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Abstract

Full Text

PHYSICAL CHEMISTRY

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EFFECT OF VULCANIZATION OF ELASTOMERS ON THEIR ADHESION TO NON-VULCANIZING POLYMERS

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According to current concepts ($^{1-3}$), the mechanisms of adhesion and of the covulcanization of rubbers have much in common. The phenomenon of covulcanization, like the adhesion of polymers, includes diffusion of macromolecules and their segments, especially intensive in the initial period of vulcanization, when crosslinks have not yet formed. The difference between covulcanization and adhesion consists only in the fact that the process of interpenetration of molecular chains in the former case is sooner or later interrupted by the superimposed process of vulcanization, which fixes the macromolecules or their portions with strong chemical bonds. This leads to the formation of an adhesive seam considerably stronger than a seam in which the diffused molecules are fixed only by weak intermolecular bonds.

It is of interest to determine how vulcanization of elastomers affects their adhesion to polymers that are incapable of forming chemical bonds with them. This case is of enormous practical importance, since rubbers are very often used in combination with plant and synthetic fibers that are incapable of vulcanizing.

Elastomers of different molecular structure, polarity, and degree of molecular mobility were taken as adhesives: butadiene-acrylonitrile rubber (SKN-26), butadiene-styrene rubber (SKS-30A), oil-extended butadiene-styrene rubber (SKS-30ARM-15), and butyl rubber. On the basis of the rubbers listed above, rubber compounds were prepared both containing and not containing vulcanizing groups (in the latter case the ingredients of the vulcanizing group were replaced by an equal amount of inert filler—chalk). The composition of the vulcanizing group was chosen to be optimal for each rubber.

As substrates, plasticizer-free films were used—cellophane (hydrated cellulose) and perfol PK-4 (polycaprolactam).

Application of the adhesive to the substrate was carried out by calender lining under conditions optimal for each elastomer (^{4}). The specimens obtained by this method were doubled and subjected to vulcanization. Vulcanization was carried out on a "Berstorff" continuous-vulcanization apparatus at 143°C and a specific pressure of ≈ 0.85 kg/cm^2. The duration of vulcanization was varied

Figure 1

Figure 1: Figure 1

from 0 to 88 min.

Figures 1 and 2 present the dependence of the specific adhesion (determined by the delamination method) of elastomer coatings on the above-mentioned substrates. As can be seen, regardless of the type of adhesive and substrate, the holding time of the bonded joint at the vulcanization temperature has a very strong effect on the magnitude of adhesion. However, whereas the adhesion of coatings not containing a vulcanizing group increases continuously (though at different rates) with increasing heat-treatment time, the adhesion of coatings containing vulcanizing groups passes through a maximum.

The continuous increase in the magnitude of adhesion in the first case may be due to the interdiffusion of molecules or their elements in the boundary layer. In the second case, the increase in adhesion during brief heat treatment of the bonded joint is evidently explained by the same reason as in the preceding case. The structuring processes at this stage, owing to the presence of an induction period of vulcanization, apparently either have not yet occurred or proceed only to a very small extent.

Fig. 1. Effect of heat-treatment time on the adhesion of coatings containing no vulcanizing groups to polyamide film PK-4 (*a*) and cellophane (*b*).
1—Butyl rubber; 2—butadiene-styrene oil-filled rubber (SKS-30ARM-15); 3—butadiene-styrene rubber (SKS-30A); 4—butadiene-nitrile rubber (SKN-26).

A sharp change in the shape of the curve upon vulcanization for more than 12–15 min is probably caused by two factors. One of these factors is a sharp decrease in the diffusion rate as a result of structuring of the adhesive. However, even a complete cessation of diffusion could lead only to adhesion ceasing to increase after some point, despite an increase in the heat-treatment time. A factor responsible for the decrease in adhesion may be the appearance, in the contact zone, of additional stresses due to shrinkage of the rubber coating caused by structuring of the elastomer. These stresses will, of course, reduce the force that must be applied in order to destroy the adhesive joint.

The data obtained also make it possible to draw a number of conclusions concerning the influence of the molecular structure of the elastomers studied on adhesion.

It is known that butyl rubber is a practically nonpolar elastomer with a linear structure, whose molecular weight is very low compared with the molecular weights of other elastomers (in our case the weight-average molecular weight of butyl rubber was 32,000). The low molecular weight of this polymer accounts for the presence in it of a considerable number of macromolecular ends, which, as is known (5), take the most active part in diffusion processes. All this provides

Figure 2

Figure 2: Figure 2

butyl rubber with maximum adhesion to both substrates.

The presence of bulky styrene side groups and a high molecular weight account for the considerably lower adhesion values of butadiene-styrene elastomers. It is very interesting to compare the adhesion of the butadiene-styrene elastomers SKS-30A and SKS-30ARM-15. The latter differs from the ordinary low-temperature butadiene-styrene rubber SKS-30A only in the content of softener introduced into the copolymer during its manufacture. Considering that the copolymers under consideration have one and the same chemical nature, it remains to be assumed that the greater adhesion

Fig. 2. Effect of vulcanization on the adhesion of a rubber coating to polyamide film PK-4 (*a*) and cellophane (*b*). The designations are the same as in Fig. 1.

of the oil-filled elastomer is due to the greater mobility of its molecular chains.

Finally, in all cases the minimum adhesion was observed for the most polar adhesive—the butadiene-nitrile copolymer. This circumstance can also be explained from the standpoint of the diffusion theory of adhesion—by the low mobility of the molecular chains and the presence of nitrile-acrylic side groups. In this case diffusion processes undoubtedly proceed at a much lower rate, as indicated by the absence of a sharp increase in adhesion at the initial stage of polymer interaction. In addition, the magnitude of the specific adhesion in the latter case may to a noticeable extent be due to intermolecular interaction of polar polymers in the contact zone.

It is significant that the curves characterizing the change in adhesion with the heat-treatment time of various adhesive joints are arranged in one and the same sequence both in Fig. 1 and in Fig. 2. This means that the particular features of rubber vulcanization cannot outweigh the influence of the nature of the adhesive on adhesion. When considering the influence of the nature of the substrate on adhesion, attention is drawn first of all to the fact that nonpolar rubbers exhibit high adhesion to polar substrates. This fact may be explained by local dissolution of the hydrocarbon chains of the adhesive in the substrate, which consists of polar groups and fairly large sections of nonpolar hydrocarbon chains (6).

A comparison of adhesion to cellulose and to capron shows that its value is always higher in the case of capron. In all probability this is due to the extremely high rigidity of the molecular chains of cellulose (7) and the very high density of their packing, caused by the presence of hydrogen bonds between hydroxyl groups (8). Moreover, unlike capron, cellulose always exists only in the glassy state (7, 9). Such a structure of cellulose and its physical state create extremely unfavorable conditions for diffusion of elements of the adhesive molecules.

Thus, vulcanization of the rubber coating causes the appearance of an adhesion maximum, which corresponds to the optimal (according to

adhesion) of the degree of vulcanization. The existence of a vulcanization optimum with respect to bond strength was verified by us for rubber–fabric materials based on fabrics made of cellulose, capron, and glass fiber. In these cases as well, an analogous character of the change in adhesion with the degree of vulcanization of the rubbers was observed. The influence of "mechanical adhesion," without changing the character of the dependence, leads only to higher values of the overall bond strength of the adhesive to the fabric in comparison with the corresponding values of specific adhesion to films.

Table 1

Influence of the degree of vulcanization on the bond strength of rubber with fabric

Rubber designation	Type of carcass fabric	Optimum vulcanization time, min., for rubber	Optimum vulcanization time, min., for adhesion	Peeling resistance, g/cm after vulcanization, 35 min.	Peeling resistance, g/cm after vulcanization, 15 min.
SKS-30A	Percale	35	15	900	1500
SKS-30A	Capron art. 1520	35	15	350	1050
SKS-30A	Glass fabric T_1	35	15	600	1350
SKN-26	Percale	35–40	15	1150	2000
SKN-26	Capron art. 1520	35–40	15	200	700
SKN-26	Glass fabric T_1	35–40	15	400	1200
Butyl rubber	Percale	40	15	2600	3900
Butyl rubber	Capron art. 1520	40	15	2000	3600
Butyl rubber	Glass fabric T_1	40	15	2700	4000

The existence of a vulcanization optimum with respect to bond strength in rubber–fabric articles and materials can be used in production practice. At present such articles are vulcanized according to regimes corresponding to the optimum in the physicomechanical properties of the rubber. However, the degree of vulcanization that is optimal with respect to bond strength is reached considerably earlier, and the magnitude of the bond strength under regimes of vulcanization optimal for the properties of the rubber is much lower than its value at the degree of vulcanization corresponding to the adhesion optimum. Table 1 gives the corresponding values of the bond strength of rubbers to fabrics of different chemical nature. The bond-strength values are given in Table 1 both for vulcanization corresponding to the optimum in rubber properties (35-40 min. at 143°) and for vulcanization according to the regime corresponding to the optimum in bond strength (15 min. at 143°). According to the data of Table 1, reducing the vulcanization time from 35 min. to 15 min. leads to an increase in bond strength by a factor of 1.8-3.

A reduction in the degree of vulcanization of these layers (in comparison with the degree of vulcanization of the main mass of rubber) can be effected without changing the currently accepted vulcanization regime for the given article, by a corresponding decrease in the content of the vulcanizing group in the boundary rubber layer. In addition to increasing the "rubber—fabric" bond strength in articles, this measure will make it possible to reduce the cost of the articles by decreasing the content of expensive ingredients of the vulcanizing group.

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