Changes in the Sorption and Adhesion Characteristics of Siloxane Block Copolymers on Exposure to Radiation

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The influence of the adsorbed dose and the type of siloxane block copolymer on the changes in the diffusion and adhesion parameters of the block copolymer coatings has been investigated together with the dose dependence of their protective properties in corrosive media. It is shown that the action of radiation on block copolymer coatings lowers appreciably their sorption capacity and increases their adhesion strength, which results in an increase in their longevity.

Polyorganosiloxanes are widely used in the preparation of radiation-, heat-, and corrosion-resisting coatings.[1] Methods for the synthesis of siloxane block copolymers (BCP) which make it possible to vary the sizes of the dimethylsiloxane (DMS) and phenylsilsesquioxane (PSSO) blocks in the macromolecule have now been developed.[2] This permits the variation of the properties of the polymer coatings obtained from them. We investigated the radiation-chemical reactions of siloxane block copolymers[3,4]; it was shown that their exposure to the action of γ-radiation entails the formation of a three-dimensional network.

This factor made it possible to put forward a procedure for the radiation-induced hardening of coatings based on siloxane block copolymers.[4] Indeed, the longevity of coatings hardened by γ-radiation at a dose equal to that for gel formation in the block copolymer is significantly greater than the longevity of analogous coatings obtained using thermal and chemical hardening methods.[4,5] However, the influence of the radiation dose on the longevity of the coatings has not been investigated. Furthermore, the protective properties of the coatings, such as permeability to moisture and adhesion strength, have not been studied.

The aim of the present study was to investigate the influence of the absobed dose and the type of siloxane block copolymers on the changes in the diffusion and adhesion parameters of the block copolymer coatings and also to determine the dose dependence of their relative longevity.

The objects of study were block copolymers having the general formula $[(CH_3)_2SiO]_m\{[C_6H_5SiO_{1.5})]_a[C_6H_5SiO(OH)]_{1-a}\}_n$. The ratio of the flexible DMS and PSSO rigid blocks (m:n), the number-average molecular weight ($\bar{M}_n$), and the content of the OH groups (wt. %) in the block copolymers investigated are indicated in Table 1. The specimens were irradiated in the dose range 30–200 kGy in evacuated glass bulbs from a ^{60}Co γ-source. The specimens were irradiated at ~30 °C, a dose rate of ~2.8 Gy s^{-1}, and a residual pressure in the bulbs of 133×10^{-6} Pa. The relative longevity was determined with the aid of metallisation stripe pattern (MSP) structures. For this purpose a coating ~5 µm thick was deposited on the MSP structure containing stripes produced by metallisation with aluminium. The longevity of each type of coating was tested on at least nine metallisation stripes. The MSP structures with radiation-hardened coatings were placed in an autoclave at 120 °C and 98% relative humidity and periodic measurements were made of the resistance of the metallisation stripes. The instant at which a sharp jump in the resistance of the aluminium metallisation stripe took place was adopted as the failure time. The relative longevity of the test coating was assumed to be equal to the time of attainment of 50% of failures. The strength of adhesion of the coatings to aluminium was determined by the normal stripping method on 5×5 mm plates. The break occurred at the polymer – support interface. The permeability to moisture was studied on free films ~ 2 mm thick. For this purpose, periodic measurements were made of the change in their weight after being kept in distilled water at 25 °C. The content of the gel fraction was determined from the results of the extraction of the soluble component with toluene at 25 °C for 24 h.

Table 1 Characteristics of the siloxane block copolymers

Block copolymer	m:n	M_n	OH groups, wt.%
BCP-1005	10:5	3580	1.78
BCP-2005	20:5	4390	1.83
BCP-8040	80:40	20140	3.02
BCP-80100	80:100	18590	5.10

The dependences of the change in the weight of the free films of the siloxane block copolymers investigated on the duration of maintenance in distilled water were obtained. The amount of absorbed moisture initially (200–250 h) increases rapidly and then the sorption slows down and the amount of sorbed water approaches asymptotically the equilibrium value determined by the absorbed dose and the type of block copolymer. Sorption equilibrium is attained after the specimen has been kept in distilled water for ~500–700 h. For shorter treatment times τ, the time variation of the weight of a specimen with a thickness d under the conditions of two-sided diffusion of water is described by equation (1),[7,8]

$$\Delta M = 4 \times \frac{\Delta m_\infty}{d} \times \left(\frac{D}{\pi}\cdot\tau\right)^{\frac{1}{2}} \tag{1}$$

where Δm is the change in the weight of the specimen expressed as a percentage of the initial weight, Δm_∞ the equilibrium amount of sorbed water (%), and D is the diffusion coefficient of water in the polymer.

Fig. 1 presents the dose dependences of the changes in the diffusion coefficient calculated by equation (1) for the block copolymers investigated. Exposure to radiation lowers the diffusion coefficients to different extents depending on the sizes and ratio of the flexible and rigid blocks. Indeed, polymer cross-linking processes are known to entail usually a decrease in their permeability.[9]

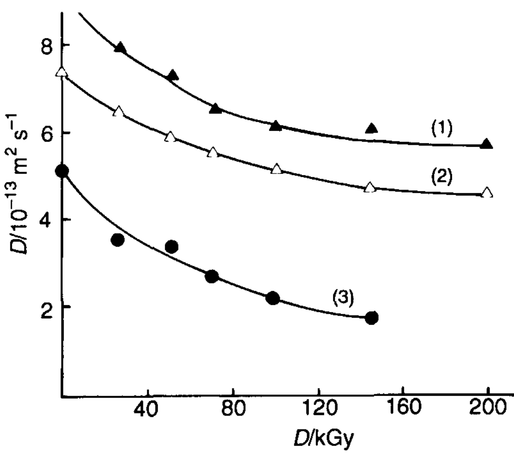

Fig. 1 The dose dependence of the diffusion coefficient for different copolymers: (1) BCP-8040; (2) BCP-80100; (3) BCP-2005

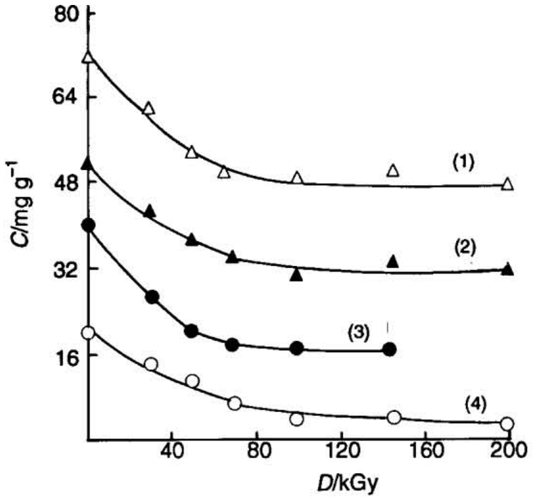

Fig. 2 Dose dependence of the sorption capacity for different copolymers: (1) BCP-80100; (2) BCP-8040; (3) BCP-2005; (4) BCP-1005

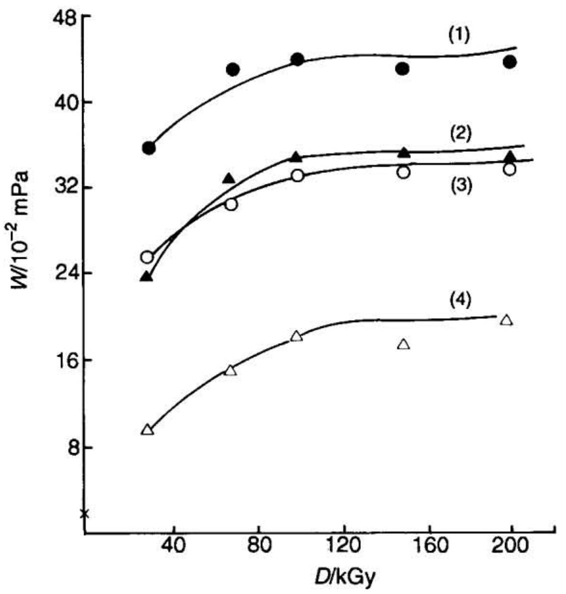

Fig. 3 Dose dependence of the adhesion strength for different copolymers: (1) BCP-2005; (2) BCP-8040; (3) BCP-1005; (4) BCP-80100; x = adhesion strength of the coating based on BCP-2005 hardened by adding γ-aminopropyltriethoxysilane

Irradiation of the block copolymers diminishes the equilibrium amount of the sorbed water, *i.e.* the sorption capacity of the films (Fig. 2). Under these conditions, the sorption capacity of the non-irradiated siloxane block copolymers is correlated with the content of their OH groups. According to Iordansrii,[10] the water sorbed in the polymer matrix is distributed preferentially in the vicinity of polar (in our case OH) groups, forming a kind of cluster. Thereafter, as the content of OH groups is reduced, a decrease in sorption capacity should be expected. The decrease in sorption capacity on irradiation can be attributed to the loss of OH groups.

Fig. 3 illustrates the dependence of the change in the adhesion strength of the test coating on the irradiation dose. It presents for comparison the adhesion strength of the coating based on BCP 2005 obtained using a chemical hardener (AGM-9). Evidently irradiation of the coatings with a dose of 30 kGy already leads to a significant increase in adhesion strength. It is known[11,12] that irradiation of polymer coatings can increase the adhesion strength as a result of processes occurring at the polymer–support interface under irradiation,

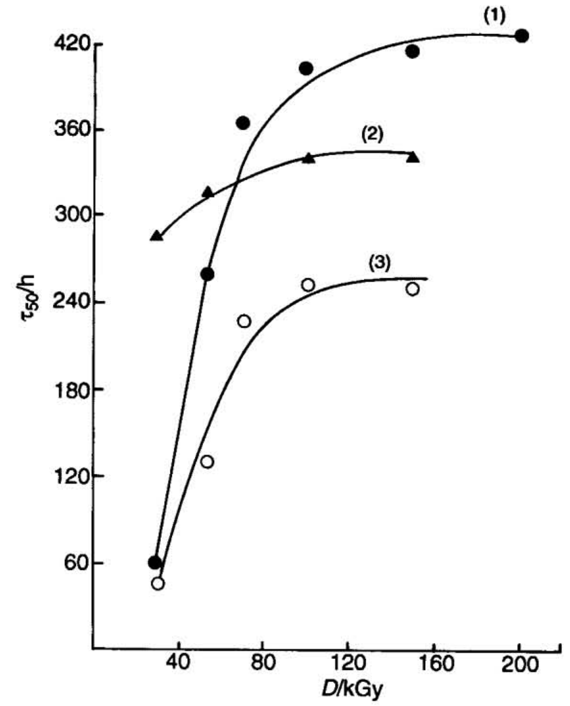

Fig. 4 Dose dependence of the relative longevities of coatings formed from different copolymers: (1) BCP-2005; (2) BCP-8040; (3) BCP-1005

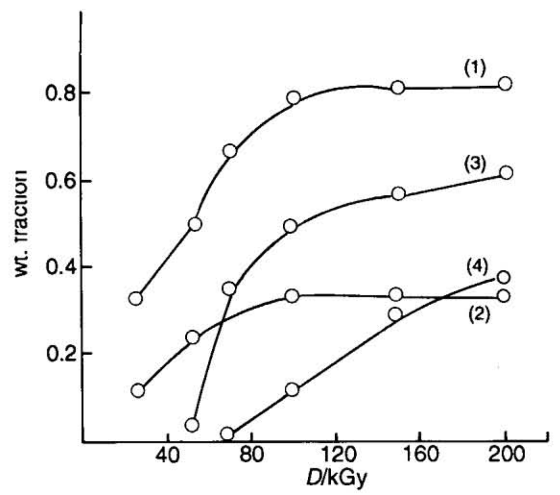

Fig. 5 Kinetic curves for the accumulation of the gel fraction in different copolymers: (1) BCP-8040; (2) BCP-80100; (3) BCP-2005; (4) BCP-1005

which leads to the formation of chemical bonds from the OH groups of the oligomers and the active centres of the support (Fig. 3). Under these conditions, the number of active OH groups in the block copolymer depends on the dimensions and relative disposition of the PSSO and DMS blocks and can differ from the values quoted in Table 1.[12] Thus, the block copolymers investigated can be arranged in the following series in terms of the decrease in their adhesion strength: BCP-2005 > BCP-8040 > BCP-1005 > BCP-80100.

Fig. 4 presents the dose dependences of the changes in the relative longevities of the test coatings. Irradiation of the coatings based on BCP-1005 and BCP-2005 with small doses does not lead to the formation of coatings with a long life, which is apparently associated with failure to complete the formation of a three-dimensional network (Fig. 5). Thus, the longevity of these coatings for a dose of 30 kGy is not more than 60 h. An increase in the absorbed dose leads to a significant increase in the relative longevity, which reaches

300–400 h. This is apparently associated primarily with the increase in the adhesion strength and the decrease in the sorption capacity of the coatings. The action of radiation on films of the block copolymers investigated also lowers the diffusion coefficient (Fig. 3), but calculations have shown that in the case of the coatings which were employed (5 μm thick) the diffusion equilibrium is established over a period of the order of 1 min, so that the observed decrease in the diffusion coefficient on irradiation of the block copolymer (by a factor of 2–4) can hardly improve significantly the protective properties of the coatings in corrosive media.

Thus, the principal properties of different protective coatings based on siloxane block copolymers, obtained as a result of radiation-induced hardening, have been investigated. It is shown that the action of radiation lowers the sorption capacity and increase the adhesion strength of the coatings, which increases their relative longevity. Irradiation of the test polymers with a dose of 50–200 kGy lowers the diffusion coefficient by a factor of 2–4.

References

1 *Oligoorganosiloksany. Svoistva, sintez, primenenie. (Oligoorganosiloxanes. Properties, synthesis and use)*, ed. M. V. Sobolevskii, Khimiya, Moscow, 1985, p. 13 (in Russian).

2 A. A. Zhdanov, B. G. Zavin and A. Yu. Rabkina, *Dokl. Akad. Nauk SSSR*, 1985, **282**, 328 [*Dokl. Phys. Chem. (Engl. Transl.)*, 1985, **282**, 147].

3 V. V. Lyashevich, L. N. Pankratova, O. Yu. Panov, E. R. Klinshpont, B. H. Zavin and A. Yu. Rabkina, *Khim. Vys. Energ.*, 1991, **25**, 238 [*High Energy Chem. (Engl. Transl.)*. 1991, **25**, 199].

4 L. N. Pankratova, O. Yu. Panov, V. B. Nesterov, L. T. Bugaenko, B. G. Zavin and A. Yu. Rabkina, Russian Pat. 1819163, 1991.

5 L. N. Pankratova, O. Yu. Panov and V. B. Nesterov, *Plasticheskie massy*, 1992, 37 (in Russian).

6 V. B. Nesterov and A. A. Teverovskii, *Elektronnaya tekhnika, Ser. Materialy*, 1986, 47 (in Russian).

7 A. A. Teverovskii and E. G. Epifanov, *Elektronnaya tekhnika, Ser. Materialy*, 1982, 65 (in Russian).

8 G. Mattael, *Microelectronics Reliab.*, 1990, **30**, 835.

9 A. E. Chalykh, *Diffuziya v polimernykh sistemakh (Diffusion in polymer systems)*, Khimiya, Moscow, 1987, p. 108 (in Russian).

10 A. I. Iordansrii, *Materials of the International Conference on Regulation of Polymeric Materials Stability*, Moscow, 1992, p. 332.

11 A. D. Zimon, *Adgeziya plenok i pokrytii (Adhesion of films and coatings)*, Khimiya, Moscow 1977, p. 266 (in Russian).

12 V. A. Belyi, N. I. Egorenkov and Yu. M. Pleskachevskii, *Adgeziya polimerov k metallam (Polymer adhesion to metals)*, Nauka i tekhnika, Minsk, 1971, p. 185 (in Russian).

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