0.44$ and for chlorobenzene up to $F_1 = 0.27$ as expected.

Oxygen Permeability

The increase of the "dissolved" oxygen permeability coefficients of the formed siloxane-methyl methacrylate copolymers with the increase of siloxane content is shown in Figure 2. The substitution of the high alcohols produced more permeable copolymers whereas phenol and mandelic acid transesterification decreased the oxygen permeability. The substitution of a polar alcohol such as 2-ethoxyethanol increased the O_2 permeability coefficient of the produced copolymer only slightly over MPTMS copolymers; however, nonpolar and linear alcohols such as n -propanol and n -butanol substitution increased the oxygen transport to a greater extent. The increase in the size of the linear molecule also increased to O_2 permeability, as seen in the comparison of the effect of n -propanol and n -butanol substitution. The most pronounced oxygen permeability increase was obtained by substituting branched alcohols. Since it was also difficult to increase the substitution ratio of these compounds to MPTMS due to the steric hinderance, the comparison can only be made by lowering the substitution ratio of linear alcohols. Thus, n -butanol-monosubstituted MPTMS obtained by short-stopping the transesterification reaction was used as a reference for isobutanol monosubstituted MPTMS. The isobutanol-containing copolymers had approximately 35% higher oxygen permeability than n -butanol-containing ones. The positive effect of the branching and large size of the pendant groups on O_2 permeability may be attributed to the larger free volume created in the copolymer by the motion of these polymer chains. However, in the case of phenol- and mandelic acid-substituted siloxanes, bulky aromatic groups cannot increase the free volume of the copolymer due to the close packing tendency of the symmetric aromatic pendant groups. This behavior was also exhibited in the swelling ratio results of the copolymers in chlorobenzene and ethyl acetate solvents in Table II.

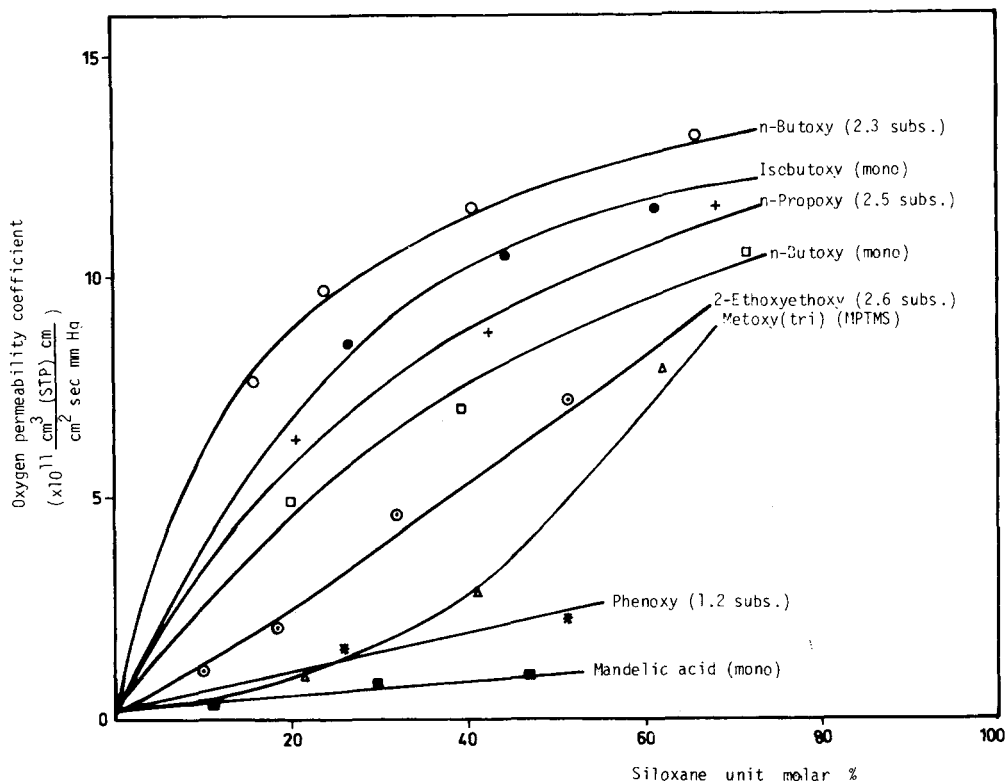


Fig. 2. The increase of the "dissolved" oxygen permeability coefficient of uncrosslinked siloxane-methyl methacrylate copolymers with their siloxane contents.

Only a slight increase of O_2 permeability was obtained by substituting MPTMS with 2-ethoxyethanol although, this molecule was expected to increase the O_2 permeability to high levels due to the flexibility of C—O bond present and the possibly high O_2 solubility.

The increase of EGDM content had two effects on the oxygen permeability of the copolymers as seen in Table III. First, cross-linking allowed the use of more siloxane monomer in comonomer feed in order to obtain mechanically resistant glassy copolymer products. Second, the higher the cross-linking, the lower the O_2 permeability resulted as expected. Thus, for the lower cross-link densities, the effect of the increase of siloxane content raised the O_2 permeability, then for highly cross-linked copolymers, O_2 permeability diminished. The effect of the substituted pendant groups on the O_2 permeability of the cross-linked copolymers was in the same order as uncrosslinked copolymers.

Surface Free Energy

The work required to pull the liquid away from the surface leaving the equilibrium-adsorbed film is given by Young-Dupré equation:

$$W_A = \gamma_{LV}(1 + \cos \theta) \quad (1)$$

where γ_{LV} is the free energy of liquid in equilibrium and θ is the contact angle of the liquid on the solid.

TABLE III
The Results of the Oxygen Permeability Coefficients and Surface Free Energy Measurements
of Siloxane-Methyl Methacrylate Copolymers

Type of siloxane	F_1 Siloxane	f_3 EGDM	Oxygen permeability coefficient $\times 10^{11}$ $\frac{\text{cm}^3 \text{ (STP) cm}}{\text{cm}^2 \text{ s mmHg}}$	Contact θ		Surface free energy ergs cm^{-2}		
				Water	Methylene iodide	γ_{SV}^d	γ_{SV}^p	
MPTMS	0.22	0	0.8	71	32	38.9	7.1	46.0
	0.41	0	2.9	72	34	38.1	6.9	45.0
	0.62	0	7.9	78	41	35.6	5.1	40.7
	0.59	0.06	5.1	72	36	37.1	7.2	44.3
	0.68	0.11	7.3	72	35	37.7	7.1	44.8
	0.78	0.22	8.8	79	43	34.7	4.9	39.6
	0.67	0.33	6.5	76	36	37.9	5.3	43.2
Product of reaction (1) in Scheme 1	0.21	0	6.2	74	33	39.0	5.8	44.8
	0.43	0	8.7	78	36	38.3	4.5	42.8
	0.68	0	11.5	83	41	36.6	3.1	39.7
	0.57	0.06	7.2	71	33	38.4	7.3	45.7
	0.67	0.11	8.1	73	36	37.3	6.7	44.0
Product of reaction (3) in Scheme 1	0.16	0	7.6	80	34	39.7	3.5	43.2
	0.24	0	9.6	82	35	39.6	2.9	42.5
	0.42	0	11.5	84	35	40.0	2.2	42.2
	0.66	0	13.2	85	37	39.2	2.1	41.3
	0.57	0.06	9.5	79	40	36.4	4.5	40.9
	0.63	0.12	Broken	—	—	—	—	—

Product of reaction (4) in Scheme 1	0.27	0	8.5	79	34	39.5	3.8	43.3
	0.44	0	10.5	80	35	39.2	3.6	42.8
	0.62	0	11.5	82	37	38.6	3.0	41.6
	0.58	0.06	9.5	77	36	38.1	4.9	43.0
	0.65	0.11	10.5	78	39	36.7	4.8	41.5
Monosubstituted product of reaction (3) in Scheme 1	0.20	0	4.9	76	32	39.9	4.8	44.7
	0.39	0	6.9	78	34	39.3	4.2	43.5
	0.72	0	10.5	81	35	39.4	3.2	42.6
Product of reaction (7) in Scheme 1	0.10	0	1.1	68	36	36.4	9.4	45.8
	0.18	0	2.0	67	37	35.7	10.1	45.8
	0.32	0	4.6	65	37	35.4	11.3	46.7
	0.52	0	7.2	58	27	38.7	13.9	52.6
Product of reaction (8) in Scheme 1	0.26	0	1.5	84	34	40.5	2.2	42.7
	0.52	0	2.2	87	36	40.1	1.5	41.6
Product of reaction (9) in Scheme 1	0.11	0	0.3	72	35	37.7	7.1	44.8
	0.29	0	0.8	75	37	37.2	5.9	43.1
	0.47	0	1.0	77	40	36.0	5.4	41.4

Owens and Wendt²⁰ proposed that the free energy of adhesion of a solid in contact with a liquid can be represented by the equation:

$$W_A = 2\left(\sqrt{\gamma_{SV}^d \gamma_{LV}^d} + \sqrt{\gamma_{SV}^P \gamma_{LV}^P}\right) \quad (2)$$

where subscripts *S*, *V*, and *L* refer to solid, vapor, and liquid, *p* and *d* to polar and dispersion, respectively.

According to their approach the surface free energy of solid or liquid is the sum of the polar (dipole-hydrogen bonding) and the London dispersion components:

$$\gamma_i = \gamma_i^P + \gamma_i^d \quad i = SV, LV \quad (3)$$

Thus, γ_{SV}^P and γ_{SV}^d can be calculated for a solid by measuring the contact angles of two different liquids for which the values of γ_{LV} , γ_{LV}^P and γ_{LV}^d are known and by using Eqs. (1)–(3).

In Table III, the surface free energy components of the siloxane-methyl methacrylate copolymers were calculated by using the values of water and methylene iodide reported by Owens and Wendt²⁰ (H_2O : $\gamma_{LV} = 72.8$ erg, cm^{-2} , $\gamma_{LV}^P = 51.0$ erg, cm^{-2} , $\gamma_{LV}^d = 21.8$ erg, cm^{-2} , CH_2I_2 : $\gamma_{LV} = 50.8$ erg, cm^{-2} , $\gamma_{LV}^P = 1.3$ erg, cm^{-2} , $\gamma_{LV}^d = 49.5$ erg, cm^{-2}). The values 50.2, 11.0, 39.2 erg, cm^{-2} were calculated for γ_{SV} , γ_{SV}^P , γ_{SV}^d , respectively, for methyl methacrylate homopolymer from the measured water contact angle of 63 degrees and methylene iodide contact angle of 28 degrees.

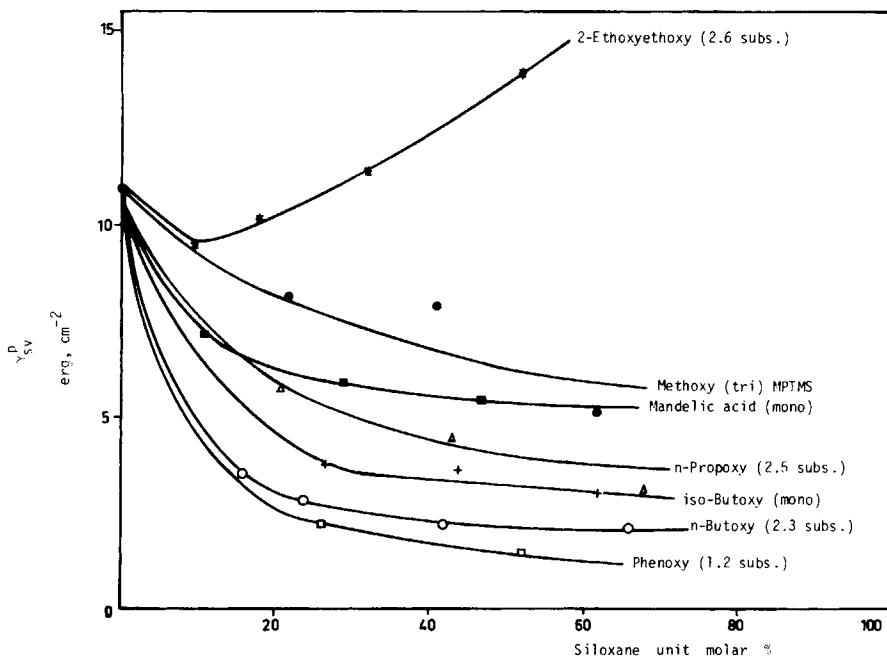


Fig. 3. The change of the polar component of surface free energy of the uncrosslinked siloxane-methyl methacrylate copolymers with their siloxane contents.

The relation of the γ_{SV}^P , γ_{SV}^d , and γ_{SV} values of the siloxane-methyl methacrylate copolymers (uncross-linked) to their siloxane contents are indicated in Figures 3-5.

Since MPTMS monomer was less polar than methyl methacrylate, the γ_{SV}^P values of the copolymers of MPTMS-MMA decreased with the increasing siloxane content as shown in Figure 3. *n*-Propoxy, isobutoxy, *n*-butoxy groups also introduced more hydrophobicity to the copolymer and their γ_{SV}^P values were found to be lower than methoxy-containing copolymers. The difference of γ_{SV}^P values of isobutoxy-containing copolymers from *n*-butoxy-containing ones were mainly due to the low substitution ratio of isobutoxy group. Phenoxy group, although substituted to only a 40% degree, decreased γ_{SV}^P values drastically due to the hydrophobicity of the aromatic group. This effect was also reflected in the γ_{SV}^P values of siloxane copolymers containing mandelic acid, although the polar carboxyl group present. Polar 2-ethoxyethanol group substitution resulted in the highest γ_{SV}^P values of the corresponding copolymers.

The γ_{SV}^d values of the copolymers of MPTMS-MMA decreased with increase of the siloxane content as indicated in Figure 4. *n*-Butoxy, isobutoxy and *n*-propoxy substitution to MPTMS resulted in higher γ_{SV}^d values of copolymers close to MMA homopolymer value. The introduction of polar groups into copolymer resulted a decrease in γ_{SV}^d values as exhibited in 2-ethoxyethanol and mandelic acid-containing copolymers.

The γ_{SV} values of all the copolymers showed similar variation of γ_{SV}^P component with the increase of siloxane content as seen in Figure 5. This is due to the fact that the difference of all γ_{SV}^d values were within $\pm 6.3\%$, however, γ_{SV}^P values varied within $\pm 44.6\%$ with the increase of siloxane content.

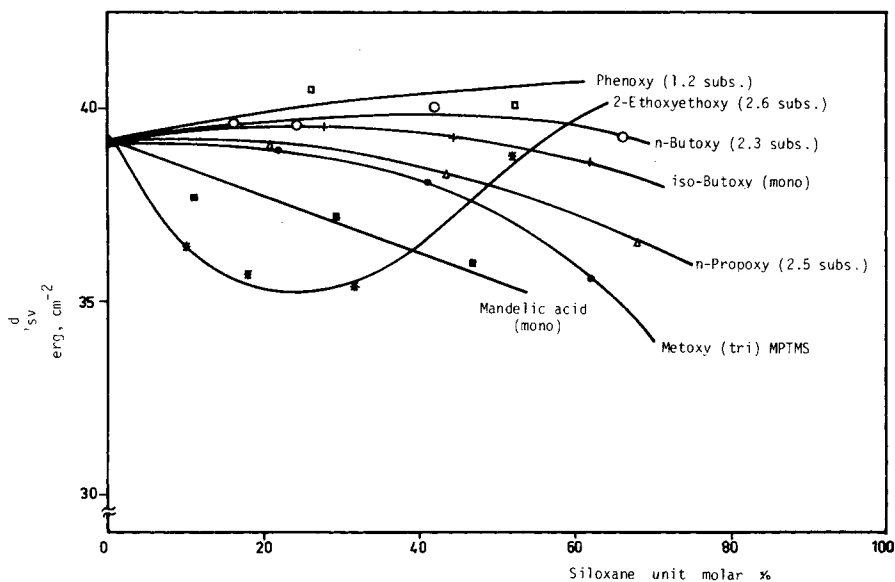


Fig. 4. The change of the dispersion component of surface free energy of the uncrosslinked siloxane-methyl methacrylate copolymers with their siloxane contents.

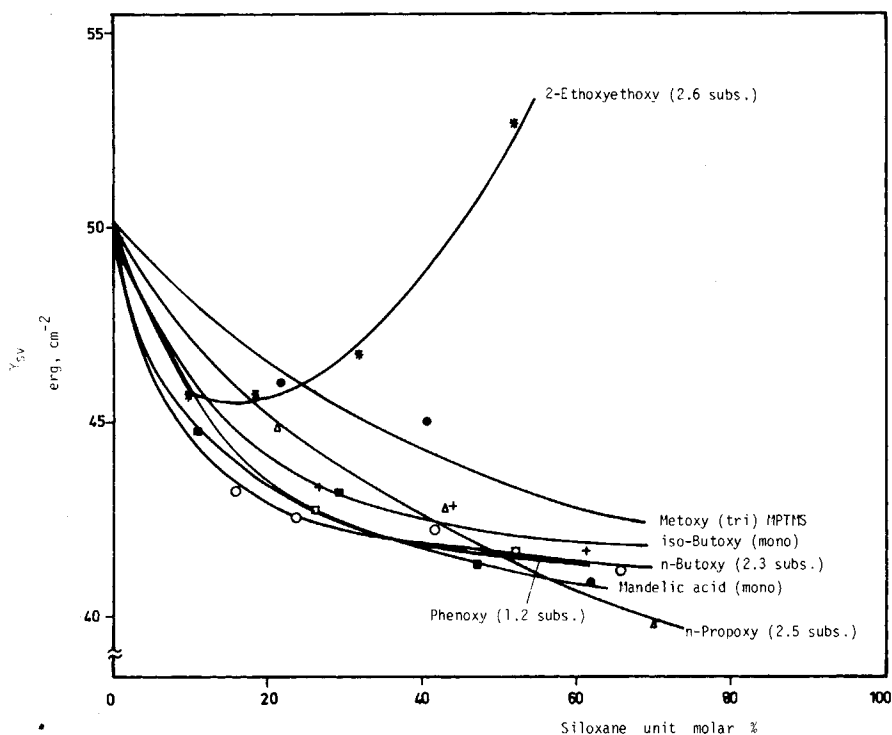


Fig. 5. The change of the total surface free energy of the uncrosslinked siloxane-methyl methacrylate copolymers with their siloxane contents.

Crosslinking did not affect the surface properties to a greater extent. Only one generalization can be made; the higher the crosslinking the lower the surface free energy.

CONCLUSIONS

The transesterification reactions of MPTMS monomer were performed by using high monohydric alcohols, branched alcohols, ether alcohols, phenol, and mandelic acid to obtain novel organofunctional siloxanes. Metallic sodium-catalyzed reactions were found most suitable whereas noncatalyzed reactions with heating or tetrabutyl titanate-catalyzed reactions could also be used to a limited extent. The substitution ratios of the branched alcohols were found to be low due to their steric hinderance.

Copolymerizations of the produced siloxane monomers with MMA and crosslinking agent EGDM were carried out and the swelling behavior and thermal properties of these copolymers indicated highly crosslinked structures with a moisture-curing mechanism at high temperatures.

The oxygen permeability and surface free energy properties of the copolymers having no EGDM content were investigated to determine the effect of the substituted group on the produced copolymer. It was found that the copolymers containing branched, nonpolar, and lengthy pendant groups were highly oxygen permeable, possibly due to the introduction of larger free volume into the copolymer by these groups.

Analysis of the surface free energy of the siloxane-MMA copolymers showed that the main variation was found to be in γ_{SV}^P values with siloxane content rather than γ_{SV}^d values, and thus similar variations were determined in γ_{SV} values as γ_{SV}^P . Since MPTMS monomer was less polar than MMA, the γ_{SV}^P values of all the siloxane-MMA copolymers except 2-ethoxyethanol decreased with the increasing siloxane content. Polar 2-ethoxyethanol substitution to MPTSM resulted in the highest γ_{SV}^P values of the corresponding copolymers.

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