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Recovery of monomers and fillers from high-temperature-vulcanized silicone rubbers—combined effects of solvent, base and fillers

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Abstract

The depolymerization of high-temperature-vulcanized (HTV) silicone rubbers containing filler silica and alumina into cyclosiloxane monomers and spontaneous recovery of fillers were studied. First, HTV silicone rubber was treated with different types of solvents in the presence of KOH to find that a triad mixture of diethylamine, methanol and hexane was appropriate not only to dissolve the silicone rubber to a suspension but also to separate fillers completely by filtration. The filtrate was distilled to remove solvent first and then give pure cyclosiloxane monomers in 76–84% yields. Second, the rubbers were treated with other types of triad mixture of solvents and bases, e.g. tetramethylammonium hydroxide, hexane and diethylamine. After filtration, residue was again treated with the amine and hexane to recover clean fillers in 83–93% yields. Cyclosiloxane monomers were also obtained from the combined filtrates in 67–78% yields. © 2002 Published by Elsevier Science Ltd.

Keywords: Silicone rubber; Monomer recycling; Fillers recovery

1. Introduction

How to solve the problem of polymer wastes particularly at the post-consumer stage is now becoming an important issue on the basis of protecting global environment and petroleum resources from depletion. The primary solution to this problem can be the depolymerization of plastic wastes to monomers. On this conceptual basis, organosilicon polymers, the worldwide production of which has reached several millions tons annually, cannot be an exception to be evaded from recycling particularly because a huge amount of energy is required for the production of organosilicon polymers [1].

It is well known that the polymerization of cyclosiloxane monomers involves a thermodynamic equilibrium between cyclic monomers and linear polymers [2–8]. Based on this fact, some recycling methods of linear poly(dimethylsiloxane) (PDMS) and cross-linked PDMS (vulcanized silicone rubbers) to cyclosiloxane monomers have been already developed [9–19].

In parallel to this study, we have reported an effective depolymerization of PDMS to cyclosiloxane monomers such as hexamethylcycloterasiloxane (D_3), octamethylcyclotetrasiloxane (D_4) by KOH-catalyzed depolymerization in combination with the use of buffer acid [20]. Indeed, not only PDMS but also vulcanized PDMS can be depolymerized to cyclosiloxanes monomers effectively by this base–acid tandem operation.

The main problem in recycling silicone rubber wastes in the form of monomers is the removal of fillers from rubbers. One method to solve the problem is the use of solvents [17–19]. However, because of strong interaction between fillers and PDMS chains that hampers the separation of fillers from PDMS chains, it is not so easy to find an effective solvent, which at the same time also facilitates the depolymerization. It is usually not easy to obtain monomers from the equilibrated depolymerization mixture while leaving the solvent and fillers. If the solvent is removed in advance to the separation of fillers, the remaining PDMS cannot be depolymerized smoothly to monomers, thus resulting in low yields. Nevertheless, this problem seems to be solvable if the fillers can be separated in advance to the removal of solvent and monomers. However, another problem remains, namely, how to separate fine fillers of nanometer-sized silica and alumina.

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In this report, we describe that a mixture of diethylamine, methanol and hexane is very effective not only to facilitate the KOH-catalyzed depolymerization of silicone rubber containing silica and alumina, but also separate fillers completely by filtration before the removal of monomers and solvents. After the removal of solvents, pure cyclosiloxane monomers can be obtained by distillation in 76–84%. In parallel, not only to improve the monomers yield but also to separate fillers effectively, an organic base was used in place of KOH. Consequently, fillers were recovered in 83–93% efficiency.

2. Experimental

2.1. Materials

Poly(dimethylsiloxane-co-methylvinylsiloxane) gum is commercially produced by Dow Corning Co. (SH410). The ratio of vinyl groups to silicon atoms in this gum was determined by ^{1}H NMR to be 0.0225. Ingredients in the silicone rubber were as follows: PDMS gum: 40%, silica: 9%, alumina: 51%. Vulcanization of the rubber was carried out at 170 °C for 10 min after kneading it with 0.8 phr of 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane. Diethylamine, toluene, methanol, hexane, and KOH were available from Wako Pure Chemical Co. Monomers D_3, D_4, D_5 and D_6 were commercially available from Shin-Etsu Co.

2.2. Depolymerization of vulcanized silicone rubber containing fillers

Vulcanized silicone rubber sheets containing fillers were cut into pieces (about $2 \times 3 \times 4\ \text{mm}^3$ in size) and they were mixed with KOH in a triad mixture of solvents in a 100 ml flask or with tetramethylammonium hydroxide in a triad mixture of diethylamine, hexane and methanol, or in a binary mixture of hexane and methanol. The mixture was agitated by a magnetic or mechanical stirrer at room temperature or under solvent reflux. When the silicone rubber was dissolved in the solvent mixture, the mixed solution was filtered. After the fillers were separated by filtration, the filtrate was transferred to a 100 ml flask, a small amount of KOH was added if needed, and the solution was heated to remove the solvent first and then subjected to distillation at 170 °C/30 mm Hg for 3 h to obtain depolymerization products. The distillates were collected in a trap cooled at −78 °C. On the other hand, the filtration residue was again treated with a mixture of diethylamine and hexane to give fillers.

2.3. Treatment of fillers

The fillers separated by filtration from the treatment with tetramethylammonium hydroxide were heated under atmospheric pressure at 150 °C for 5 h. The weight of remaining fillers was measured as W_f (g), and the recovery yield was calculated on the basis of ingredients (60.8%) originally contained in the rubber specimen. After this treatment, 0.5 g of the recovered fillers was added to a 10 ml mixture of methanol and H_2O (v/v = 1:1), and after stirring the mixture at room temperature for 2 h, pH of the solution was measured.

2.4. Characterization

The swelling ratio of silicone rubber in different solvents was measured as follows. A specified amount of rubber (W_r, in grams) which was cut into small pieces of about ($5 \times 5 \times 5\ \text{mm}^3$) in size was immersed in a specified amount of solvent or solvent mixture in a conical flask for 48 h at room temperature. Then the swollen rubber was taken out, solvent on the surface of the rubber was wiped quickly by a filter paper, and the weight of the rubber (W_s in grams) was measured quickly. The weight swelling ratio W_r/W_s was calculated. The composition of monomers was analyzed by gas chromatography on GC-14B (Schimadzu Co.) using commercially available cyclosiloxanes D_3, D_4, D_5 and D_6 as the standard substances. The chromatographic conditions were as follows: solvent, acetone; concentration of samples, about 0.05 g/ml; temperature programming, 10 °C/min for 50–320 °C; injector and detector temperatures, 320 °C.

3. Results and discussion

3.1. Dissolvability of solvent for filler-containing vulcanized silicone rubbers in the presence of KOH

Table 1 lists the results of dissolution of silicone rubber in toluene, methanol, and diethylamine. Our preceding study [20] indicated that vulcanized silicone rubbers containing no fillers can dissolve well in toluene in the presence of KOH. However, toluene was not effective for the dissolution of silicone rubber containing silica and

Table 1
Time required for dissolving filler-containing silicone rubber by two-step mixing of DEA and methanol

Entry	Amount of solvent (ml)				Solubilization time (min)[a]
	Initially added under reflux		Secondly added after the first		
1	DEA	17.5	MeOH	6.5	5
2	DEA	20.0	MeOH	7.0	10
3	MeOH	17.5	DEA	7.0	40
4	MeOH	10.0	DEA	10.0	30

Amount of filler-containing silicone rubber = 4.9–6.2 g.

[a] Time required under solvent reflux after the secondary solvent was added. The refluxing time in the initial solvent was 4 h.

Table 2
Time required for dissolving filler-containing silicone rubber in the prepared mixture of DEA and methanol in the presence of KOH

Entry	Solvent mixture (ml)		KOH (g)	Solubilization time (min)[a]
	CH_3OH	DEA		
5	6.0	20.0	0.73	30
6	10.0	11.5	0.78	40
7	14.5	7.0	0.55	70
8	10.0	11.5	0.78	90

Amount of silicone rubber specimen in each entry was 6.2 g. A mixture of methanol and DEA was used from the beginning.

[a] Time required under solvent reflux for entries 5–7 and at room temperature for entry 8.

alumina even under the presence of KOH at a high content of 30 wt% and refluxing for 10 h. The reason may be attributed to strong interactions between fillers and PDMS chains in comparison with those between fillers and toluene. It has been reported [17,18] that amines are useful solvents for KOH-catalyzed depolymerization of silicone rubbers and, therefore, diethylamine (DEA) was chosen to dissolve filler-containing silicone rubber in our experiments. However, DEA was also found not effective to dissolve silicone rubber (Table 1). This is probably due to the fact that the rubber was not room temperature vulcanized (RTV) but high temperature vulcanized (HTV) and, due to the difference in cross-linking structures between RTV and HTV rubbers, DEA cannot attack the cross-linking bonds of HTV [21,22]. In addition, methanol was also found ineffective for the dissolution of the rubber albeit it has a good ability to dissolve KOH.

Nevertheless, we found that the combined use of DEA with methanol was effective to dissolve the filler-containing silicone rubber in the presence of KOH. After warming the rubber in refluxing DEA with KOH, methanol was added and a suspension of fillers containing depolymerized rubber was formed quickly (Table 1). The reversed treatment, namely, heating the rubber in MeOH with KOH and then adding DEA, also dissolved the rubber in a short period to form an emulsion but not a suspension. Further, with a prepared mixture of DEA and methanol, the silicone rubber was dissolved much quickly to form a filler suspension (Table 2).

The dissolution of silicone rubber basically depends on the breakage of Si–O bonds of PDMS by KOH and, thereby, two important factors should be considered to facilitate the depolymerization, i.e. concentration of KOH catalyst in the solvent and swelling ratios of silicone rubber in the solvent. Swelling ratios of vulcanized silicone rubbers with or without fillers, determined by independent swelling experiments, are listed in Table 3. The swelling ratio is the largest in DEA and smallest in methanol. Because the addition of methanol to DEA leads to decrease in swelling ratio, the effective dissolution of the rubber in the mixture of DEA and methanol is undoubtedly attributed to the increased solubility of KOH in methanol.

It is intriguing to find that the solubility of silicone rubber without fillers in DEA alone or a mixture of DEA and methanol showed no obvious difference, which was not the case for the rubber filled with silica and alumina. This discrepancy probably can be explained as follows. As the silicone rubber gets swollen, silanol groups on the surface of silica react with KOH to form potassium silanolates, but the basicity of the silanolates is too weak to initiate the depolymerization of PDMS, i.e. the chain transfer from the silanolate on the silica surface to the PDMS is not likely. After most of silanol groups are transformed to silanolates, the depolymerization takes place smoothy by KOH in solution. In DEA solvent, the KOH concentration in solution is low even when a high content of KOH is added and most of KOH in solution reacts with the silanol groups on the surface of silica. As methanol is added, concentration of KOH in the mixed solvent increases considerately to initiate the depolymerization of PDMS leading to a quick dissolution of silicone rubber, although some KOH is competitively consumed by the reaction with silanol groups. This explanation can also be supported by the observation that most of the KOH remained in the fillers (vide infra).

Table 3
The weight swelling ratio of silicone rubbers in various solvents

Silicone rubber	Solvent	Swelling ratio
With filler	Toluene	1.69
	Methanol	1.02
	DEA	2.03
	DEA + methanol (w/w = 1:1)	1.20
Without filler	Toluene	3.34
	Methanol	1.04
	DEA	3.95
	DEA + methanol (w/w = 1:1)	1.37

Without KOH.

3.2. Monomers recovery from suspension formed after dissolution of silicone rubbers

After the dissolution of silicone rubber in the experiments listed in Table 1, the reaction mixture was heated under solvent reflux for 3 h. The suspension formed in the dissolving treatment of entry 1 (Table 1) was distilled directly in vacuo to remove volatile substances giving a hard and fragile residue. The observed weight loss in the silicone rubber was about 7%. Since additional heating of the residue at 170 °C/30 mm Hg for 3 h showed no weight loss, the observed small decrease in the weight of recovered rubber indicated that the fillers did affect the depolymerization of PDMS.

Separation of fillers from the emulsions formed in entries

Table 4
Yield and composition of monomers obtained from depolymerization in a mixed solvent of DEA and methanol

Entry[a]	Composition of monomers (%)						Yield[b] (%)	Yield[c] (%)
	D_3	D_4	D_5	D_6	D_7	D_8		
2	3.6	67.2	23.4	4.6	0.9	0.3	31.5	79
5	6.3	73.9	18.7	1.1	–	–	32.1	80
6	10.6	70.8	15.6	2.2	0.8	–	27.6	69
7	14.8	76.1	7.7	1.1	–	0.3	22.6	57
8	11.4	72.6	13.8	1.3	0.7	0.2	21.9	55

[a] Entry numbers correspond to those in Tables 1 and 2.
[b] Based on the amount of filler-containing silicone rubber.
[c] Based on PDMS.

3 and 4 (Table 1) was impossible, whereas with the suspensions in entries 2 (Table 1) and 5–8 (Table 2) the filtration was easy. Filtrates were nearly clear solutions except a trace amount of fine particulates. The filtrate was heated at 110 °C to remove methanol and DEA giving finally a viscous liquid residue. Then the residue was subjected under distillation at 170 °C/30 mm Hg for 3 h to obtain monomers. The yield and composition of monomers are listed in Table 4. The monomers mainly consisted of D_4, D_5, and D_3, together with a small amount of D_6, D_7 and D_8. Though the reason is not clear, the formation of ten-membered monomer D_5 tends to be favored over six-membered D_3. No other compound was found by the GC analysis.

3.3. Increased effect of triad solvent mixture on the separation of fillers

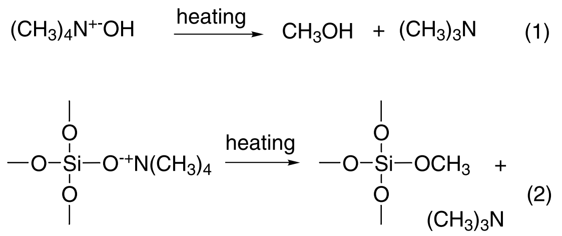
In most case of the above described experiments, though mostly successful, fillers could not be separated perfectly. This is because very small particles of fillers (silica and alumina), formed by the collapse of their aggregates, can pass through the filter. The amount of inseparable fillers was sometimes not negligible resulting in lowering of the monomers yield as listed in entries 7 and 8 in Table 4.

In order to achieve a complete separation of fillers, a hydrocarbon solvent such as hexane was added as the third solvent component to the mixture of DEA and methanol. It was found that by the addition of hexane the filtrates became clear without any suspending particulate. The reason for this change is clear. In a non-polar solvent hexane, polar small particulates of silica and alumina become unstable and, as a consequence, they form aggregates. Indeed, the use of this triad solvent mixture improved the monomers yield and the efficiency was not affected by the amount of solvents and KOH (Table 5). For entries 3 and 4 in Table 5, where the initially added amount of KOH were smaller than that in other entries, additional amount of KOH 0.02 g was added after the removal of solvent because without it the depolymerization was very slow. This indicates that most of the initially used KOH was consumed by the reaction with silanol groups on the surface of silica fillers.

Table 5
Yield of monomers obtained from depolymerization in a triad solvent mixture

Entry	Silicone rubber (g)	Solvent (ml)			KOH (g)	Yield (%)	
		Hexane	DEA	Methanol		A[a]	B[b]
1	6.28	12	5	8	0.56	30.3	76
2	6.55	24	10	16	0.99	33.7	84
3	6.20	24	10	16	0.23[c]	31.5	79
4	6.22	12	5	8	0.25[c]	32.3	81

Refluxing time in the solvent mixture was 5 h.
[a] Based on the total amount of silicone rubber.
[b] Based on PDMS.
[c] Additional KOH (0.02 g) was added to this amount before distillation.



Scheme 1. Decomposition of $(CH_3)_4NOH$ and ammonium silanolate on the surface of silica.

3.4. Recovery of fillers by use of tetramethylammonium hydroxide [$(CH_3)_4NOH$] in triad solvent mixtures

The fillers separated in the above-described process may not be re-used for re-manufacturing silicone rubbers without further purification. This is because most of the KOH remain in the fillers even after filtration and it would afford a poor thermo-stability to the re-produced silicone rubber. The post-treatment involving neutralization of the recovered fillers and removing the salts formed is somewhat complicated. Therefore, in order to recover the fillers not contaminated by alkali metal cations from vulcanized silicone rubber and cyclosiloxane monomers as well, $(CH_3)_4NOH$ was used as a base catalyst for the depolymerization of vulcanized silicone rubber. Because $(CH_3)_4NOH$ is easily decomposed at high temperatures (Scheme 1, Eq. (1)), the fillers containing this base can be purified for re-use simply by a heating treatment (Scheme 1, Eq. (2)). Indeed, after separating the fillers from the treatment with $(CH_3)_4NOH$, the fillers were heated in air at 150 °C for 5 h, and their aqueous suspension was found neutral to the pH test. This is because $(CH_3)_4NOH$ absorbed on the surface of silica easily decomposed to volatile CH_3OH and $(CH_3)_3N$ under heating (Scheme 1). On the other hand, the filtrate was treated with KOH to depolymerize PDMS to cyclosiloxane monomers. Thus, both fillers and monomers were recovered (Table 6).

In all the experiments described up to this stage,

Table 6
Yields of monomers and fillers obtained by use of $(CH_3)_4NOH$ in a mixed solvent

Entry	Solvent (ml)		$(CH_3)_4NOH$ (25% in MeOH) (g)	Yield of monomers (%)	Yield of fillers (%)
	Hexane	DEA			
1	20	10	0.6	67	85
2	15	15	0.6	75	93
3	10	20	0.6	78	83

Amount of silicone rubber specimen in each entry was 10 g. Refluxing time in the solvent mixture was 5 h.

vulcanized silicone rubbers filled with a binary mixture of silica and alumina were used as the substrates. Because of this binary composition, characterization of separated fillers was somehow difficult. Therefore, we prepared a model silicone rubber filled only with silica, a typical rubber of industrial use. The preparation procedure of model silicone rubber filled with 30 phr silica was as follows: a 15 g of PDMS gum was dissolved in 80 ml of toluene, to which was added 4.5 g of silica and 0.15 g of 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane. The mixture was agitated with a magnetic stirrer at room temperature for 4 h. The solvent was removed in vacuo and vulcanization was carried out in an oven heated at 170 °C for 4 h.

Depolymerization of the model waste was performed as follows: A mixture of 10 g of vulcanized rubber, 15 ml of DEA, 15 ml of hexane and 1.2 g of 25% methanol solution of $(CH_3)_4NOH$ were agitated under the solvent reflux for 5 h. However, the suspension of fillers showed a very high viscosity and filtration was impossible. By adding 10 ml of methanol, the viscosity was decreased abruptly, thus enabling filtration. This phenomenon can be explained in terms of the disrupture of strong hydrogen bonding between silanol groups covering the surface of silica. This bonding must be attenuated by the addition of methanol because methanol can replace one of the counterparts of the bonding between silanols. The separated fillers and filtrate were again subjected to the same treatment as described above and finally monomers were obtained in 69% and recovered silica in 93% yield.

The recovered silica was dried under heating and its aqueous suspension was neutral to the pH test. FT-IR spectra of both the recovered and original silica were almost the same (Fig. 1) and, therefore, poly(siloxane)s were completely removed from the fillers affording pure recycled silica.

4. Summary

The binary mixture of diethylamine and methanol was found useful to dissolve HTV silicone rubber containing silica and alumina as fillers. Most of the fillers can be easily separated by filtration from the suspension formed after dissolution of silicone rubbers by KOH-catalyzed depolymerization. Complete separation of fillers by filtration was achieved by the use of triad solvent mixture consisting of

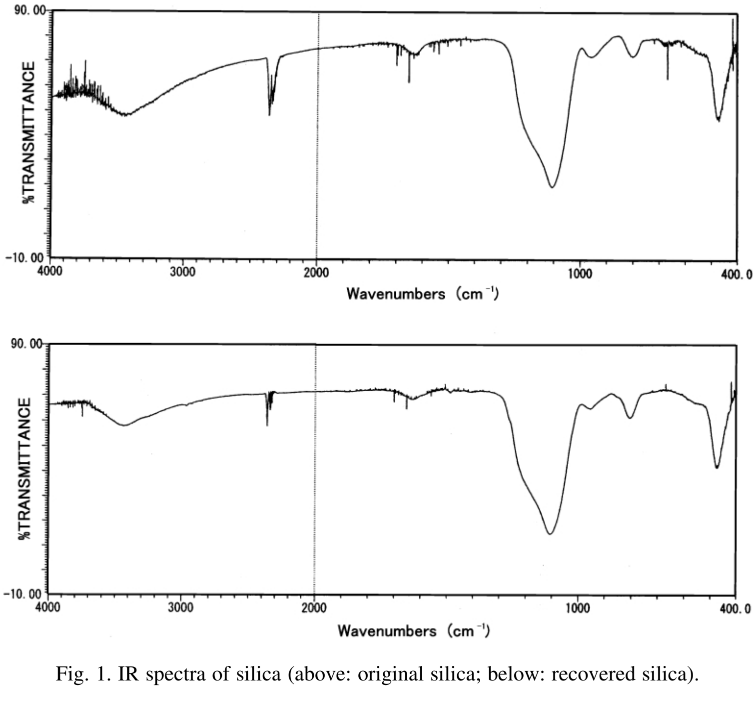


Fig. 1. IR spectra of silica (above: original silica; below: recovered silica).

DEA, methanol and hexane. After the removal of fillers and solvents, the residue was heated and distilled to give pure monomers consisting mainly of D_3, D_4 and D_5 in the yields varying from 76 to 84%. To recover the fillers efficiently, $(CH_3)_4NOH$ was more appropriate as a base catalyst than KOH and, in combination with the use of triad solvent mixtures, fillers were recovered in 83–93% yields.

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