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Experiments with a C-14 tagged silicone mold release have given no evidence of its diffusion through polyethylene or the elastomers Buna N, Buna S, butyl, Hypalon, natural, or urethane. Hexane rapidly removed the mold release from rubbers which it did not swell (urethane, Buna N, and Hypalon). Buna S, natural, and butyl rubbers retained a low level of the mold release agent, even after repeated treatment with hexane. This is presumably related to the fact that the latter three rubbers

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20 ABSTRACT (contd)

swell in the silicone. Removal of the silicone from polyethylene which had been molded against a surface coated with the mold release proved difficult.

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INTRODUCTION

Silicone release is used extensively in molding polymers. When it is used on the mold it gradually becomes incorporated into the polymers being molded. If the silicone can migrate it can change the bulk properties of the polymers. Even if it does not migrate and remains primarily at or near the surface, it will change surface properties, such as printability, coatability, and bondability. Therefore, it is of interest to know how much silicone remains within the polymer, whether it migrates and how easy it is to remove.

DISCUSSION

Elastomers

The silicone oil was brought into contact with the elastomers in a hexane solution. Although the total volume of the drop was less than 0.1 ml and the hexane evaporated in less than a minute, it is possible that there could have been local swelling of the elastomer network. In this case some of the silicone could have penetrated into the swollen rubber and remained trapped upon the subsequent evaporation of the hexane. Paul and others (Ref 1) found that no separation of components occurred in hydraulic permeation of a binary mixture into a highly swollen, lightly crosslinked natural rubber.

Polyethylene

When the oil is first dropped onto the aluminum sheet before molding the polyethylene, there is an excess of the silicone oil. This excess is incorporated into the bulk of the plaque to a considerable degree, in some cases being visible as a cloudy area in the polyethylene. On subsequent pressing, less, though a still detectable amount, is removed from the surface of the aluminum (Table 1). An effort was made to clear the oil from these plaques to see how firmly it was bound to the bulk of the polyethylene. For this purpose a reflux vapor degreaser was used with hexane. This cleaning was followed by hexane soaks.

It is believed that the occluded oil is not chemically bound to the polyethylene, though there is some Van der Waals attraction. It is, therefore, able to show mobility within the polyethylene, being mainly limited by the pore sizes and by the balance of forces of attraction and repulsion within the bulk of the material. If the balance is wrong the molecule cannot even enter the pores, even though it could physically fit.

The silicone oil used in this work was polydimethyl siloxane (PDMS) $(\text{-O-Si}(CH_3)_2\text{-})n$. The methyl groups are the entity primarily exposed when the molecule is in the coiled position. The oxygen atoms tend to be sterically shielded by the bulky methyl groups so that they show little hydrogen bonding ability. A methyl group has little tendency to interact with other groups and has a critical surface tension of about 22 dyne/cm (Ref 2). In some configurations, all the methyl groups are arranged along one side of the molecule, leaving the -Si-O-Si-O linkages exposed along the other side. These exposed oxygen atoms would then be available for electrostatic interactions with their surroundings. As the molecules straighten when going through narrow pores, more of these oxygen atoms become exposed. Normally steric hindrance of the methyl groups tends to coil the molecule, leaving the methyl groups exposed. The surface tension of dimethyl siloxanes is 19 dynes/cm (Ref 3).

The size and shape of the silicone molecule play a major role in its diffusion through the polyethylene matrix. A long chain molecule can move through a tortuous path with much more facility than can a rounder molecule of the same weight. On the other hand, in a long molecule the segments move semi-independently, restrained only at their ends. The longer the molecule, the less likely that all of its parts are going in the same direction at the same time (Ref 4). If there is no driving force (electricity, pressure), a segment jump can be either forward or backward. The driving force in diffusion is entropic, i.e., a backward jump is precluded because there is another segment or molecule occupying that spot. Each segment acquires the energy necessary for a jump independently. At higher energies, the probability is greater that several adjoining segments will have sufficient energy for a coordinated jump. After the first 10 or 12 monomer units, the effective shape of the PDMS molecule does not change.

PDMS forms a helix with a large (about 5.3Å) diameter in the crystalline state (Ref 5). This helix probably does not exist in solution. Flory and Shih (Ref 6) have published a value of 3.36Å for the radius in solution, based on "geometric considerations." Tancrède, and others, found that all linear dimethyl siloxanes act as chemically identical species which disorder the n-alkanes similarly (Ref 7). The methyl exteriors of the dimethyl siloxane chains are chemically similar to those of the alkanes. The large size of the PDMS molecules in the coiled state makes it difficult for them to diffuse through a polymer. In solution, the PDMS molecules are probably more extended, and thus find it somewhat easier to diffuse. In addition, if the solvent swells the polymer network, the paths through which diffusion may occur are larger and more accessible.

Cicchetti and coworkers (Ref 8) found that the energy of activation for diffusion of hydroxy-alkoxy-benzophenones in polypropylene varies with the number of carbon atoms in the diffusing molecules, reaching a maximum and then declining. They attributed the decline to increasing chemical compatibility between the penetrant and polymer which overcomes the steric effect of the larger volume of the penetrant. If the penetrant is incompatible with the polymer, the effect of the molecular size predominates, making the energy of diffusion higher for the larger molecules.

EXPERIMENTAL MATERIALS AND PROCEDURE

Experimental Materials

Rubbers: Buna N, compound BA-7226, bondable, Buna S, compound BR-14720; butyl grade-CR-115; Hypalon grade 1H-22-20; natural, compound BR-2582; urethane, compound RS-12010-6. All were 1/16 inch (0.16 cm) thick and from Minor Rubber Company, Inc, Bloomfield, New Jersey.

Polyethylene: Ethylene butene BMN 5565, 01-2-1750, fluff, melt index 6.5 from Phillips Chemical Company, Bartlesville, Oklahoma.

Radio Active Silicone: Synthesized by Dow-Corning Corporation, Midland, Michigan. Polydimethyl siloxane with the C-14 in the methyl group, viscosity 10,000 cps, specific activity 1.0 mc/g.

Mold Release Agent: Eccoslip H-48, batch 11487811, silicone in hexane from Emerson and Cumings, Canton, Massachusetts.

Mold Release

Eleven ml of mold-release compound was poured into a small vial with a polyethylene-lined cap. Then 0.01 ml of the radioactive oil was removed quantitatively from its septum-topped bottle with a syringe and ejected into the vial. The mixture was allowed to sit at least overnight.

Rubber

The rubbers were cut into 2 inch x 2 inch (5 cm x 5 cm) squares and washed several times with hexane-soaked tissues. They were allowed to dry overnight, after which they were bonded to a 3-1/4 inch x 2-3/4 inch (8 cm x 7 cm) aluminum counting plate which had a 1-1/4 inch (3.2 cm) diameter central hole. A drop of the radioactive mold release was placed in the center of the hole and allowed to spread (Ref 10, 11). The assembly was not moved until the next day. A small square of cardboard was attached to the plate by a strip of tape so that it could cover the hole or could be flipped out of place to allow the radioactivity to be counted. In some cases, another counting plate was put on the back of the rubber, at right angles to the first.

Polyethylene

The entire molding procedure had to take place in a glove box to avoid contamination of the rest of the room. A heavy iron hot plate was used as the source of heat with a thick aluminum slab plate, previously heated on the hot-plate, providing heat from above. An 8 inch x 6 inch x 1/32 inch (20. cm x 15. cm x 0.08 cm) sheet of aluminum was covered with inactive mold release and an aluminum, 4 inch x 4 inch x 1/32 inch (10 cm x 10 cm x 0.08 cm) with a 1-1/2 inch (3.8 cm) diameter circle cut out of its center, was placed on it. A drop of radioactive oil was deposited in the center of the hole, and a small amount of polyethylene fluff (about 5 ml) was poured on top. When the hot-plate and slab were at the correct temperature, 150°C, the slab was momentarily removed from the hot-plate, the aluminum assembly was placed on the plate, and another 8 inch x 6 inch (20 cm x 15 cm) aluminum sheet coated with inactive mold release was put on top. The slab was replaced with a 2.26-kg lead weight put on top. At this point, timing began. After 3-1/2 minutes the assembly was removed from the hot-plate. The two aluminum sheets, with the shim and the polyethylene, were laid directly onto the floor of the box and the slab put back onto the hot-plate. After a half hour, the upper sheet was removed and the shim picked up. It was possible to remove the polyethylene plaque from the shim with tweezers. The inactive side was put over the hole in a counting plate. A piece of aluminum foil was placed over the active side and fastened to the plate with adhesive tape.

Counting

A thin window counter was used to measure the level of radioactivity in the samples. The tube was mounted vertically, looking down on a sample holder which had slots that accepted the rectangular plates at several distances from the window. Most of the counting was done using the center slot. The counting on other shelves was correlated by counting standard samples on both shelves and taking the ratio of the two counts, thus obtaining the necessary multiplication factor. Most of the counting periods were three minutes, although some weak samples were counted for longer times to improve the statistics. Background counts were taken for at least ten minutes.

Removal of Silicone

Circles were cut out of the rubber and PE by using the center holes of the counting plates as patterns. Each rubber was then completely immersed in hexane for two minutes. After removal from the hexane with tweezers, the rubber was air dried (about 30 seconds) and counted on both sides. The process was repeated on each of the next two days. After the three immersion extractions, the sample was placed in a Roweg extractor in such a way that it was immersed in the vapor but was not covered by the refluxing hexane liquid. The rubber remained in this extractor for one syphoning, after which it was removed and counted. This was repeated twice, or until the counts were at a background level. Rubbers which still showed substantial activity were put in individual glass bottles and allowed to soak in hexane for extended periods. Both the circles and the hexane extract were counted after each soak.

The polyethylenes were treated similarly, except that the first treatment was the Roweg extractions.

Hexane Extract

The hexane from the sample soaking was evaporated to dryness in polystyrene caps. A simple rinse was also included. The caps fit into the central holes of the counting plates.

RESULTS

Diffusion

The mold release agent was placed onto one side of the rubber and allowed to evaporate. The opposite side was radioactively counted. In a few cases, there was a small initial increase in counting rate on this opposite side. After the first few days there was no increase, and in no case was the level more than eight counts above background. This was presumably due to contamination of some sort since diffusion would have caused the counting rate to gradually increase.

The molded polyethylene plaques were thinner than the rubber ones, and some of the oil was incorporated into them by wicking when the polyethylene fluff first came into contact with the coated surface before molding. Thus, some of the polyethylene plaques showed a fairly high initial counting rate on the side not directly in contact with the oil. This rate did not change significantly for any of the plaques during the experiment.

Cleaning

Much of the oil was loosened from the surfaces during the course of the diffusion experiments and was easily removed by the first attempt at cleaning (Table 1). However, some of the oil was much more tightly bound. The counting rates for the rubbers declined with repeated hexane soaks, but those for the polyethylene remained approximately the same after the initial surface cleaning.

CONCLUSION

No evidence has been found for the diffusion of the silicone oil through polyethylene or rubbers (Buna N, Buna S, butyl, natural, Hypalon, urethane). Oil placed on the rubber's surface is not easily removed from rubbers (Buna S, natural, butyl) that swell in the solvent (hexane). The mold release agent taken up by polyethylene is held tightly, and is therefore difficult to remove.

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Table 1

Removal of silicone from rubbers and polyethylene

SAMPLE	TOTAL C/M BEFORE CLEANING	C/M AFTER 2 MINUTE HEXANE RINSE	C/M AFTER 2ND 2 MIN. RINSE	C/M AFTER 3RD 2 MIN. RINSE	C/M AFTER VAPOR DEGREASER 5 MINUTES	C/M AFTER 2ND VAPOR DEGREASER 5 MINUTES	C/M AFTER 2ND VAPOR DEGREASER 10 MINUTES	C/M AFTER 1 HOUR HEXANE SOAK	C/M AFTER 89 HOUR HEXANE SOAK	C/M HEXANE EXTRACT FROM 89 HOUR SOAK	C/M AFTER 41 HOUR HEXANE SOAK	C/M HEXANE EXTRACT FROM 41 HOUR SOAK
RUBBERS												
I Urethane	1385	23	7	10	10		1					
I Buna S	3797	88	49	45	28		25	13	7	16	9	0
II Buna N	1750	16	7	6	7							
II Hypalon	1361	39	13	10	6							
II Natural	1187	29	12	14	13		8	4	7	4	4	2
II Butyl	2361	65	43	32	17		29	20	19	8	23	4
II Urethane	1491	16	2	8	5		6	5	0	0		
II Buna S	1736	83	18	28	19		17	12	17	3	7	
III Buna N	993	30	4	0								
III Natural	1130	30	9	4								
III Butyl	1252	31	20	19	14		7	12	15	0		
III Urethane	1071	10	1									
III Buna S	181	1	4	0	4							
POLYETHYLENE												
a. 1	987				446	437		413	396	16	366	
b. 2	109				69	71		65	53	0		
c. 3	31				12	13		2	10	3		
a. 4	631				339	347		327	311	32	272	3
b. 5	133				85	82		84	70	2		
a. 6	1078				693	810		601	663	61	630	11
b. 7	132				81	89		86	71	0		
a. 8	263				206	176		100	163	41	186	
b. 9	23				7	7		6	4	0		

a. Molded immediately after oil was dropped onto mold.

b. Molded with no new application of oil.

c. Molded after two other samples with no new application of oil.