AUTOHESION OF COMMERCIAL ELASTOMER SYSTEMS

Part 3. Effect of Migration of Pseudosofteners on the Autohesion of Elastomer Systems


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In experiments on P-200 and SKN-40 elastomers plasticized with pseudosofteners (dibutyl phthalate and medical liquid petrolatum, respectively) it has been established that their autohesion strength falls with increase in storage time. When various amounts of incompatible plasticizers are introduced, the autohesion strength falls to a certain limit, after which it remains constant. Radioactive measurements on P-200 plasticized with radioactive dibutyl phthalate have shown that the autohesion strength of an elastomer system is directly related with the amount of pseudosoftener migrating to the surface.

The system rubber—incompatible plasticizer is thermodynamically unstable and separates with time, as a result of which the plasticizer migrates to the surface [1].

The negative effect of the duration of storage of rubber blends before layering on a number of technical characteristics due to migration of low-molecular components to the surface was noted in [2, 3]. The nature and rate of migration of plasticizers and other ingredients to the surface were investigated in [4–7]. The possible effect of introducing plasticizers on the autohesion of elastomer systems was also examined in [8]. The present authors have shown the the introduction of increasing amounts of incompatible plasticizers into rubbers leads to a continuous decrease in the autohesion strength of the system.

Fig. 1. Effect of storage of autohesion elements composed of P-200 elastomer plasticized with dibutyl phthalate on the autohesion strength of the system at different plasticizer contents: 1) P-200, 2) P-200 with 5 parts by volume DP per 100 parts by volume polymer, 3) P-200 with 7 parts by volume DP per 100 parts by volume polymer, 4) P-200 with 10 parts by volume DP per 100 parts by volume polymer, 5) P-200 with 15 parts by volume DP per 100 parts by volume polymer.

Effect of storage of autohesion elements before layering on autohesion strength. We investigated SKN-40 butadiene-acrylonitrile copolymer and P-200 polyisobutylene, which represent types of elastomers with different polarity and differ substantially in autohesion properties.

P-200 elastomer was plasticized with dibutyl phthalate, and SKN-40 with medical liquid petrolatum. The amount of plasticizer introduced was 5–15 parts by volume for dibutyl phthalate and 3–5 parts by volume for liquid petrolatum per 100 parts by volume polymer. The lower limit of the amount of plasticizers introduced exceeded their previously determined [10] compatibility with the elastomers, while the upper limit was determined from the maximum amount of plasticizer that could be introduced into the polymer without losing the technical properties of the system.

The procedures for introducing the plasticizers, preparing the autohesion elements, and determining the autohesion strength were the same as those previously described in [9]. In all cases the elements of the autohesion joints were in contact for 30 min.

Fig. 2. Effect of storage of elements made from SKN-40 elastomer plasticized with medical liquid petrolatum on the autohesion strength of the system at different plasticizer contents: 1) SKN-40, 2) SKN-40 with 3 parts by volume liquid petrolatum per 100 parts by volume polymer, 3) SKN-40 with 5 parts by volume liquid petrolatum per 100 parts by volume polymer.

However, insufficient data are available on the nature of the relationship between autohesion strength and the duration of storage of rubbers plasticized with pseudosofteners, and we still lack experimental data that would directly confirm the dependence of autohesion strength on the amount of plasticizer migrating to the surface. This is the subject of the research reported in this paper.
Figure 1 shows the autohesion strength as a function of the duration of storage for autohesion bonds obtained from P-200 polymer plasticized with dibutyl phthalate at different plasticizer contents. As may be seen from the straight line 1, the autohesion strength of pure P-200 is almost independent of storage time. However, the autohesion properties of plasticized P-200 rapidly deteriorate with storage of the autohesion elements. Thus, the autohesion strength of P-200 containing 5 parts by volume dibutyl phthalate (curve 2) falls more than 25% below the initial value after the first 3 hr storage, after which the rate of fall slows down somewhat. After approximately 8–10 hr the autohesion strength is about 50% of the initial value and then remains constant.

The nature of the variation of the autohesion strength for P-200 plasticized with a large quantity of dibutyl phthalate remains as before (curves 3–5). However, as the amount of plasticizer increases, the autohesion strength falls to its constant value more and more rapidly. It is interesting to note that the limiting autohesion strength remains the same for all the samples, irrespective of plasticizer content.

The relationship between autohesion strength and storage time for elements prepared from SKN-40 plasticized with medical liquid petrolatum (Fig. 2) is similar in character. An initially rapid and then slower fall in autohesion strength leads to a constant value at different amounts of plasticizer. Pure SKN-40 exhibits almost no change in autohesion strength with time (Fig. 2), curve 1.

The presence of a limiting autohesion strength independent of the plasticizer content may be explained as follows. The plasticizers employed are almost incompatible with P-200 and SKN-40 elastomers. Consequently, the plasticizer gradually migrates to the surface during storage, accumulates at the surface in the form of a thin film and thus reduces the autohesion strength determined for the same contact time. However, the incompatibility is, of course, relative: a certain amount of dibutyl phthalate still dissolves in the P-200 and, conversely, a certain amount of P-200 is dissolved in the plasticizer that migrates to the surface. The same applies to SKN-40 plasticized with liquid petrolatum. Whatever the plasticizer content, the layer formed on the surface as a result of migration will be a maximally saturated solution of the elastomer in the plasticizer, always with the same percentage content of high-molecular component.

Consequently, the limiting autohesion strength corresponding to a sufficiently long storage time will always have a constant value corresponding to the autohesion strength of the saturated, probably gel-like solution of the polymer in the plasticizer.

A certain initial increase in autohesion strength after the introduction of relatively small amounts of plasticizer (Fig. 1 and 2, curves 2) is apparently associated with a decrease in the viscosity of the system and hence improved mobility of the polymer chains [8]. However, even after 30 min the plasticizer appearing on the surface reduces the autohesion strength to a value less than that for the pure elastomer.

The proposed explanation is perfectly probable. However, since it presupposes the presence of a direct relation between the amount of plasticizer migrating to the surface and the deterioration of the autohesion properties of the elastomer system, it needs experimental confirmation by direct measurements. Accordingly, we carried out radiometric measurements that enabled us to estimate the rate of accumulation of radioactive plasticizer on the surface of the autohesion element.

Radiometric investigation of the migration of radioactive plasticizer. Plasticizer migration was investigated in relation to P-200 elastomer plasticized with radioactive dibutyl phthalate (5 parts by volume plasticizer per 100 parts polymer). Dibutyl phthalate tagged with carbon 14 was synthesized in the usual way [11, 12]. The product obtained after purification was subjected to additional vacuum distillation; the fraction boiling at 168–172° C (residual pressure 3–4 mm Hg) was drawn off. The purity of the dibutyl phthalate obtained was checked with respect to the refractive index, whose value coincided with tabulated data (nD = 1.4925).

The procedure for introducing the tagged dibutyl phthalate (specific activity 0.002 mC/g) into the P-200 and preparing the autohesion elements was the same as that previously described in [9]. From the autohesion elements we cut samples 3 cm in diameter which served as sources of β-radiation. The amount of plasticizer migrating to the surface was estimated from the change in the β-radiation counting rate. For this purpose we used an end-window counter for soft β-radiation. The pulses were counted on a B-2 mechanical counter. The radiation intensity was measured every 30 min. For each point three measurements were made in a 3-min interval and averaged.

Figure 3 shows the autohesion strength (curve 1) and the β-radiation counting rate (curve 2) as functions of storage time. Since the radiation intensity gives the amount of plasticizer migrating to the surface, the curves obtained should be considered graphic confirmation of the presence of a direct relation between the autohesion strength of the elastomer system and the migration of plasticizer to the surface.

The relationship between autohesion strength and counting rate (amount of plasticizer migrating to surface) is also confirmed by the linear dependence of these two quantities (Fig. 4).

SUMMARY

1. It has been shown that the autohesion strength of P-200 and SKN-40 elastomers plasticized with pseudosofteners (dibutyl phthalate and medical liquid petrolatum, respectively) falls with increase in storage of the elements of the autohesion bond.

2. When various amounts of incompatible plasticizers are introduced, the autohesion strength falls to a certain limit, after which it remains constant.

3. Radiometric measurements on P-200 plasticized with radioactive dibutyl phthalate confirm that the autohesion strength of an elastomer system is directly related with the amount of pseudosoftener migrating to the surface.