



Silane-Functionalized Organic Macrocyclic Compounds-Modified UV-Curable Polyurethane Coatings: Synthesis and Properties

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Abstract

Three-dimensional polymer based porous calix[4]resorcinarene has many applications due to its special properties. The special structure of this polymer and having hydroxyl groups in it can provide the necessary conditions for making derivatives with other functional groups so that we can prepare other compounds with other applications. To create functional groups and modify the surface of the polymer, silane coupling agent can be a good option to create new properties and effective applications in the porous surfaces of polymer calix[4]resorcinarene. This research intends to provide a simple method for the use of poly(calix[4]resorcinarene) in ultra violet curable organic coatings. For this purpose, first the poly(calix[4]resorcinarene) was synthesized and then, by surface modification, double carbon-carbon bonds were created on it so that we could use it in radiant coatings. Then, after characterizing the synthesized materials, the structure and properties have been studied. The results confirmed the structure of the synthesized materials. Surface modification improved the distribution of particles in the polymer matrix and provided better coatings also thermal stability of urethane acrylate resin increased.

Keywords: Poly(calix[4]resorcinarene), Porous polymer, UV-curable coatings, Surface modification.

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Introduction

Due to the high efficiency of porous polymers in chemical transformations, it can be expected that the three-dimensional polymer-based porous calix[4]resorcinarene will be used as a new high-performance polymer substrate for the preparation of various polymers and finally polymer reactants. Today, porous polymer structures, as an important group of materials, are widely and rapidly advancing in various fields of science and technology [1-3]. In fact, the porous nature of these species has given these compounds special physical and chemical properties, such that these days they are widely used in various fields such as sensors, gas separation and storage, catalytic applications, energy storage and conversion, de-colorization of colored wastewater and many other cases are used [4-7].

By binding monomeric components, polymers, through known polymer chain diffusion processes, such as radical, anionic, cationic, and compression processes, lead to sub-branching in the growing polymer chain and ultimately to the production of the desired 3D polymer network. The special structure of these three-dimensional and porous polymer species provides a suitable substrate for the addition of other compounds, including homogeneous catalytic species to these compounds and thus the production of inhomogeneous catalytic species. The special properties of these porous polymer structures, including effective and noticeable active surface, high mechanical and thermal stability, easier recovery from the reaction medium, proper distribution of pore size and in many cases their easy and low cost synthesis from simple materials and in Availability has turned them into promising options for producing suitable structural networks for catalytic purposes [8-10]. In recent decades, the modifying porous surfaces to increase their efficiency as adsorbents, bio-hosts, sensors, catalysts etc. has attracted a lot of attention. The desired substrate or surface can be synthetic resin, organic, biological and inorganic polymers, macroporous and mesoporous structures of silica and zeolites [11-13].

Due to the success of the use of calix[4]resorcinarene in the formation of porous and porous polymer species, in this study, an attempt was made to use the polymer form of these species in the functionalization of these structures. Polymer to be used in various applications [14, 15]. The characteristics of this polymer network include the existence of many cavities, high thermal stability, the necessary potential for functionalization due to the presence of aromatic rings and abundant hydroxyl groups [3, 8]. Modification of polymers is a good way to improve the properties in order to increase their efficiency in various fields. The use of silane coupling agent with different agents is one of the common methods. In addition, in recent years, the use of UV-curable polymers as environmentally friendly polymers that have fast curing speeds with low energy and high efficiency can be effective in production [16-18].

Due to the high effectiveness of three-dimensional polymer-based porous calix[4]resorcinarene polymers in chemical transformations, this study aims to modify its surface by silane coupling agent and create a carbon-carbon double bond at the end of its structure for ability to contribute in crosslinking with UV-curable resins to provide a quick way to prepare coatings with different applications of these compounds. Although in this research, a silane coupling agent with a dual carbon-carbon bond has been used, but with the appropriate choice of end groups, various other applications can be achieved.

Experimental

Materials and Methods

Resorcinol, acetaldehyde, formaldehyde, vinyltrimethoxysilane (VTMS), isopropyl alcohol, benzophenone, triethanolamine and sodium hydroxide were purchased from Merck Company (Germany). Ethanol (96%) and hydrochloric acid (37%) were purchased from Dow Jones Company (South Korea). Argon gas was purchased from an Iranian company. Copper chromite ($\text{CuCr}_2\text{O}_4 \cdot \text{CuO}$) nanocatalyst with average particle size of 50 nm and UV-curable urethane acrylate is synthesized according to our previous work [16,19].

Preparation of calix[4]resorcinarene and its polymer

Calix[4]resorcinarene was synthesized according to the method reported previously [20] but to achieve more yield, copper chromite ($\text{CuCr}_2\text{O}_4 \cdot \text{CuO}$) nanocatalyst is used. For preparation poly(calix[4]resorcinarene), under an argon atmosphere, 40 mL of 10% sodium hydroxide (NaOH) solution was added to 14 mmol (7.6 g) of prepared calix[4]resorcinarene. The solution was mixed by a magnetic stirrer for 1 h at ambient temperature, and a red solution was obtained. Then 42 mmol (1.26 g) formaldehyde was dropwise added to the solution in 30 min. The flask was heated to 90 °C and maintained at this temperature for 20 min while stirring. After completing the reaction, the solution was rinsed with cold distilled water to remove excess sodium hydroxide. To convert phenoxide groups into phenol groups, the solid was grinded and the resulting powder was dispersed in 50 mL of 0.1 M HCl for 1 h. The polymer was filtered, rinsed several times with distilled water and dried in an oven for 10 h at 100 °C. The polymer based on calix[4]resorcinarene was obtained as a brown solid.

Modification of polymer based on calix[4]resorcinarene

10 g of poly(calix[4]resorcinarene), 100 ml of isopropyl alcohol and 1 ml vinyltrimethoxysilane (VTMS) were mixed by a magnetic stirrer for 1 h at ambient temperature.

Then 2 ml 10% HCl solution was added and mixed for 24 h [21-23]. The modified polymer was rinsed several times with distilled water and dried in an oven for 8 h at 70 °C. Figure 1 shows all the steps of synthesis and modification.

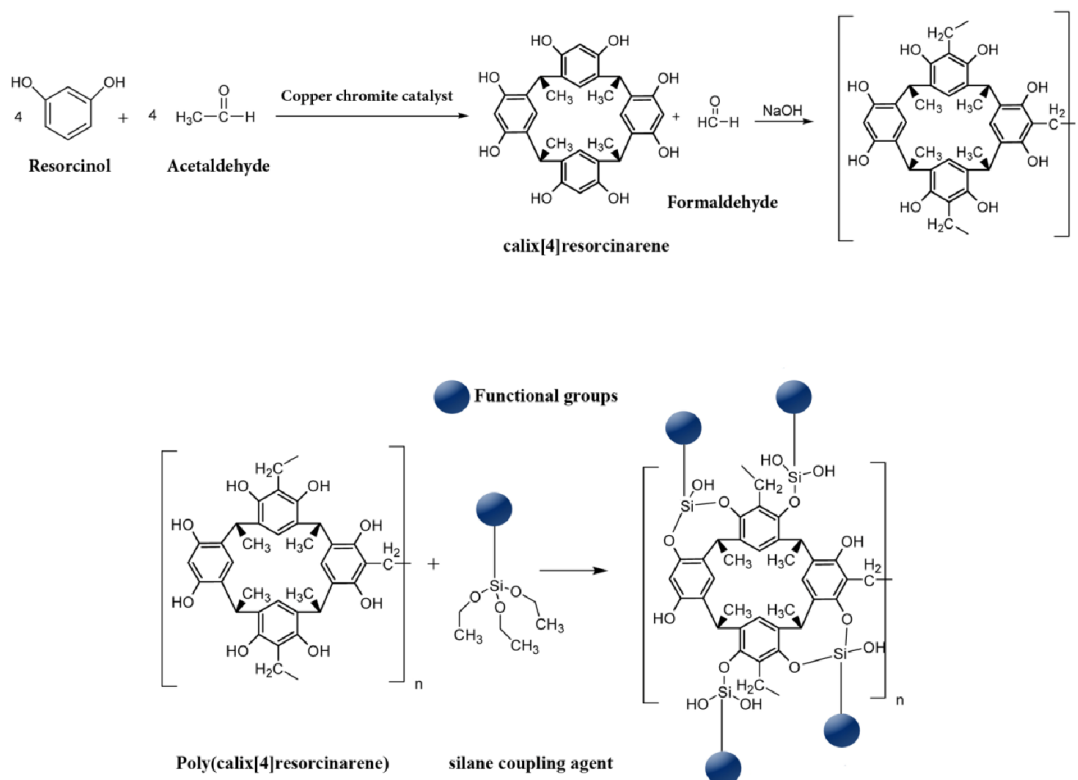


Figure 1. Schema all the steps of synthesis and polymer modification.

Coatings preparation

Three samples of pure resin, resin containing 3% modified, and resin containing 3% unmodified poly(calix[4]resorcinarene) were prepared and mixed. Then 4% by weight of benzophenone as a photoinitiator and triethanolamine as a co-photoinitiator was added and mixed well. After preparing the film, each was cured by ultraviolet irradiation.

Instrumental methods

Fourier-transform infrared spectroscopy (FTIR, BOMEMMB-Series 1998) with a spectral resolution of 4 cm^{-1} and a scanning rate of 21 cm^{-1} , also, ^1H NMR and ^{13}C NMR spectra were recorded in dimethyl sulfoxide (DMSO) by Bruker Advanced DPX 500 MHz spectrophotometer using tetramethylsilane as the internal reference was used to study chemical structure of products. Thermal stability of the samples was studied by Thermogravimetric analysis (TGA), NETZSCH STA 409 PC/PG (Germany) under nitrogen gas with rate of 10 $^{\circ}\text{C}/\text{min}$. A laboratory

oven (UF30/UN30 MEMMERT, Germany) with a temperature range of +8 above the ambient temperature to 300 °C was used to dry the samples at the desired temperature. Optical microscope and atomic force microscope (AFM) of the DME Dual Scope C320 model were used to study the morphology. Precipitates were filtered by a Buchner funnel and a vacuum pump (VE135, VALUE, China) operated with a power of 0.33 hp.

Results and discussion

FTIR spectroscopy of calix[4]resorcinarene and its polymer

In FTIR spectra of calix[4]resorcinarene. As can be seen in Figure 2, the appeared wide strong peak at 3367 cm^{-1} is related to OH group. Stretching vibration peaks at 2972 cm^{-1} and 2929, 2874 cm^{-1} are indicated aromatic and aliphatic C-H, 1617 and 1518 cm^{-1} are assigned to for C=C aromatic, 1118 and 1096 cm^{-1} related to C-O and also bending vibration peaks of CH_3 appeared in 1424 and 1372 cm^{-1} .

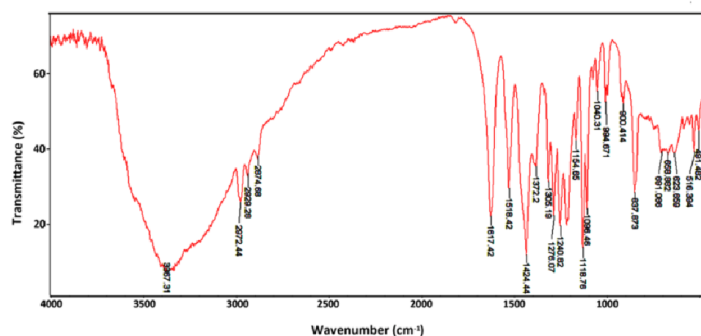


Figure 2. FTIR spectrum of calix[4]resorcinarene.

NMR spectra of calix[4]resorcinarene

In order to confirm the molecular structure of calix[4]resorcinarene, ^1H -NMR and ^{13}C -NMR spectra were done which is shown in Figures 3 and 4, respectively. Results indicated the peak of hydrogen atoms belonging to CH_3 (a) appeared at the range of 1.048-1.305 ppm. The peak of hydrogen atoms in carbon connected to methyl group (b) emerged at 3.585 ppm. The hydrogen of OH group (c) appeared at the range of 4.433-4.460 ppm. Hydrogen peak in carbon between two OH groups (d) and in the opposite direction (e) was observed at 6.140 and 6.770 ppm, respectively.

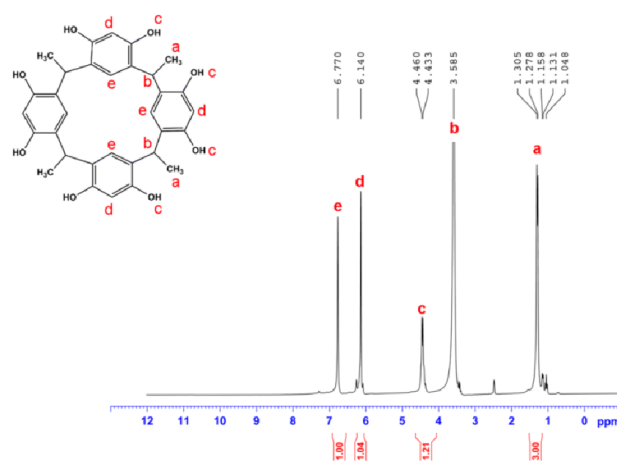


Figure 3. ¹H NMR spectrum of calix[4]resorcinarene.

In CNMR spectrum of calix[4]resorcinarene the peak of carbon atom in CH₃ was observed at the range of 22.18-29.99 ppm. The peak of carbon atoms connected to methyl group appeared at the range of 40.07-41.41 ppm. The carbon in aromatic ring between two OH groups merged at 103.57 and carbon in the opposite direction was observed at 126.76 ppm. Carbon peak in carbon connected to OH groups appeared at 153.32 and carbon in the opposite direction was observed at 124.62 ppm.

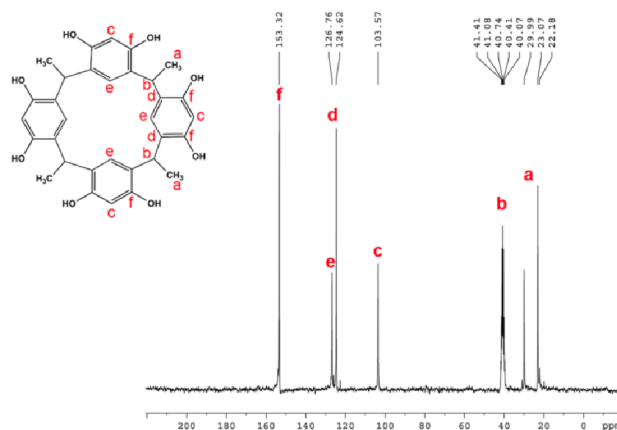


Figure 4. ¹³C NMR spectrum of calix[4]resorcinarene.

FTIR spectroscopy of modified and unmodified calix[4]resorcinarene polymer

FTIR spectrum of polymer based on calix[4]resorcinarene is shown in Figure 5-a. In this Figure, broad strong peak at 3446 cm⁻¹ is the intra-molecular hydrogen bond for OH group. Peaks appeared at 2928 and 721 cm⁻¹ are for connecting aliphatic C-H of calix[4]resorcinarene rings and aromatic

C-H which should be around 3050 cm^{-1} due to overlap with the OH group peak is not observed. Aromatic ring C=C and C-H can be seen at $1616, 1475\text{ cm}^{-1}$, respectively. Peak at 1095 cm^{-1} is related to C-O and 1212 cm^{-1} is for C-OH. Also the peaks of 1377 cm^{-1} are corresponded to bending CH_3 .

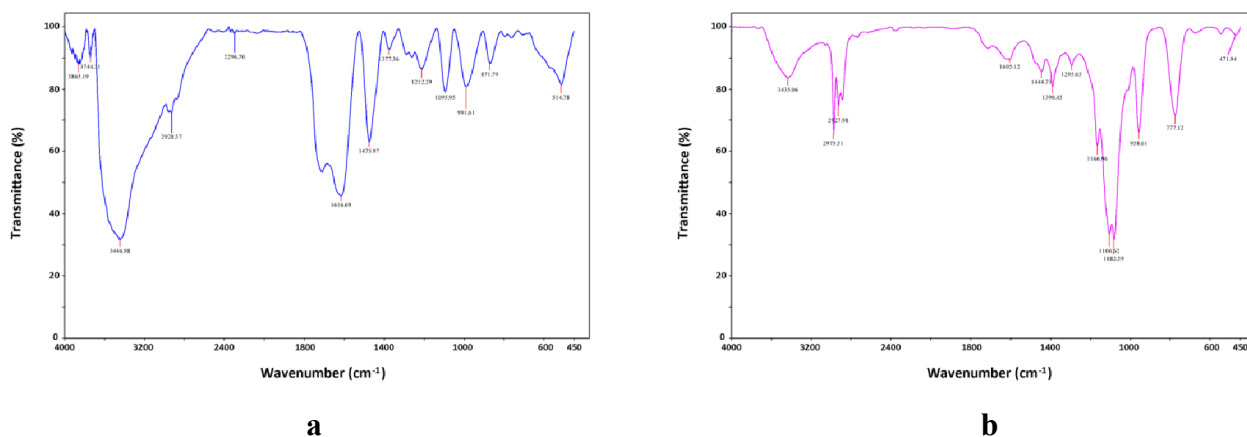


Figure 5. FTIR spectra of modified (a) and unmodified (b) calix[4]resorcinarene polymer.

FTIR spectrum of modified calix[4]resorcinarene polymer is shown in Figure 5-b. In this Figure, the broad strong peak at 3435 cm^{-1} is the intra-molecular hydrogen is bond for OH group. Peaks appeared at 2975 and 777 cm^{-1} are for connecting aliphatic C-H of calix[4]resorcinarene rings. Aromatic ring C=C and C-H can be seen at $1605, 1444\text{ cm}^{-1}$, respectively. Peaks at 1106 and 1082 cm^{-1} are related to Si-O-Si and 958 cm^{-1} is for Si-OH which are confirm the modification.

Morphology

Microscopic images of modified and unmodified calix[4]resorcinarene polymer particles are shown in Figure 6. It is clear that the modified particles have a smaller size than the unmodified sample. Smaller size is probably due to the addition of chemical modifier and the creation of a gap between the molecular chains.

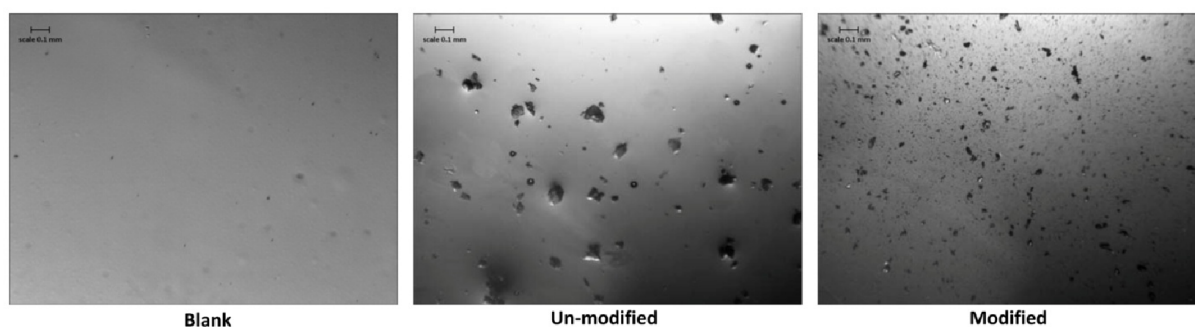


Figure 6. Images of unmodified and modified calix[4]resorcinarene polymer.

With modified and unmodified particles of calix[4]resorcinarene polymer and UV-curable urethane resin films were prepared. The results obtained from AFM images and from the surfaces of these samples (Figure 7) indicated that dispersion of modified particles is better than unmodified calix[4]resorcinarene polymer. The reason can be attributed to the existence of carbon-carbon double bond at the end of the silane coupling agent, which act like the other components of the UV curable resin and participates in the radical reaction and crosslinking of the coating [16].

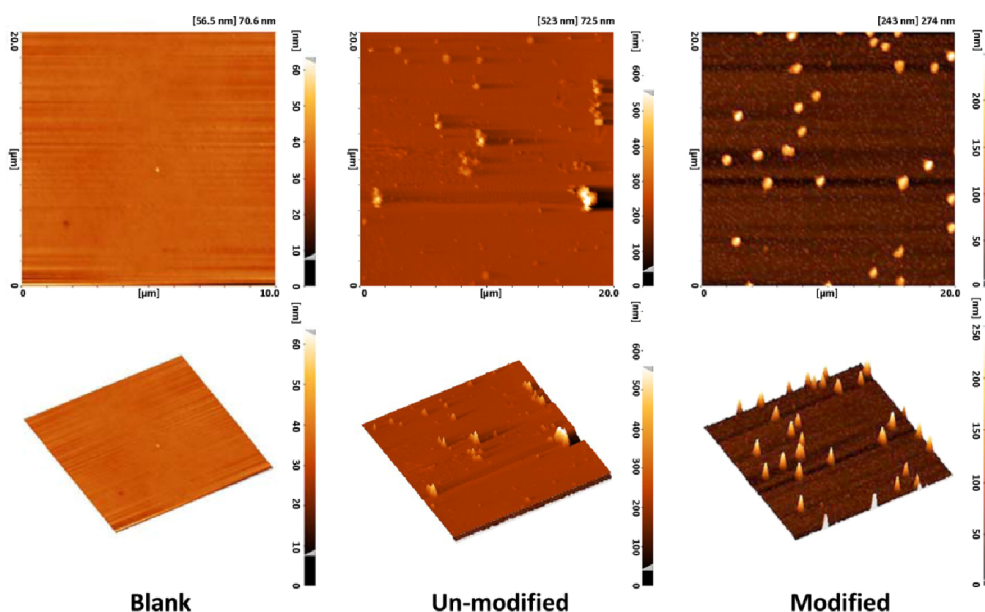


Figure 7. Images of unmodified and modified calix[4]resorcinarene polymer.

Thermal stability of coatings

The results obtained from TGA test are given in Figure 8 and the details are presented in Table 1. As the results show, the modified calix[4]resorcinarene polymer sample has higher thermal stability than the unmodified one, as the reduction difference of 5% and 25% has a temperature difference of 44.87 and 91.1 °C, respectively. Also, complete degradation has not been done up to 600 °C, and this stability is higher for the modified sample.

Table 1. Thermal behavior of samples.

Samples	Loss weight Temperature (°C)					Residue @612 °C (%)
	5%	25%	50%	75%	100%	
PoCalix powder	64.33	298.74	362.51	>600	>600	29.30
M-PoCalix powder	109.20	389.84	620	>600	>600	51.86
Blank film	185.92	349.92	410.85	438.45	620	0.70
PoCalix film	180.29	366.78	418.30	441.91	>600	3.95
M-PoCalix film	182.25	364.00	415.09	444.67	>600	6.60

Interestingly, the polymer films prepared with modified and unmodified calix[4]resorcinarene polymer exhibit almost the same thermal behavior, which can only be related to the behavior of the resin. In all samples, high thermal stability is observed, which can be attributed to the existence of multiple benzene ring structures.

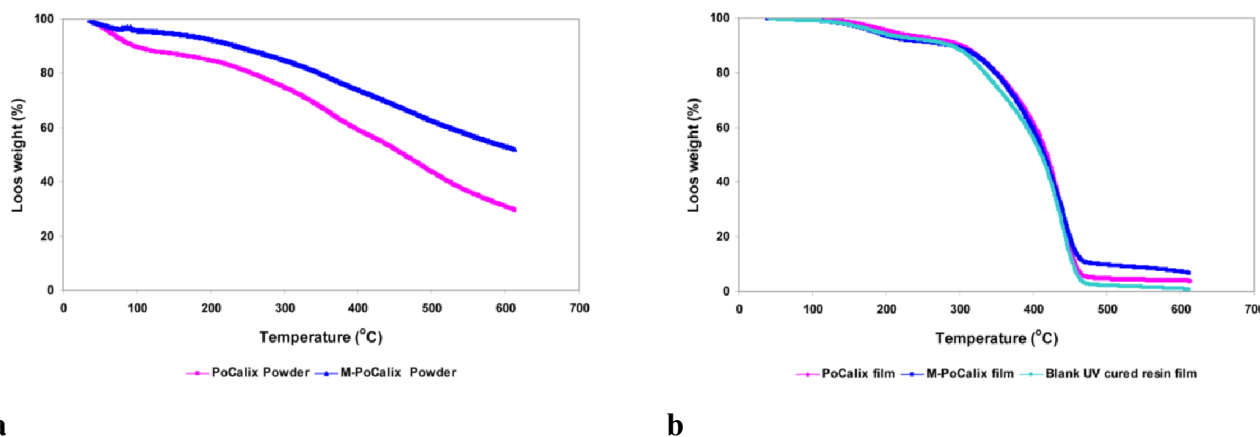


Figure 8. TGA results of materials in powder form and cured film.

Conclusion

In this study, calix[4]resorcinarene polymer was synthesized and surface modification was done. FTIR and NMR results confirmed the structure and successfully synthesize. Microscopic images showed that the modified calix[4]resorcinarene polymer particles were smaller in size than the unmodified sample and were dispersed better in the polyurethane resin matrix. The prepared polymer coatings showed high thermal stability. The simple surface modification method with silane compounds can be a good solution for creating different functional groups and applications for calix[4]resorcinarene polymer in organic coatings.

Acknowledgments

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