

Modification of Cyclohexanone–Formaldehyde Resins with Silicone Tegomers

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ABSTRACT: Cyclohexanone–formaldehyde resins were modified *in situ* with α,ω -diamine polydimethylsiloxanes and α,ω -dihydroxy polydimethylsiloxanes. Melting points, solubilities in organic solvents, gel permeation chromatographs, Fourier transform infrared spectra, and NMR spectra of the modified resin were determined, and the surface properties of the resins were investigated by contact angle

measurements. A small amount of silicon compounds seemed to effect the physical properties of the cyclohexanone–formaldehyde resins significantly. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 97–101, 2005

Key words: modification; polysiloxanes; resins

INTRODUCTION

In earlier studies, the synthesis of copolymers of ketonic resins with polydimethylsiloxane (PDMS) has been achieved with isophorone diisocyanate as a coupling agent.¹ This method has a number of steps, and the overall copolymer yield is not very high. PDMSs containing ketonic resins showed unique properties with the combination of a high surface activity of siloxane segments and a good compatibility of ketonic resins.

The *in situ* modification of cyclohexanone–formaldehyde (CF) resins has been previously studied.^{2–5} Modifier compounds are usually added to the reaction flask either at the beginning of polymer preparation or the later stage of resin formation, depending on their reactivity. The proper choice of modifier compounds usually results in satisfactory physical properties, such as solubility, melting point, and chemical reactivities. Polysiloxanes possess unique combinations of many interesting properties, especially high surface activities and low solubility parameters. These properties lead to the thermodynamic incompatibility of polysiloxanes with most other organic polymer systems. One method used to overcome this difficulty is the use of siloxane-containing copolymers as compatibilizers with organic polymers. In siloxane-containing copolymers, siloxane segments migrate to the air–polymer surface, but the organic segments in the copolymers act as an anchoring group for the siloxane blocks, and then permanent surface modification can be

achieved.^{6,7} In this article, the synthesis of copolymers of CF resins with α,ω -diamine polydimethylsiloxanes and α,ω -dihydroxy polydimethylsiloxanes with a one-step method of *in situ* modification of ketonic resin is reported.

EXPERIMENTAL

Materials

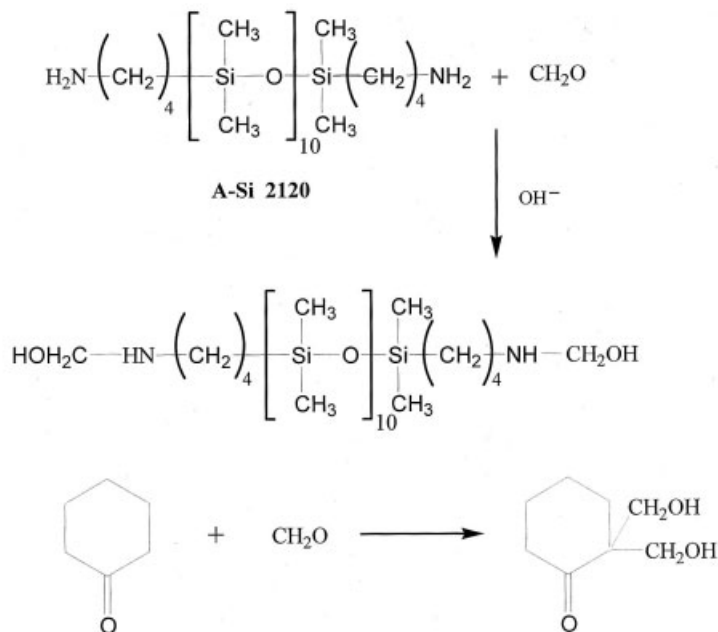
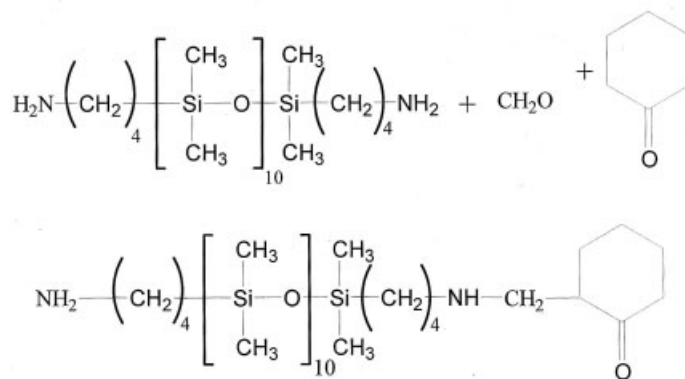
α,ω -Diamine polydimethylsiloxanes (tegomer A—Si 2120) and α,ω -dihydroxy polydimethylsiloxanes (tegomer H—Si 2311; PDMS) were the products of Goldschmidt Chemical Corp. (Essen, Germany). Tegomers A—Si 2120 and H—Si 2311 had molecular weights of 980 ± 30 and 2500 ± 250 , respectively. The solvents and other chemicals used were products of Merck (Darmstadt, Germany). A. G. Formaldehyde is used as formaline (37%).

Thin-layer chromatography (TLC) plates (Silicagel 60, 0.20 mm) with 254-nm fluorescent indicators were used.

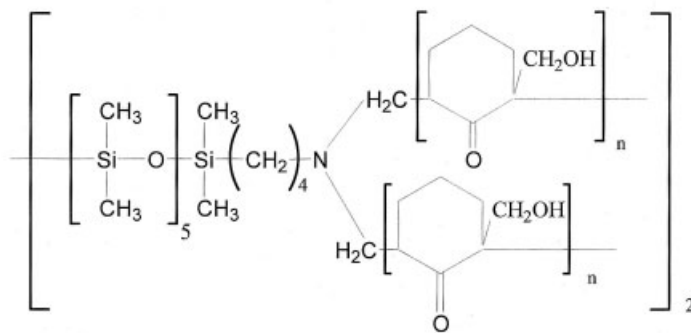
Analysis

Fourier transform infrared (FTIR) spectra were recorded on a Mattson FTIR 1000 spectrometer and a Jasco 5300 FTIR spectrometer (Tokyo, Japan). ¹H-NMR spectra were taken on Bruker AC (200 MHz) and Bruker (250 MHz) spectrophotometers (Darmstadt, Germany) in CDCl₃ and a *d*₆-dimethyl sulfoxide (DMSO) solution without tetramethylsilane. The gel permeation chromatograph was equipped with a differential refractometer and an ultraviolet (254 nm) detector with tetrahydrofuran (THF) as the eluent at a flow rate of 1 mL/min. Molecular weights were calculated with polystyrene standards.

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Aldol like reaction:**The Mannich type reaction:**

The structure of silicon / resin copolymer

**Scheme 1**

The solubility properties of the block copolymers were investigated as follows. 20 mg of solid sample in 2 mL of solvents was mixed in a test tube at room

temperature and shaken. If dissolution occurred in 5 min, it was considered to be soluble. If dissolution was not completed, it was slightly soluble at room temper-

TABLE I
Physical Properties of the Modified CF Resins with Silicone Tegomers

Sample	Tegomer (wt % of cyclohexanone)	Melting point (°C)	M_n (g/ mol)	M_w (g/ mol)	Solubility					
					THF	DMSO	CHCl ₃	CH ₃ OH	(CH ₃) ₂ O	C ₆ H ₅ CH ₃
CF	0	110	1000	1000	s	s	s	sl	sl	sl
CF-2120-01	0.1	90	3640	3700	s	s	s	sl	s	sl
CF-2120-1	1	80	3460	3520	s	s	s	sl	s	sl
CF-2120-5	5	98	3150	3460	s	s	s	sl	s	sl
CF-2120-5 ^a	5	70	3300	3340	s	s	s	s	s	sl
CF-2120-35	35	Crosslinked	—	—	—	—	—	—	—	—
CF-2311-10	10	125	3480	3420	s	s	s	s	s	s

^a Method II.

M_n , number-average molecular weight; M_w , weight-average molecular weight.

S, soluble; SI, slightly soluble.

ature. Then, the solution was heated up to the boiling point of the solvent, and the same observation was repeated at that temperature. If the dissolution did not occur even in the hot solvent, it was considered insoluble.

Contact angle measurements of the copolymeric films were carried out on a Kernco model GIII contact angle meter at room temperature with distilled water. The measurements were made immediately at the beginning, then after 10 s, and finally after 3 min for water droplets on the films prepared by casting from a 1% (w/v) chloroform solution.

Preparation of the modified CF resins

Method I

Into a three-necked flask, 88 g of cyclohexanone, 30 g of formaline, 20 g of cyclohexane, and silicone tegomer were added and heated to 60°C with stirring; then added was 0.36 mL of 20% NaOH in equal portions. When the temperature of the mixture rose to 75–80°C, refluxing began. Then, 100 g of formaline and 3.64 mL of 20% NaOH were mixed and added continuously at a gradually increasing rate sufficient to maintain vigorous refluxing. After 2 h, the reaction was completed. The upper phase was decanted. It was then washed several times with hot water and dried at 120°C *in vacuo*.

Method II

Into a three-necked flask, 88 g of cyclohexanone, 30 g of formaline, and 20 g of cyclohexane were added and heated to 60°C with stirring; then 0.36 mL of 20% NaOH in equal portions was added. When the temperature of the mixture rose to 75–80°C, refluxing began. Then, 90 g of formaline and 3.64 mL of 20% NaOH were mixed and added continuously at a gradually increasing rate sufficient to maintain vigorous refluxing. After 2 h, the modifier compound and 10 g

of formaline were added, and the stirring was continued for 2 h more; then, the reaction was completed. The upper phase was decanted. It was then washed several times with hot water and dried at 120°C *in vacuo*.

RESULTS AND DISCUSSION

The formation of CF resin starts with an aldol-like reaction following a base-catalyzed elimination reaction of water from methylol derivatives of cyclohexanone.^{2,8} α,ω -Dihydroxy polydimethylsiloxanes (tegomer H—Si 2311), with hydroxyl chain ends, probably combines to the resin molecules from its hydroxy chain ends by the effect of the base-catalyzed condensation reactions.

α,ω -Diamine polydimethylsiloxanes (tegomer A—Si 2120) with an amine chain end probably acted as an amine component of the Mannich-type reaction⁹ under the conditions of the resin preparation. Because the molar ratio of formaldehyde to amine was rather high, each —NH₂ groups should have reacted with 2 mol of formaldehyde and 2 mol of ketones. The intermediate formed from aldol-like reactions and Mannich-type reactions combined by the effect of the base catalyst to form modified resin similar to base-catalyzed ketonic resin formation (Scheme 1).

The amount of silicone tegomer was kept low to inhibit crosslink reactions. In one experiment, an insoluble crosslinked product was obtained. The physical properties of the modified CF resins are shown in Table I. The solubilities of the modified CF resins were investigated with different organic solvents. The addition order of tegomer to the reaction media resulted in copolymers with slightly different solubilities, melting points, and molecular weights. The melting points of the copolymers were lower than those of the CF resins. The advantages of tegomer addition for the resin preparation were as follows: the reaction rate increased, the formation of the resin started much earlier, and the removal of water from the resin was much easier.

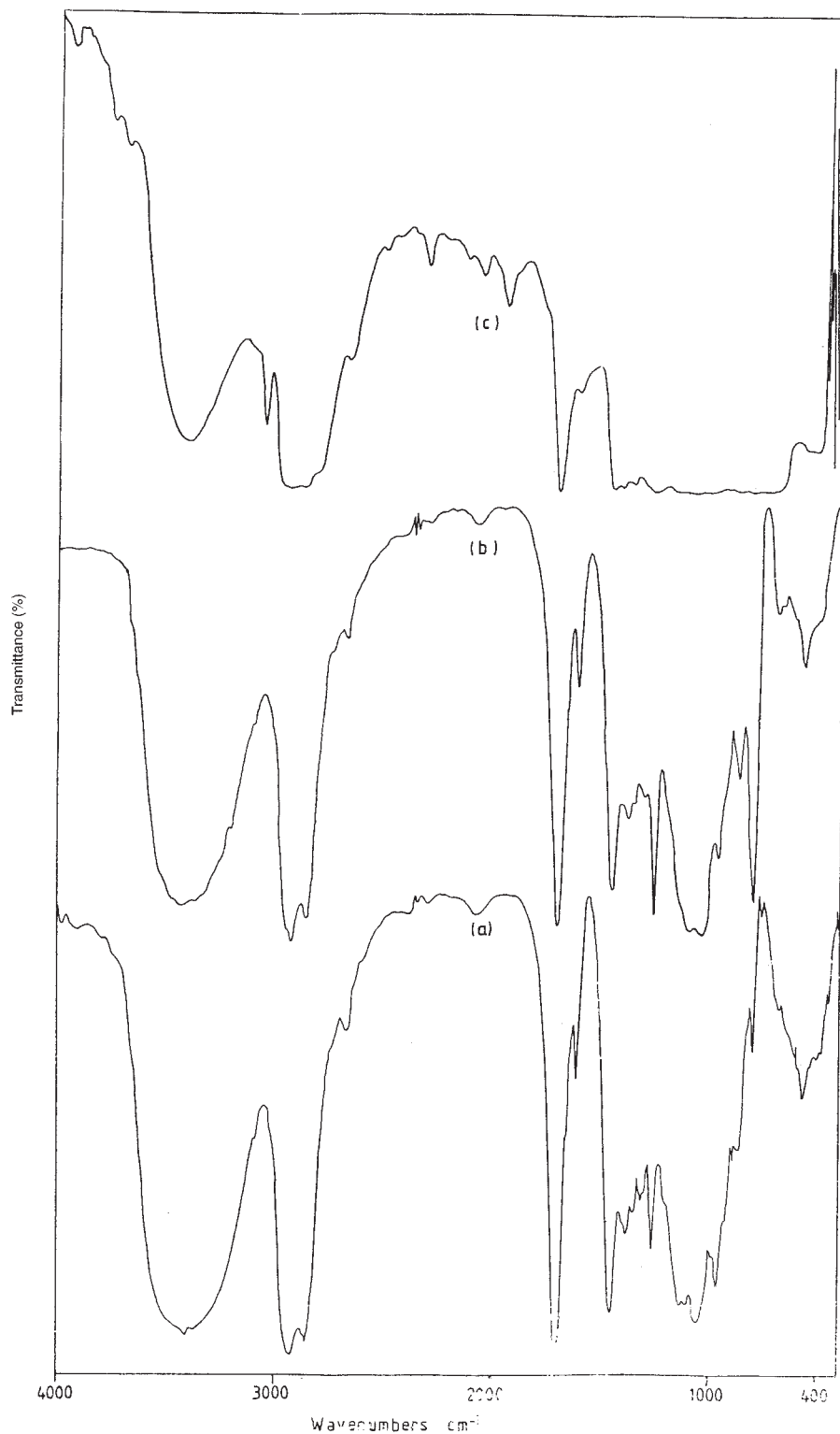


Figure 1 FTIR spectra of (a) CF-2120 (5%, method I), (b) CF-2311 (10%), and (c) CF-2120 (35%).

The FTIR spectrum of modified CF resins with both amine chain ends and hydroxyl chain ends are shown in Figure 1. The modified resins showed a peak at 3400 cm^{-1} due to hydroxyl groups, and the peak at 1700 cm^{-1} due to carbonyl groups was clearly seen. CF resins mod-

ified with both tegomer A—Si 2120 and tegomer H—Si 2311 showed a signal due to Si—O—Si groups at about 1100 cm^{-1} . The peaks at $940\text{--}970$ and 1080 cm^{-1} due to Si—O bonds of —Si—O—CH₂ and at 1250 and $850\text{--}750\text{ cm}^{-1}$ due to Si—CH₃ groups were present.

The $^1\text{H-NMR}$ spectra were recorded from the deuterated solvent solution without a TMS internal standard. The $^1\text{H-NMR}$ spectra of the tegomer-modified CF resins are shown in Figure 2. The peaks appearing at about 0.05–0.1 ppm were due to $-\text{Si}-\text{CH}_2$ and $\text{Si}-\text{CH}_3$ protons.

The modified resins were examined with TLC. Tegomer A—Si 2120, tegomer H—Si 2311, the CF res-

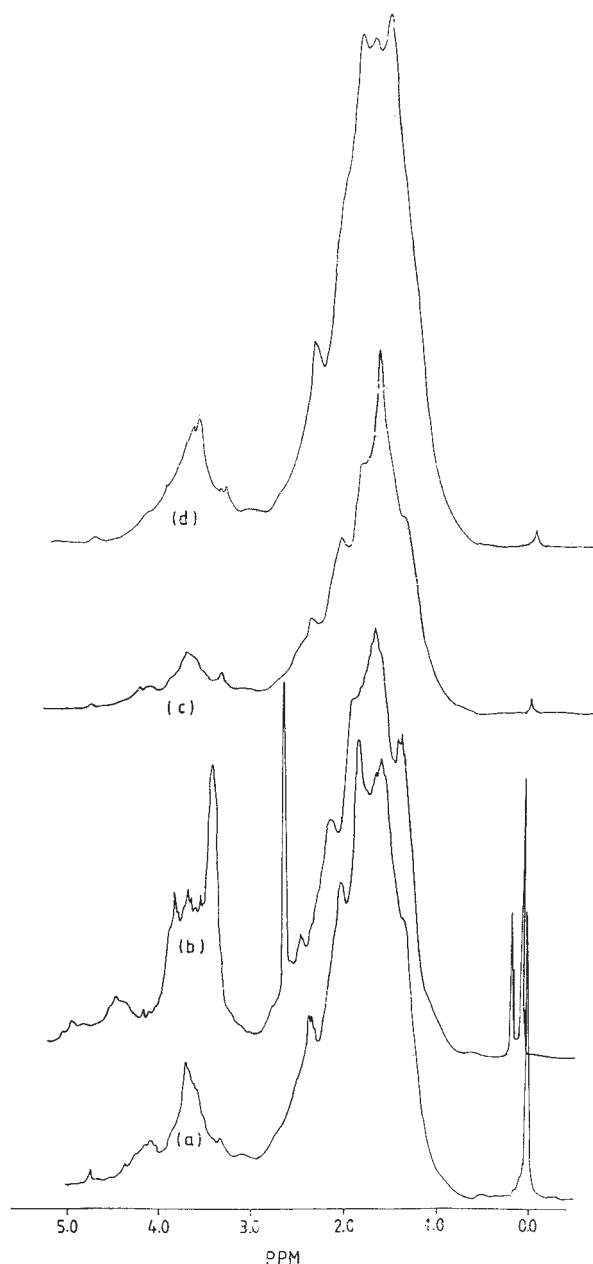


Figure 2 $^1\text{H-NMR}$ spectra of (a) CF-2120 (5%, method I, in CDCl_3), (b) CF-2311 (10%, in d_6 -DMSO), (c) CF-2120 (1%, in CDCl_3), and (d) CF-2120 (0.1%, in CDCl_3).

TABLE II
Contact Angle Values of the Modified Resin Films

Resin	Cast film from dichloromethane air side
CF	75
CF-2120 (5%)	78
CF-2311 (10%)	93

ins, and the modified resins were applied to the TLC plate eluted with chloroform/benzene (3/1 mixed solvent), and then each sample showed their own R_f values. TLC results indicate that those products were not the blends of CF resin and the tegomers, but they were block copolymers.

Contact angle measurements were made on modified resin films prepared by casting from a dichloromethane solution on a glass slide. The results are given in Table II.

The inclusion of the silicon tegomers resulted in a considerable increase in the contact angle values of the CF resins.

CONCLUSIONS

The addition of a small amount of silicon tegomer as the modifier to a mixture of cyclohexanone and formaldehyde during resin preparation gave a number of advantages, including an increase in resin formation speed, easy removal of water from the final product, and higher contact angle values of the modified resins. The silicon-modified resins may have some advantages in application areas where the surface angle is important. In addition, silicon-modified resins may find new applications in the areas of surface coating, printing, inks, and silicon resin compatibilization.

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