Surface Behavior of Blends of SBR with Ultrasonically Devulcanized Silicone Rubber

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Received 22 September 1997; accepted 13 February 1998

ABSTRACT: The application of silicone polymers as additives in commercial polymers for improving their surface properties is an attractive method. Use of reclaimed silicone rubber for blending with commercial organic polymers is an equally attractive possibility. Ultrasonically devulcanized silicone rubber was mixed with virgin and ultrasonically devulcanized styrene–butadiene rubber (SBR). The surface and bulk mechanical properties and curing behavior of the blends of SBR with ultrasonically devulcanized silicone rubber were investigated. Contact angles of these blends were measured, and the concentration of silicone rubber on the surface was calculated. It was shown that the soluble part of devulcanized silicone rubber migrates to the surface. The addition of 5 phr of devulcanized silicone rubber led to the formation of a continuous surface layer containing 100% silicone rubber. In general, the mechanical properties of the blends remain intact and, in some cases, are even better than those of SBR. Curing behavior shows that the blends have the similar cure kinetics as virgin or devulcanized SBR, but a lower final torque. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2691–2696, 1998

Key words: silicone; silicone rubber; PDMS; SBR; ultrasound; devulcanization; revulcanization; gel; sol; blends; surface properties; surface concentration; contact angle; cure behavior; mechanical properties

INTRODUCTION

Ultrasonically devulcanized silicone rubber (polydimethylsiloxane; PDMS) under optimum processing conditions has good mechanical properties after revulcanization and can be used by itself or by blending with virgin silicone rubber.[1] A very interesting practical application can be achieved by blending organic polymers with silicone polymers. It is well known that the surface composition of a multicomponent polymer system, such as a copolymer or a blend, may differ greatly from its composition in the bulk. This is due to the difference in the surface energies of the components. Surface–bulk compositional differences are particularly pronounced in polymers containing silicone. This is because of the extremely low surface energy of 2.2 N/m^2 for PDMS.[2] The high extent of surface segregation typical of silicone-containing polymers can be used in practice to obtain a polymer with remarkable surface properties. This can be accomplished without significant changes in the bulk properties of the base polymer. There is a wide range of surface applications of PDMS. Some specific applications are in antifoaming agents, surfactants, water repellency and dewatering applications, lubricants, release agents, and pressure-sensitive adhesives.[2] Of great utility may also be the ability of silicone rubber to form, under the action of some oxidizing agents, ultrathin quartz-like surface layers with excellent protective and gas separation properties.[3–5] The presence of a small amount of silicone rubber in a

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Contract grant sponsor: The National Science Foundation; contract grant number: DMI-9312249.

Journal of Applied Polymer Science, Vol. 69, 2691–2696 (1998)
 CCC 0021-8995/98/132691-06

Table I Processing Conditions for Devulcanization and Specifications of Devulcanized SBR and Devulcanized Silicone Rubber Used in Blends

	Processing Conditions				Structural Characteristics	
Material	Barrel Temperature (°C)	Amplitude (μm)	Die Gap (mm)	Flow Rate (g/s)	Crosslink Density (10^{-2} kmol/m^3)	Gel Fraction (%)
PDMS	180	10	0.63	0.32	0.71	69.0
SBR	120	10	1.52	0.63	2.40	65.0

blend with an organic polymer can also improve the processibility of the latter.

Block copolymers having silicone chains are known to manifest an interesting surface behavior that the silicone segments are accumulated or enriched, particularly on air-side surfaces. Some of these copolymers are PDMS–polycarbonate (PC) block copolymer,[6–10] PDMS–polyurethane (PU) block copolymer,[11] PDMS–polystyrene (PS) block copolymer,[12] PDMS–poly(methyl methacrylate) (PMMA) block copolymer,[13,14] and PDMS–polysulfone (PSF) block copolymer.[15,16]

In addition to using PDMS-containing copolymers, pure silicone can also be used to modify the surface properties of commercial polymers. In the research of blends of PDMS with PVC,[10] it was found that at a silicone bulk concentration of about 6 wt%, the corresponding surface concentration is about 80%. In other research on blends of PDMS with PC or PSF,[17,18] electron spectroscopy for chemical analysis (ESCA) measurements indicated that for blends of PDMS and PC, the surface concentration of PDMS reaches about 95 wt% at 1 wt% bulk concentration of PDMS. In the case of blends of PDMS and PSF, the surface concentration of PDMS can also reach about 95 wt% at 1 wt% bulk concentration of PDMS.

Certainly, there is a possibility that an addition of reclaimed silicone rubber, obtained from the waste of silicone rubber industry, will also improve the surface properties of many commercial polymers, such as PVC, PC, SBR, and natural rubber (NR). Therefore, the purpose of the present article is to demonstrate how ultrasonically devulcanized silicone rubber can be used as a blend with SBR to change its surface properties.

MATERIALS AND EXPERIMENTAL PROCEDURES

Three types of blends of SBR and silicone rubber were prepared: (1) virgin SBR–virgin silicone rubber, (2) virgin SBR–devulcanized silicone rubber, and (3) devulcanized SBR–devulcanized silicone rubber. Polydimethylsiloxane, SE64, made by General Electric Company (Schenectady, NY), was used. It has a number-average molecular weight M_n of 2.34×10^5 g/mol, a weight-average molecular weight M_w of 4.14×10^5 g/mol, and a polydispersity of 1.77 measured by gel permeation chromatography (GPC). It contains 0.6 mol% vinyl groups. The virgin SBR used was Duradene 706 made by Firestone Synthetic Rubber and Latex Company (Akron, OH). It contains 23.5% bound styrene, 76.5% butadiene, and a nonstaining antioxidant stabilizer system. Virgin silicone rubber was compounded with 0.5 phr dicumyl peroxide (DCP) on a laboratory two-roll mill. It was precured by compression molding at 170°C for 15 min into slabs of dimensions $12 \times 260 \times 260$ mm^3. It was then post-cured in a ventilated oven at 200°C for 2 h. Virgin SBR was compounded with 2 phr of sulfur and 1.3 phr of Santocure on a laboratory two-roll mill. It was then vulcanized by compression molding at a temperature of 170°C and a pressure of 10 MPa for 10 min into slabs of dimensions $12 \times 260 \times 260$ mm^3. The vulcanized slabs were ground into particles in a Nelmor grinding machine. The devulcanization of silicone rubber and SBR was carried out in a rubber extruder with an ultrasound die attachment.[19] A 3000-W ultrasonic power supply, a converter, and a booster were used to provide longitudinal vibrations to the horn at a frequency of 20 kHz. The screw speed was 20 rpm, and both die and horn cooling water flow rates were set at 0.09 m^3/h. Other processing conditions and structural characteristics of the chosen devulcanized SBR and silicone rubber are listed in Table I. The revulcanization recipes of the blends were virgin or devulcanized SBR, 100 parts; sulfur, 2 phr; Santocure, 1.3 phr; and various amount of virgin or devulcanized silicone rubber. The blends were compounded on a two-roll mill. Then the com-

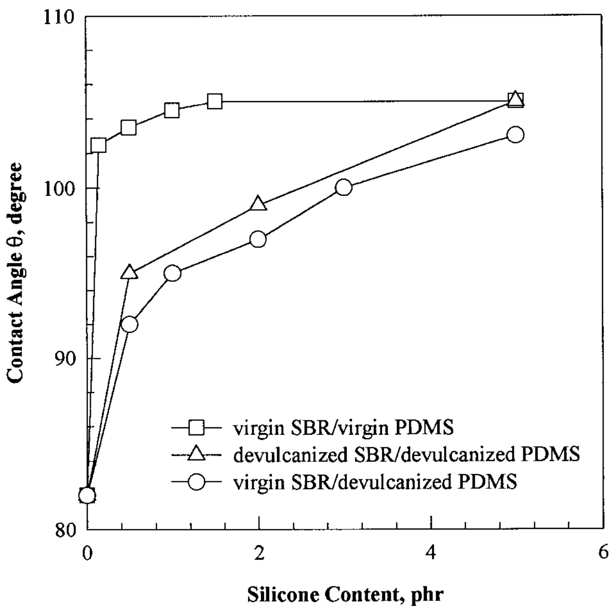

Figure 1 Contact angle of blends of SBR–silicone rubber as a function of silicone rubber content.

pounds were vulcanized by compression molding at a temperature of 170°C and a pressure of 10 MPa for 10 min into sheets of dimensions 180 × 130 × 3 mm^3. The mechanical properties of the vulcanizates were measured by a Monsanto tensile tester (T2000) following ASTM D412-92 at room temperature. Type-C dumbbell-shaped specimens were punched from the compression-molded sheet. The extension rate was set at 500 mm/min. Curing behaviors of the blends were measured by means of a Monsanto Curometer (Model R-100) according to ASTM D2084-93 at a temperature of 170°C. Contact angle measurements were made using a KERNCO microscope with a contact angle measurement attachment. Distilled water was used as a medium on the fresh surface.

RESULTS AND DISCUSSIONS

Surface Properties

Contact angle measurements indicate that the contact angle is 82° for virgin and revulcanized SBR and 105° for silicone rubber. The dependence of contact angle on the amount of silicone rubber in the blends is presented in Figure 1. It can be seen from this figure that for blends of virgin SBR and virgin silicone rubber, the contact angle increases dramatically with increasing amounts of silicone rubber. At 1-phr bulk concentration of silicone rubber, the contact angle of the blend practically achieves the contact angle of pure silicone rubber. For the blends of devulcanized and virgin SBR with devulcanized silicone rubber, increasing the silicone rubber content in the blends also increases the contact angle. In these cases, the contact angle increases somewhat slowly. At 5 phr of devulcanized silicone rubber, the contact angle of the blend of devulcanized SBR and devulcanized silicone rubber reaches a value corresponding to the contact angle of pure silicone rubber.

Devulcanized silicone rubber consists of gel and sol, while virgin silicone rubber does not contain any gel. It is clear that gel particles of the devulcanized silicone rubber will remain inside SBR matrix and only the silicone rubber molecules from sol can diffuse to the surface. As seen from Table I, the devulcanized silicone rubber contains 31% sol. Based on the sol fraction, the concentration of silicone rubber sol in the blends can be calculated. Figure 2 presents the dependence of surface contact angle for the same blends on the amount of the sol content of silicone rubber in the blend. From these data, it is clear that, at 1.5 phr, the concentration of silicone rubber sol in the blend, the contact angle of a blend of devulcanized SBR and devulcanized silicone rubber achieves the contact angle of pure silicone rubber.

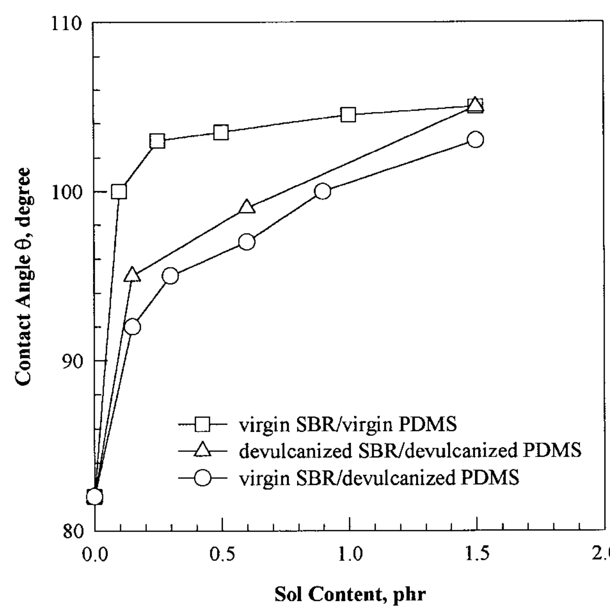

Figure 2 Contact angle of blends of SBR–silicone rubber as a function of sol content of devulcanized silicone rubber.

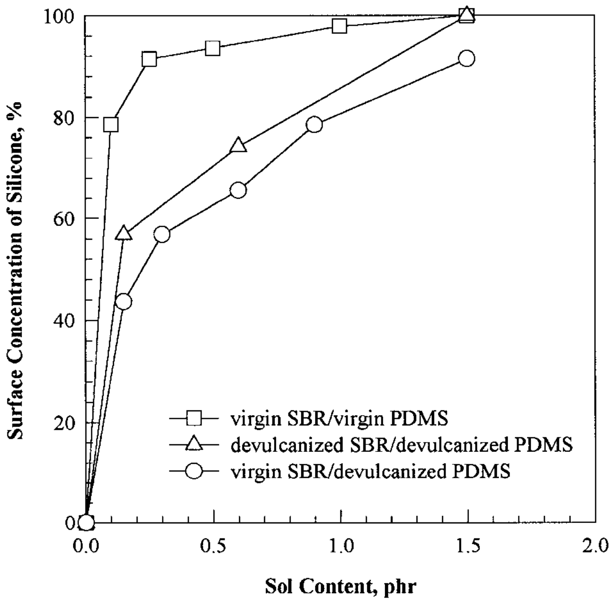

Figure 3 Calculated surface concentration of silicone rubber as a function of sol fraction of devulcanized silicone rubber.

This means that by changing conditions of ultrasound devulcanization of silicone rubber, one can achieve an increase in the sol fraction of devulcanized rubber. Then, the total amount of ultrasonically devulcanized silicone rubber in the blend with SBR, which can make surface contact angle equal to that of pure silicone rubber, will decrease.

The surface concentration of a multicomponent polymer system such as a copolymer or a blend can be calculated from contact angle θ.[14] Applying the linear relationship proposed by Cassie[20] between cosθ and the surface area fraction for heterogeneous surfaces composed of 2 components, the surface concentration φ of silicone rubber in a blend can be calculated by using the following equation:

$$\cos \theta = \varphi \cos \theta_{PDMS} + (1 - \varphi) \cos \theta_{SBR}$$

The calculated results are presented in Figure 3. It can be seen that at 1.5 phr of sol of the devulcanized silicone rubber, the surface of the blend of devulcanized SBR and devulcanized silicone rubber is fully covered by the silicone layer.

As reported earlier,[1] GPC measurements on sol of ultrasonically devulcanized silicone rubber show $M_w = 5.39 \times 10^5$g/mol and $M_n = 9.64 \times 10^4$ g/mol, indicating a higher M_w and the polydispersity index of the sol in comparison with the virgin uncured PDMS. The sol of ultrasonically devulcanized silicone rubber contains branched soluble fragments. Some of these fragments have high molecular weight, leading to a lower mobility of the molecular chains. This can be the reason for the difference in the slopes of the curves for the blends of SBR with virgin and devulcanized silicone rubber, as seen from Figures 1–3.

Curing Behavior

The cure curves of the blends are illustrated in Figure 4. The cure curves of pure SBR (virgin or devulcanized) and pure silicone rubber (virgin or devulcanized) are also shown in this figure for comparison. It can be seen that the blends of virgin SBR with virgin (curve 2) or devulcanized silicone rubber (curve 3) have the similar cure behavior as the virgin SBR (curve 1) but a lower final torque. The same phenomena is also observed when comparing the cure curve of the blend of devulcanized SBR with devulcanized silicone rubber (curve 5) with the cure curve of pure devulcanized SBR (curve 4). This indicates that the blends have similar cure kinetics as the virgin SBR or pure devulcanized SBR. The reason for the decrease in the final torque for the blends is

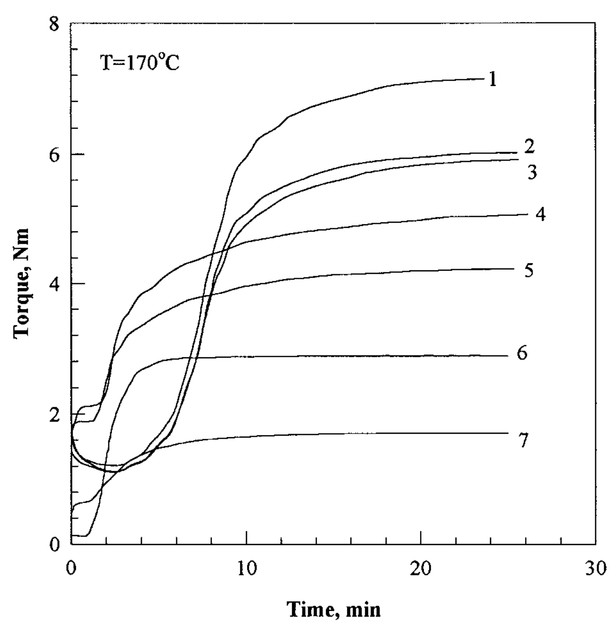

Figure 4 Cure curves for virgin (curve 1) and devulcanized (curve 4) SBR, virgin (curve 6) and devulcanized (curve 7) silicone rubber and 95/5 blends of virgin SBR–virgin PDMS (curve 2), virgin SBR–devulcanized PDMS (curve 3), and devulcanized SBR–devulcanized PDMS (curve 5).

that the virgin or devulcanized silicone rubber has a lower final torque, as indicated respectively by curves 6 and 7 in Figure 4. Another reason may be the change in the surface properties of the blends. In particular, the surface enriched with silicone rubber may result in a wall slip effect during the torque measurements and thus lower the final torque. Furthermore, torque curves 2 and 3 are essentially the same. This is due to the fact that there is a little difference in the PDMS surface concentration between the 95/5 blend of virgin SBR with devulcanized PDMS and the 95/5 blend of virgin SBR with virgin PDMS, as is evident from Figure 3.

Mechanical Properties

The stress–strain curves for the vulcanized blends of virgin SBR–devulcanized silicone rubber and devulcanized SBR–devulcanized silicone rubber are presented in Figures 5 and 6, respectively. It is seen from Figure 5 that the tensile strength of the vulcanized blend of virgin SBR and devulcanized silicone rubber is practically the same and the elongation at break is slightly higher than that for virgin SBR. For the vulcanized blend of devulcanized SBR and devulcanized silicone rubber, the elongation at break and the tensile strength are slightly higher than that for the pure devulcanized SBR vulcanizate, as indicated in Figure 6. The reasons for these observed effects are presently unknown.

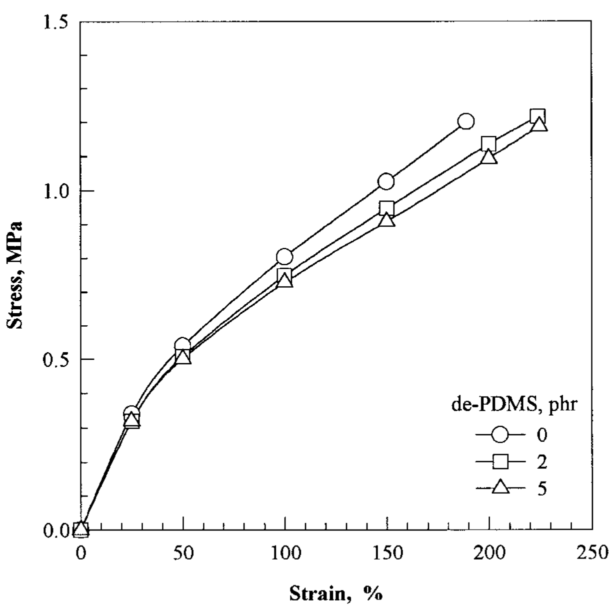

Figure 5 Stress–strain curves of virgin SBR–devulcanized silicone rubber blends.

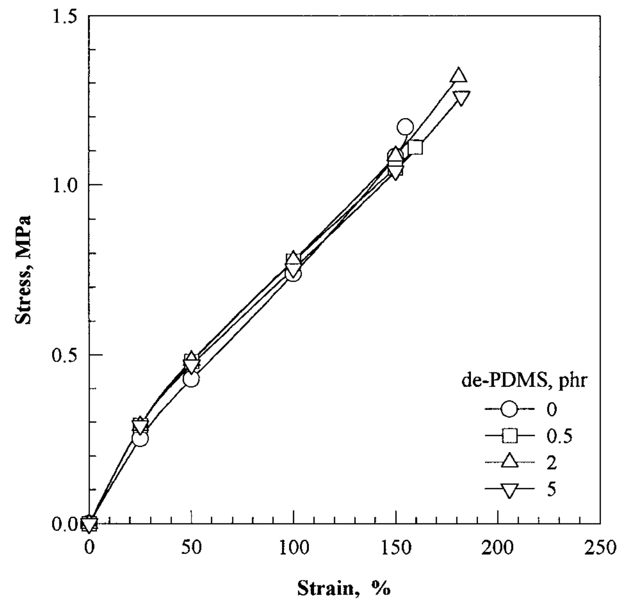

Figure 6 Stress–strain curves of devulcanized SBR–devulcanized silicone rubber blends.

CONCLUSIONS

Contact angle results indicate that soluble part of devulcanized silicone rubber migrates to the surface. The addition of a small amount of devulcanized silicone rubber led to the formation of a continuous surface layer containing 100% silicone rubber. The cure behavior of the blends indicates that the blends have the similar cure rates as the virgin or pure devulcanized SBR but a lower final torque. In general, the mechanical properties of the blend vulcanizates remain intact and, in some cases, are even better than those for the virgin SBR vulcanizates.

REFERENCES

1. B. Diao, A. I. Isayev, and V. Y. Levin, *Rubber Chem. Technol.,* submitted.
2. J. Owen, in *Siloxane Polymers,* S. J. Clarson, and J. A. Semlyen, Eds., PTR Prentice Hall, Englewood Cliffs, 1993.
3. J. Kulig, in *Proceedings of the 44th Research Symposium, Department of Macromolecular Science, Case Institute of Technology, Case Western Reserve University,* Cleveland, 1990.
4. C. A. Arnold, J. D. Summers, and J. E. McGrath, *Polym. Eng. Sci.,* **29,** 2734 (1989).
5. M. M. Gorelova, V. Y. Levin, A. J. Pertsin, and E. G. Krasheninnikov, *Proceedings of the International*

Symposium of Membranes of Gas and Vapor Separation, Suzdal, Russia, 1989, p. 109.
6. G. LeGrand and G. L. Gaines Jr., *Polym. Prepr. (Amer. Chem. Soc., Div. Polym. Chem.),* **11,** 442 (1970).
7. W. Dwight, J. E. McGrath, A. R. Beck, and J. S. Riffle, *Polym. Prepr. ACS Div. Polym. Chem.,* **20,** 702 (1979).
8. W. Dwight and H. R. Thomas, *Polym. Prepr. ACS Div. Polym. Chem.,* **22,** 302 (1981).
9. E. McGrath, D. W. Dwight, J. S. Riffle, T. F. Davidson, D. C. Webster, and R. Viswanathan, *Polym. Prepr. ACS Div. Polym. Chem.,* **20,** 528 (1979).
10. M. Gorelova, A. J. Pertsin, V. Y. Levin, L. I. Makarova, and L. V. Filimonova, *J. Appl. Polym. Sci.,* **45,** 2075 (1992).
11. K. Sha'aban, S. McCartney, N. Patel, I. Yilgor, J. S. Riffle, D. W. Dwight, and J. E. McGrath, *Polym. Prepr. ACS Div. Polym. Chem.,* **24,** 130 (1983).
12. T. Clark, J. Peeling, and J. M. O'Malley, *J. Polym. Sci., Polym. Chem. Ed.,* **14,** 543 (1976).
13. K. Varshney, and C. L. Beatty, *Org. Coat. Plast. Chem.,* **45,** 152 (1981).
14. Inoue, A. Matsumoto, K. Matsukawa, A. Ueda, and S. Nagai, *J. Appl. Polym. Sci.,* **41,** 1815 (1990).
15. N. M. Patel, D. W. Dwight, J. L. Hedrick, D. C. Webster, and J. E. McGrath, *Macromolecules,* **21,** 2689 (1988).
16. J. Pertsin, M. M. Gorelova, V. Y. Levin, and L. I. Makarova, *J. Appl. Polym. Sci.,* **48,** 1985 (1993).
17. M. Gorelova, V. Y. Levin, L. I. Dubchak, A. A. Zhdanov, L. I. Makarova, I. P. Storozhuk, and S. S. Koroleva, *Polym. Sci. USSR,* **31,** 643 (1989).
18. M. Gorelova, V. Y. Levin, and A. J. Pertsin, *Makromol. Chem., Macromol. Symp.,* **44,** 317 (1991).
19. A. Tukachinsky, D. Schworm, and A. I. Isayev, *Rubber Chem. Technol.,* **69,** 92 (1996).
20. A. B. D. Cassie, *Discuss. Faraday Soc.,* **3,** 11 (1948).