A Novel Type of Si-containing Acrylic Resins: Synthesis, Characterization, and Film Properties

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ABSTRACT: A novel type of Si-containing acrylic resins was prepared by two steps and investigated their usage as surface coatings materials. At first a reactive polysiloxane intermediate Z-6018 was reacted with 2-hydroxyethyl methacrylate (HEMA) in toluene at 110°C under N_2 atmosphere. After the condensation reaction was stopped, reacted with different acrylic ester monomers such as ethyl acrylate (EA) and methyl methacrylate (MMA) at different mole ratio (1/3 and 1/4) by the free radical addition polymerization. Structures of Si-containing acrylic resins were characterized by Fourier Transform Infrared Spectrometer (FTIR) and thermal properties of these resins were investigated by thermogravimetric analysis and differential scanning calorimetry DSC techniques. Surface coating properties of the films prepared from these resin were also determined. The results showed that all films are flexible, glossy or semi gloss and have excellent drying and adhesion properties. All films also exhibit abrasion resistances moderately. Water resistance of the films was generally modified by cured in oven and alkaline resistance of the films prepared from resins containing ethyl acrylate units are excellent. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3324–3331, 2007

Key words: silicone acrylic resins; surface coatings; polysiloxane intermediate; methyl methacrylate; ethyl acrylate

INTRODUCTION

Acrylic resins find use in a variety of paint and coatings that support the automotive, appliance, and coil industries. The key attribute of acrylic coatings is their resistance to hydrolysis during extended exterior exposure (weathering). In this respect, acrylic latex exterior paints exhibit superior performance to their solvent borne analogs. Acrylic coatings also form the basis for a large number of radiation curable formulations. Acrylic resins, which are used as both a thermoplastic and thermoset material, are prepared through the polymerization of acrylic and methacrylic acids or their corresponding esters. The copolymerization of acrylic acid with unsaturated compounds (i.e., vinyl toluene, vinyl chloride, and vinyl acetate) provides versatility in the properties exhibited by acrylic resins. Acrylic resins used in coatings are classified as being either thermoplastic or thermosetting depending upon their cure properties. Thermoplastic resins form hardened coatings simply through solvent evaporation. Thermoset resins form a crosslinked structure through a chemical reaction with itself or various other types of resins. Coatings formed from thermosetting acrylic polymers offer improved hardness, toughness, and chemical resistance over their thermoplastic counterparts. For use as a thermoset material, the acrylic resin must be functionalized with reactive groups, such as carboxyl, hydroxyalkyl, amino, or epoxy, to allow for crosslinking either with itself, with various other resins, such as epoxies and melamine formaldehyde (MF), or with polyisocyanates.[1]

Silicone polymers are of high scientific and technological interest owing to their unique characteristics such as high flexibility and hydrophobicity, excellent thermal stability, high gas permeability and low surface energy, low glass transition temperature (T_g). On the other hand, the low tensile strength and costs limit their applications.[2,3]

It thus appears of interest to incorporate polysiloxane polymers into film-forming polyacrylic lattices to take advantage of the properties of the polydimethylsiloxane (PDMS) homopolymers as well as have the mechanical strength and cohesiveness of the acrylic matrix.[2]

There have been some papers on coatings containing silicone/acrylic resins. Park et al. has synthesized silicone-acrylic resins that prepared *n*-butyl acrylate, methyl methacrylate, and *n*-butyl methacrylate as acrylic monomers and 3-methacryloxypropyltrimethoxysilane (MPTS) as a silicone monomer. These resins were used as super weatherable paints for building materials.[4]

It is known that silicone containing polymers have low surface energy of low polarity. The presence of silicone in polyacrylate film would increase its water

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resistance. This is of importance in the paint industries.[3]

On the other hand, silicone-acrylic coatings can easily be applied to various materials because their film hardness can be easily controlled. In addition, they can be made into one-component curable coatings whose curing is initiated by moisture at room temperature.[4] Hou and Kuo have synthesized a copolymer of methyl methacrylate and novel monomer that prepared from an aliphatic silane coupling compound such as 3-glycidoxypropyltrimethoxysilan (Z-6040) and HEMA.[5] Park et al. have reported that a weather resistant silicone acrylic resin coating.[6] Rao and Babu have synthesized a copolymer of vinyltriacetoxysilane and bromomethacrylate and investigated its thermal behavior.[7] Yasuyuki et al. have investigated phase separation of silicone acrylic rubber prepared by grafting silicone emulsion and acryl emulsion.[8] Witucki has indicated that a silicone acrylic emulsion were prepared by cold blending of alkoxy silane and acryl emulsion two step process. He reported that the existence of 10% silicone increases gloss retention and decreases chalking and color difference.[9] Azuma et al. have developed a high solid system which contains acrylic oligomers for automotive clear coatings.[10] Ito et al. synthesized a novel crosslinking system with hydroxyl-containing polymer, alicyclic polepoxide and polyalkoxysilane.[11] Weather resistant coatings were prepared and the weatherability of the prepared coatings tested.[12,13] There have been some patents similar to these works. Kanegafuchi Kagaku Kogyo Co. holds two patents on weather resistant coatings, in which curing catalyst are used.[14,15] DuPont Co. also holds a patent on weather resistant coatings that consist of hydroxyl group containing acrylic polymer/hydroxyl or alkoxy group containing siloxane. The coatings are not the moisture curing type, but two component reactive types.[16] PPG Co. also patented weather resistant coatings that use a cure accelerating catalyst.[17] However, there have been few papers reporting on the synthesis of the silicone/acrylic resins that is cured by moisture at room temperature and its application to weather resistant coatings.[18–20] Kuo et al. have synthesized copolymers containing polysiloxane side chains.[21,22] Mamiya et al. reported that a silicone modified nonaqueous polymer dispersions and their characteristic properties.[23] There have been also some papers about UV-curable,[24] nonionic[25] and waterborne silicon acrylic coatings.[26]

The present article describes the synthesis of a novel type of Si-containing acrylic resins and the investigation of their film properties. A novel type of Si-containing acrylic resins was synthesized by two steps. In the first step, a macromer (MC) was prepared by the condensation reaction of a reactive polysiloxane intermediate (Z-6018), which has an aromatic groups, and 2-Hydroxyethyl methacrylate (HEMA) by using azoisobutyronitrile (AIBN) as initiator, in toluene as solvent at 110°C under nitrogen atmosphere. Then, to obtain *R*-3MMA, *R*-4MMA, and *R*-3EA, *R*-4EA, MC was reacted with ethyl acrylate (EA) or methyl methacrylate (MMA) as acrylic ester monomers at different mole ratios (1/3, 1/4). The chemical structures were investigated by FT-IR analysis and thermal properties of these modified resins were investigated by using TGA and DSC techniques. Surface coating properties of these resins were also determined.

EXPERIMENTAL

Materials

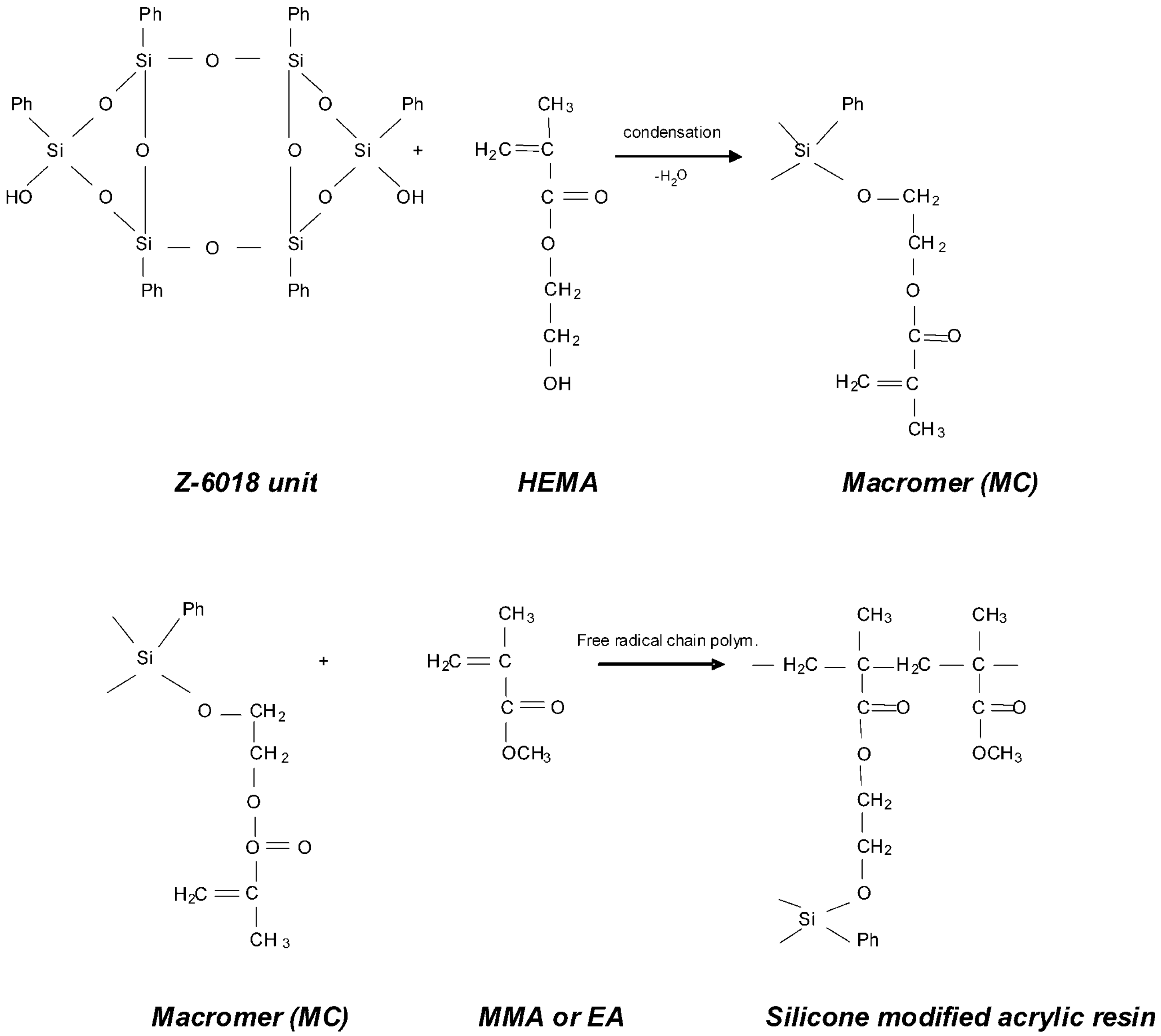
Reactive polysiloxane intermediates (Z-6018) (melting point: 75°C, hydroxyl value HV: 3.9%, viscosity average molecular weight (Mv) 1600[27] and Si content 22.5%[28]) containing free hydroxyl groups and phenyl substitute siloxane rings was obtained from Dow Cornings. 2-Hydroxyethyl methacrylate (HEMA) and methyl methacrylate (MMA), ethyl acrylate (EA) were Merck ''synthesis'' or ''analytical'' grade. MMA, EA and HEMA were purified before use. All the other materials including 2,2′-azoisobutyronitrile (AIBN), toluene, and hexane were from Merck.

Synthesis of macromer

MC was obtained by the condensation reaction of Z-6018 and 2-HEMA in toluene as solvent under nitrogen atmosphere. The details of the preparation were given elsewhere.[29] This macromer was used for the preparation of the Si-containing acrylic resins.

Synthesis of Si-containing acrylic resins

A novel type of Si-containing acrylic resins was synthesized by using MC and acrylic ester monomers MMA or EA. Reactions were carried out in toluene as solvent at 110°C for 3 h in the presence of AIBN as initiator (2.5% wt of the total reaction mixture) under N_2 atmosphere. Polymerization reaction was carried out in a glass reactor equipped with a stirrer, a reflux system, a temperature control system, heating mantle, and an N_2 gas inlet-outlet system. The reaction mixtures composed of different MC/MMA or MC/EA mole ratios (1/3, 1/4) were heated to 110°C while being stirred and the reaction was continued at this temperature for 3 h. At the end of the reaction period, reaction mixture cooled at room temperature, resins were precipitated in cold hexane (+4°C) and filtered. Then the resins were dried to constant weight under vacuum at 40°C for 24 h to give opaque white powder. In the case of MC/MMA molar ratios 1/3, 1/4 and MC/EA molar ratios 1/3, 1/4; resins were called



Scheme 1 The chemical structures MC and Si-containing acrylic resin.

as, *R*-3MMA, *R*-4MMA, and *R*-3EA, *R*-4EA respectively.

The chemical structures MC and modified acrylic resins are shown Scheme 1.

Instruments

Thermogravimetric analyses (TGAs) of the resins were carried out with Shimadzu TGA-50 thermal analyzer with a heating rate of 10°C/min in air. The mass was approximately 25 mg. Differential scanning calorimetry (DSC) analyses of the resins were carried out under N_2 atmosphere, with approximately 25 mg samples by heating up to 350°C, at a heating rate of 10°C/min. with Setaram 131 model apparatus (France). FTIR spectra of dried samples were recorded on a Digilab Exalibur-FTS 3000 MX model (USA) in the range 400–4000 cm^{-1}. The dry sample powders were thoroughly ground with KBr (IR grade, Merck-Germany) at a ratio of 1/200 and pressed into a pellet and the spectrums was then recorded.

Film preparation and determination of their properties

The films of the resins were prepared from the 30% solid content toluene solutions by using 50 μ Erichsen applicator. Drying time was determined at (20 ± 2)°C, (60 ± 5)% relative humidity by Erichsen Type 415/E tester, which gave results according to DIN 53 150. Drying time was determined at the 5th, 10th, 15th minutes, at every 15 min up to 4 h, at every 30th minute up to 8 h and 24th, 48th, and 72nd h, after application of the films.

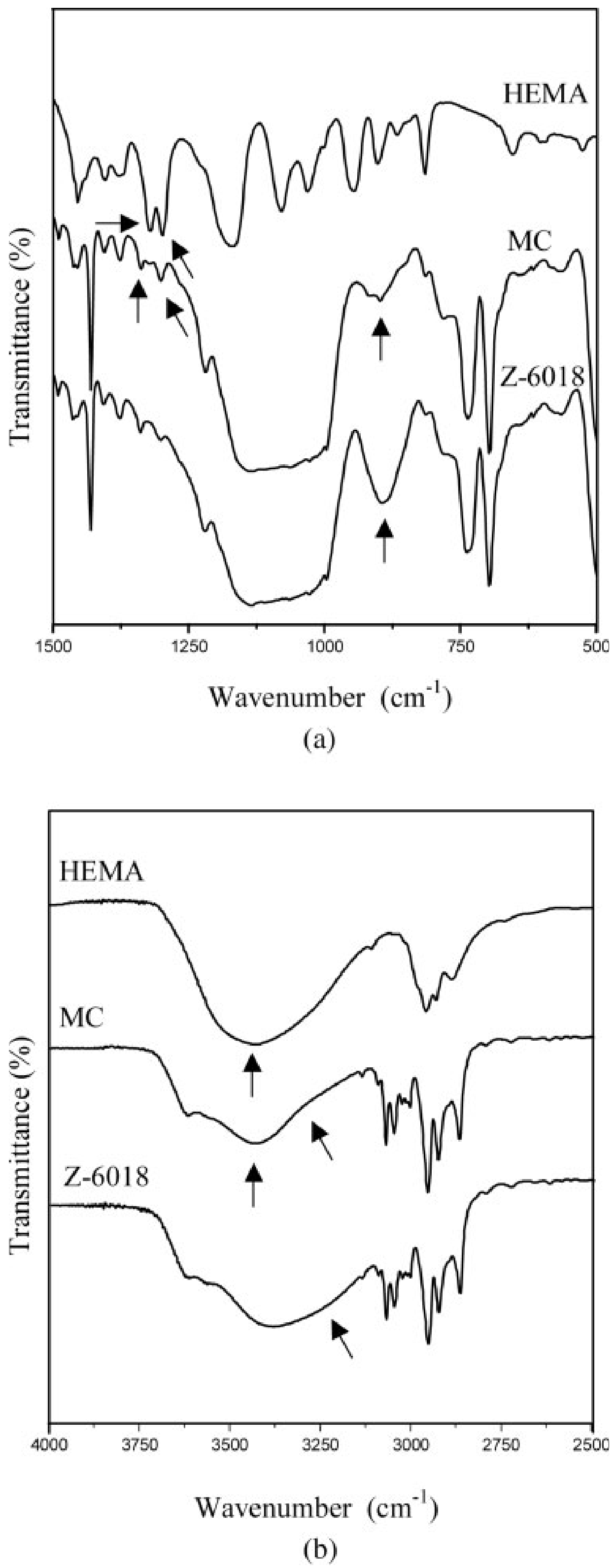


Figure 1 (a) The FTIR spectra of HEMA, MC, and Z-6018 (500–1500 cm^{-1}). (b) The FTIR spectra of HEMA, MC and Z-6018 (2500–4000 cm^{-1}).

Hardness was determined by König Pendulum, which gave results according to DIN 53 157, 72 h after application of the films. Adhesions of the films were tested by the crosscut method according to ASTM D 3359-76.

The impact resistance was determined on films according to ASTM D 2794-69, 72 h after application by FTMS 6226 Impact Flexibility Tester, which determines failure between 0.5 and 60% elongation of the film after impact.

Gloss of films was determined by Gardner Multi-Angle glossmeter according to ASTM D 523.

Abrasion resistance is usually performed with a falling sand abrasion tester. Sand is dropped down a vertical tube onto the panel that is mounted at a 45° angle. The results are given as the amount of sand required removing a certain thickness of coating. Abrasion resistance was determined by Ericsen Sand Abrasion Tester, type 2511-11, which gave results according to ASTM 9685.

Effect of water immersion was determined according to ASTM D1647-59 by 18 h of immersion in water, 48 h after application of the films. The conditions of the films were determined immediately after wiping dry and 20 min, 1 h, 2 h, and 24 h later. This test was realized again for oven-cured (1 h at 110°C) films.

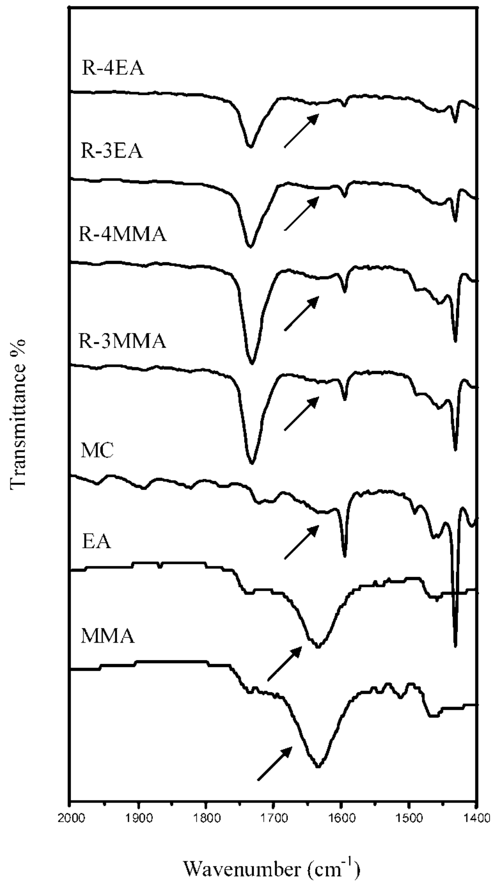


Figure 2 The FTIR spectra of *R*-3EA, *R*-4EA, *R*-3MMA, *R*-4MMA, MC, EA, and MMA.

TABLE I
Thermal Properties of the Si-Containing Acrylic Resins

Sample	T[a] (°C)							Residue (%)	Final degrd. temp. (°C)
	5%	10%	20%	30%	40%	50%	60%		
R-3EA	317	342	379	430	543	612	653	34	707
R-4EA	309	330	372	410	532	609	652	33	703
R-3MMA	266	287	374	464	564	630	672	37	691
R-4MMA	262	277	342	405	520	605	648	35	679
MC	365	450	529	614	667	717	–	49	736

[a] The temperature where various weight loss has occurred.

Alkali resistance test was determined according to ASTM D 1647. Films were prepared on glass test tubes by dipping and the tubes were inverted and supported on vertical pegs during the drying period (72 h). Then, the tubes immersed in alkali solution. The tubes were removed from the solutions after immersion for 15 min, 30 min, 1, 2, 4, 8, 16, and 24 h, and the appearances of films were observed. This test was realized again for oven-cured films (1 h at 110 °C). The all tests were repeated for three times to confirm the repeatability of the tests. The results of all tests are given in Tables I–IV.

RESULTS AND DISCUSSION

FTIR spectra of the resins

The FTIR spectra of MC, HEMA, Z-6018 are given in Figure 1(a,b). The intensity of the peak at 895 and 3250 cm^{-1} which is attributed to Si—OH groups and free —OH groups stretching in Z-6018 decreased. On the other hand; 1322, 1299 and 3200–3350 cm^{-1}(max. at 3426 cm^{-1}) peaks indicating free -OH stretching and acrylates ester C—O stretching in HEMA transformed to small peaks or shoulders at 915, 899, 1302, 1337, and 3435 cm^{-1} because of the formation MC.[30] It was not observed that the new absorption peaks at 1100–1075 cm^{-1} due to the formation of Si—O—C_2H_5 groups during the formation of MC because of the interaction.[30]

FTIR spectra of *R*-3MMA, *R*-4MMA, *R*-3EA, *R*-4EA, EA and MMA are given in Figure 2. The formation of the resins is connected with the disappearance of the absorption peak at about 1680–1620 cm^{-1} max. at 1636 cm^{-1} due to the —C = C-stretching vibrations of vinyl groups in acrylate monomers such as EA and MMA.

Thermal properties of the resins

Thermal properties of the resins were investigated by using TGA and DSC techniques.

Thermal oxidative degradations of the modified resins were investigated by TGA under air atmosphere with a heating rate of 10°C/min. Results were presented in Table I and Figure 3.

The TGA curves indicate that all resins show almost same degradation behaviors and degradation has occurred two or three step. We believe that the introduction of Si linkages in the polymer structure would improve the thermal stability. But the introduction of ester bonds as weak bonds in the copolymer structure was caused to the decreasing the thermal stability of the resins. So, MC has a higher thermal stability than *R*-MMA and *R*-EA. *R*-3EA and *R*-4EA have higher thermal resistance up to about 330–340°C than other resins *R*-3MMA and *R*-4MMA and weight loss was approximately 10% at this temperature range. However after 340°C all resins exhibit more or less the same thermal and oxidative degradation stability, so they are thermally stable materials. *R*-3MMA has higher thermal resistance after about 350°C.

DSC curves of the *R*-3EA, *R*-4EA, *R*-3MMA, *R*-4MMA, and MC are given Figure 4. The melting points of the *R*-3EA, *R*-4EA, *R*-3MMA, *R*-4MMA and

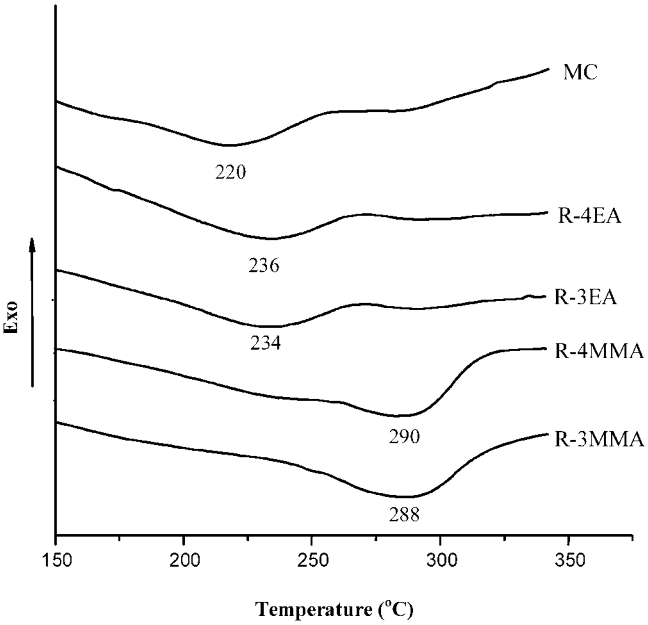


Figure 3 The DSC curves of *R*-3EA, *R*-4EA, *R*-3MMA, *R*-4MMA, and MC.

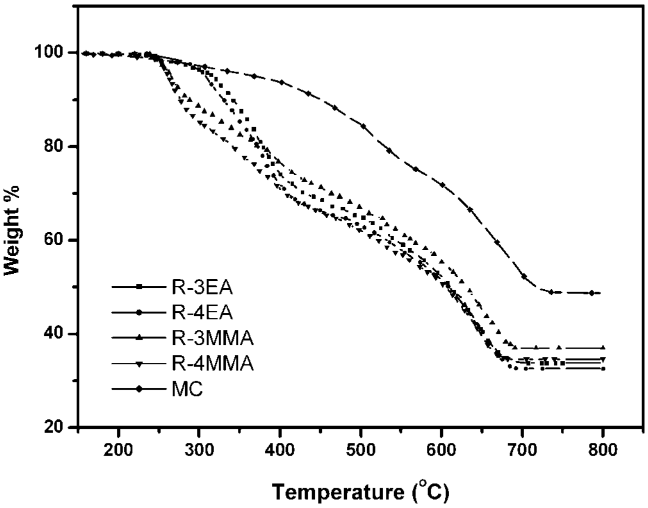


Figure 4 The TGA curves of *R*-3EA, *R*-4EA, *R*-3MMA, *R*-4MMA, and MC.

MC were determined as, 234, 236, 288, 290, and 220 °C, respectively.

The copolymerization of MC with EA or MMA resulted in a product having a higher melting point than this of MC, as expected also, the melting points of the resins including MMA units, having a higher than that of EA.

Film properties of the products

The drying time test results of the film from prepared *R*-3EA, *R*-4EA, *R*-3MMA and *R*-4MMA and MC are given Table II. It was observed that *R*-3MMA and *R*-4MMA reach up to 7th drying stage in a satisfactory and short time than those of MC. When the acrylate monomer units incorporate with the copolymer structure drying time is extremely short for 6th stage. Also the films of *R*-3MMA and *R*-4MMA prepared by using MMA in the copolymerization reaction have excellent drying properties.

The hardness, impact resistance, abrasion resistance, adhesion and gloss results of the films prepared from *R*-3EA, *R*-4EA, *R*-3MMA and *R*-4MMA and MC are given Table III. As seen, the determined hardness values are higher than this of MC. When the acrylate monomer units incorporate with the copolymer structure, hardness of the films is increase. But hardness values of all films are not close to glass hardness of 250 könig second. It was indicated that these films are relatively flexible.

On the other hand, the all films which prepared from *R*-3EA, *R*-4EA, *R*-3MMA and *R*-4MMA have same impact resistance values but these values are slightly higher than this of MC.

Abrasion resistance determined with falling sand particles depends more on elasticity of film. There is no significant difference in abrasion resistance but the films which prepared from *R*-3EA, *R*-4EA, *R*-3MMA, and *R*-4MMA show better performance than the films which prepared from MC.

All films exhibit superior adhesion to the glass substrate and have glossy and semi glossy properties. Also, the more increase the amount of acrylate monomer in the copolymer structure, the more increase glossy of the films.

As seen from Table IV the appearance of the films except prepared from *R*-3EA generally became clear at the end of the 24 h, these properties of the films were modified by cured in oven.

As seen from Table V, alkaline resistance of the films prepared from *R*-3EA and *R*-4EA are excellent. Also, alkaline resistance of the films from prepared *R*-3MMA, *R*-4MMA is improved by cured in oven for 1 h.

SUMMARY AND CONCLUSIONS

In this work, novel acrylic resins were obtained successfully from a reactive polysiloxane intermediate (Z-6018), which has aromatic groups, 2-Hydroxyethyl methacrylate (HEMA), ethyl acrylate(EA)/methyl methacrylate (MMA), for the first time.

The novel Si-containing acrylic resins have been synthesized by two steps. At first a macromer was prepared as silicone modified acrylic intermediate, and then this macromer was reacted with acrylic ester monomers such as EA and MMA to obtain Si-containing acrylic resins. These silicone modified acrylic resins were identified by FTIR Spectrometer and thermal

TABLE II
Drying Time of the Films Prepared from Si-containing Acrylic Resins

	Drying time stage[a]						
Sample	1	2	3	4	5	6	7
MC	–	–	–	5 min	–	5 h 15 min	24 h
R-3EA	–	–	5 min	30 min	–	1 h 30 min	1 week
R-4EA	–	–	5 min	60 min	–	2 h 45 min	1 week
R-3MMA	–	–	–	5 min		15 min	3 h 45 min
R-4MMA	–	–	–	5 min	–	10 min	4 h

[a] Time required reaching a certain drying time.

TABLE III
Hardness, Abrasion Resistance, Impact Resistance, Adhesion and Gloss of the Films Prepared from Si-containing Acrylic Resins

Sample	Hardness (König sec.)	Abrasion resistance (mL sand)	Impact resistance (%)	Adhesion (%)	Gloss
MC	137	500	2	100	60
R-3EA	199	700	5	100	74
R-4EA	198	700	5	100	87
R-3MMA	199	700	5	100	70
R-4MMA	192	700	5	100	90

properties of these resins were also determined by DSC and TGA techniques. Some of their film properties were investigated. The properties of the Si-containing acrylic resins were found to be compatible and comparable with the properties of the resins that had been given in the literature before.[31–33]

Our results show the following:

- As expected that, because of the aromatic rings and siloxane units in the backbone, the macromer shows better thermal stability than the acrylic resins prepared with only EA or MMA that had been given in the literature before.[34,35]
- The introduction of acrylate monomers such as MMA and EA units into macromer backbone has not significantly improved the thermal stability.
- All films prepared in this study are flexible, glossy, or semiglossy.
- The drying and adhesion properties of the all prepared films were found to be excellent.
- All films have moderate abrasion resistance and the films which are prepared from *R*-3EA, *R*-4EA, *R*-3MMA and *R*-4MMA show better abrasion resistance than these of macromer.
- Alkaline resistances of the films prepared from *R*-3EA and *R*-4EA are excellent and water resistances of the films were generally improved by curing in oven.
- The introduction of silicone units and aromatic groups into acrylic resins improved the thermal and mechanical properties. So this type of novel Si-containing acrylic resins can be used as surface coating materials.

TABLE IV
Water Resistance of the Films Prepared from Si-containing Acrylic Resins

	Water resistance[a]									
	Dried					Oven cured				
Sample	0 min	20 min	1 h	2 h	24 h	0 min	20 min	1 h	2 h	24 h
MC	C	C	C	C	C	C	C	C	C	C
R-3EA	T	ST	C	C	C	C	C	C	C	C
R-4EA	T	ST	ST	ST	C	C	C	C	C	C
R-3MMA	T	T	T	T	C	C	C	C	C	C
R-4MMA	T	T	T	T	C	C	C	C	C	C

W, white; T, turbid; ST, slightly turbid; C, clear.

[a] Appearance of the film after immersion in water for 18 h.

TABLE V
Alkaline Resistance of the Films Prepared from Si-containing Acrylic Resins

	Alkaline resistance[a]															
	Dried								Oven cured							
Sample	15 min	30 min	1 h	2 h	4 h	8 h	16 h	24 h	15 min	30 min	1 h	2 h	4 h	8 h	16 h	24 h
MC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
R-3EA	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
R-4EA	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC
R-3MMA	NC	B/SR	R						NC	NC	NC	NC	NC	B/SR	B/SR	R
R-4MMA	NC	B/SR	R						NC	NC	NC	NC	NC	B/SR	B/SR	R

NC, no change; B/SR, blistering and slight removal of film; R, removal of film.

[a] Appearance of the film after immersion in alkaline solution.

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