

# Adhesion of UV-Treated Rubbers to Epoxy Adhesives

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## SYNOPSIS

The adhesive joint strength behavior of vulcanized rubbers with epoxy adhesives during the ultraviolet (UV) treatment of rubber surfaces has been studied. The change in rubber surfaces and the interphase layer structure of joints has been investigated. A model for the joint strength behavior is suggested, with which one can predict the appropriate use of UV treatment of rubber surfaces to improve the joint strength. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

The ultraviolet (UV) treatment of polymer materials has often been employed to improve adhesion. The results have not always been positive. Because of this, skepticism has been associated with the selection of this technique to modify the surface of polymers in technological processes, despite the ease of UV treatment. Thus the studies of the effect of UV treatment on the structure of exposed polymers and the interface and strength of adhesive joints may establish more definite limits for the use of UV treatment for polymers.

UV treatment of polymer surfaces is known to improve or retain their adhesion abilities.<sup>1</sup> However, this treatment can reduce or completely destroy the adhesive ability.<sup>2,3</sup> The changes in polymers' adhesive properties have been associated with the modification of the structure of exposed polymers.<sup>4</sup> Here, "structure" means preferably the multilevel structural organization of polymers. Such a hierarchy of structural levels was given by Lipatov,<sup>5</sup> who distinguished four levels, namely: molecular (molecular groups), topological (presence of polymer network, molecular weight, macrochain branches), supermolecular (crystallinity, ordering of macrochain packing), macromolecular (heterogeneity of a polymer: presence of filler particles, gas-air inclusion, surface roughness). This classification of structural levels allows the various phenomena at the interface to be considered more clearly by using

the various available theories of adhesion of polymer materials.<sup>6,7</sup>

In the simplest case, the strength of a joint has been determined as the strength of the weakest phase of joint (usually the adhesive). The processes at the interface of substrate and adhesive, which influence the joint strength, are not taken into account here. As the adhesive is believed to be uniform, the strength of a joint under particular loading conditions must coincide with the strength of the pure adhesive. This will apparently be an ideal adhesive joint, where the effect of interface is absent and the joint strength is maximum.

However, the definition itself of an adhesive joint implies a prescribed deviation of structure uniformity because of the presence of two phases, the substrate and the adhesive. This causes the occurrence of an interface and a leap (or nonuniformity) of the structure. Various physico-chemical processes are also likely to occur at the interface, which change the structure of the boundary layers of adhesive and substrate. Thus, in most cases, the real adhesive joints have a lower strength than that of an ideal adhesive joint. When the stresses in a joint are uniform (or invariable) under loading, the strength of the joint is determined only by the modification of structure; namely, by the nonuniformity of joint structure at the substrate-adhesive interface.

The structure of a material and its strength are interrelated in a complex manner. But in the case of an adhesive joint, it is necessary to establish only the relationship of differential characteristics: the modification of structure and the respective change of strength. So from a certain type of material one

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may distinguish a main structural level that is the primary influence on its strength. According to the distinguished levels of structure, some theories of adhesion are available which account for the joint-strength behavior in changing any structural level at the interface.

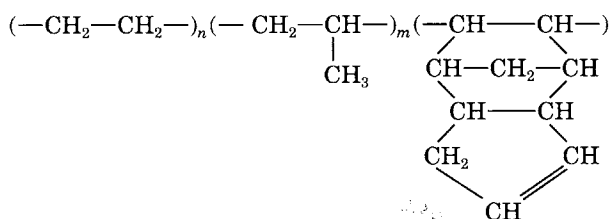
In UV modification of a polymer surface, several adhesion theories may be applied which explain the joint-strength behavior<sup>8</sup>: mechanical theory,<sup>7</sup> thermodynamic theory,<sup>9</sup> and chemical theory of adhesion.<sup>10</sup> These theories are related to molecular, topologic, and macromolecular structural levels, respectively. These theories and changes of structural levels at the interface are associated with the modification of the structure of the substrate surface layer during UV treatment.

Under the action of UV light on a polymer in the presence of air, the photooxidative reactions begin, their routes and kinetics determined by the nature of the polymer and the spectral composition of UV light.<sup>11</sup> The integral result of the reactions in an exposed polymer is the destruction of polymeric chains, the formation of crosslinks, and the appearance of additional oxygen-containing groups. In turn, this influences the change in surface energy of exposed substrate, the change in chemical reactivity of the surface layer, and deformation characteristics of the surface layer, as well as the morphology of the substrate surface. These modifications may be the reasons for the change in nonuniformity of the structure at the interface in an adhesive joint. The investigation of the relationship between these surface changes and the change in structure and joint-strength allows us to construct a model for the joint-strength behavior during UV treatment of the substrate surface.

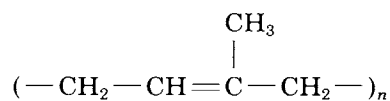
## EXPERIMENTAL

### Materials

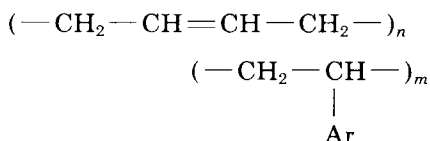
Industrial vulcanized rubbers (substrates) (see Table I) were based on ethylene-propylene rubber (EPDM-40)



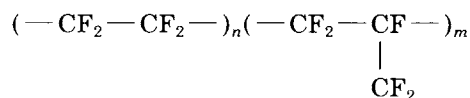
isoprene rubber (SKI-3)



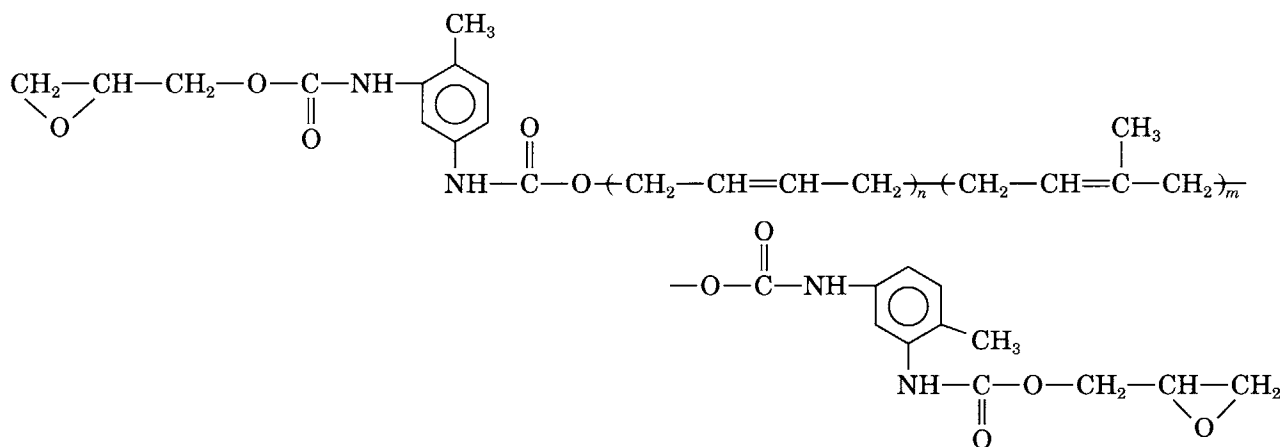
divinylstyrene rubber (SKDS)



and fluorinated rubber (SKF-26)



The adhesive contained divinylisopreneurethane diepoxide rubber (PDI)



**Table I** Composition of Substrates

Substrate	Components (in mass parts)
1	EPDM-40 rubber (100), sulfur (2.0), tetramethylene thiuramdisulphide (2.0), 2-mercapto-benzthiazol (1.0), carbon black PM-75 (50), stearic acid (1.0), ZnO (5.0), dioctylsebacinate (20).
2	SKI-3 rubber (40), SKDS rubber (60), sulfur (2.0), di-2-benzothiazolyldisulphide (2.0), carbon black PM-75 (85), ZnO (5.0), dioctylsebacinate (15).
3	SKF-26 rubber (63), <i>N,N</i> -bis(furalident)-1,6-hexamethylenediamine (2.0), carbon black PM-75 (13), phenol-formaldehyde resin (6), urothropine (1.0), MgO (13).

and divinyl nitrile carboxyl-containing rubber (SKD). The adhesive was cured at 343 K for 10 days. The joint-formation procedure was previously described in more detail.<sup>12</sup> For model experiments, the pure nonvulcanized and Co<sup>60</sup> radiation-vulcanized rubbers as well as adhesive-based epoxy resin ED-20 and carboxy-terminated butadiene acrylonitrile rubber SKN were employed. Diterbutyl antraquinone was used as UV sensitizer.

### Irradiation

The substrate surface was irradiated by using intermediate-pressure mercury quartz lamps PRK-2 and PRK-7 (analogized Hanovia type A, 673A, and others) without light filters with a rheostat power unit. The distance between lamp and samples was 0.1 m. A parameter "radiation dose" was used for quantitative measurements, determined on the basis of the power density scattered by the lamp. As previously studied,<sup>13</sup> this parameter adequately describes the change in the substrate surface within small radiation doses studied during variation of the lamp's scattering power and operating volume, and the geometry and lighting time of the sample.

### Analysis

The strength of joints was determined in tension on an RM-500 tearing machine (analogized Instron) at a 293-K temperature and 100-mm/min loading speed. The wetting angle was determined by the geometric dimensions of a droplet of adhesive on

the substrate surface by using an optical microscope (MBS-9; LOMO, Russia). The substrate surface photographs were obtained using the same microscope with an attachment and "Zenit E" camera (LOMO, Russia). Infrared (IR) transmission and IR attenuated total reflectance (ATR) spectra were obtained on UR-20 and Specord M-80 spectrometers (Jena, Germany). In order to obtain ATR spectra, a specially designed ATR accessory with crystals KRS-5 and Ge was used, the incident angle was 45 degrees, and the number of reflections was 19.

## RESULTS AND DISCUSSION

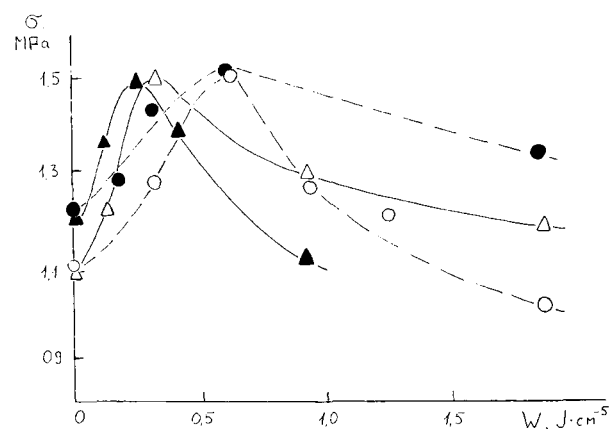
### Strength of Adhesion Joints

Figure 1 shows the characteristic dependence of joint strength on the UV-treatment dose of substrate. Two sections may be distinguished in the plot, which correspond to two mutually opposed processes. The ascending section of dependence corresponds to the increase in the adhesion ability of the substrate surface and the increase in the joint strength. Let us formally approximate this section of dependence:

$$\sigma = \sigma_0 + K_1 W \quad (1)$$

where  $\sigma_0$  is the strength of the initial joint with unexposed substrate,  $W$  is the UV-treatment dose, and  $K_1$  is a certain coefficient.

The descending section of the dependence corresponds to the drop of substrate strength at high UV-treatment doses and to the drop in total joint



**Figure 1** Dependence of joint strength of substrate 1 and adhesive 1 on the UV treatment dose at different pretreatments of substrate surface: (O) without UV sensitizer; (Δ) with UV sensitizer; (light marks) without roughening; (dark marks) with roughening.

strength. The functional dependence of polymer material strength on the UV-treatment dose is determined exponentially.<sup>14</sup> Thus, in the same manner, we also approximate the joint-strength behavior in this section:

$$\sigma = \sigma_2 + \sigma_{20} \text{EXP}\{-K_2 W\} \quad (2)$$

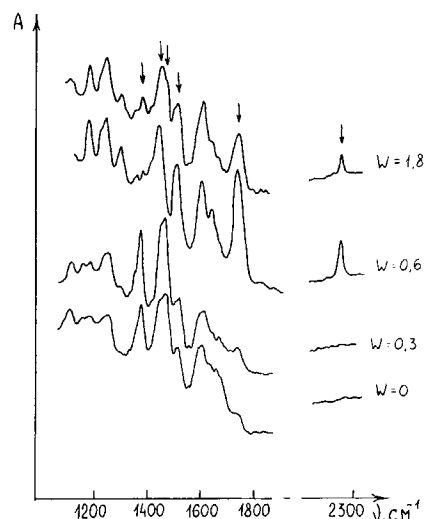
where  $(\sigma_2 + \sigma_{20})$  is the substrate strength. As the UV treatment modifies only a thin substrate surface layer, the strength characteristics  $\sigma_2$  and  $\sigma_{20}$  are not related to the entire substrate sample but only to its surface layer. This makes it difficult to compare these characteristics to the substrate strength determined under standard conditions, but does not exclude a comparative examination.

But can UV treatment produce a maximum joint strength? The adhesive strength under identical conditions and geometry of adhesive deformation in a joint is 1.47 MPa, which is close to the maximum joint strength.

The coincidence of strength values confirms the character of joint failure. A pure radiation-vulcanized EPDM-40 rubber and a model adhesive based on the rubber SKN and epoxy resin ED-20 were used for experiment. The IR ATR spectrum of the failed surface on the substrate side (Fig. 2) shows the changes in the failure character with increasing UV-treatment dose. The first section of the strength dependence (Fig. 1) corresponds to the adhesion character of failure. There are no absorption bands  $\nu(\text{C}\equiv\text{N}) = 2230 \text{ cm}^{-1}$  and  $\nu(\text{C}=\text{O}) = 1720 \text{ cm}^{-1}$  of adhesive rubber SKN. This indicates that the adhesion ability of the substrate surface is insufficient, and the joint strength is determined by the strength of the substrate-adhesive interface.

The change in the failure character is observed at the transition to the extreme section of the strength dependence. The spectrum of the substrate surface does not exhibit the EPDM-40 rubber bands (for example the band  $\delta(\text{CH}_3) = 1380 \text{ cm}^{-1}$ ) and it corresponds to the cured adhesive [resin ED-20 bands  $\nu(\text{Ar}) = 1518, 1610 \text{ cm}^{-1}$ ,  $\nu(\text{C}-\text{O}-\text{C}) = 1255 \text{ cm}^{-1}$ , and bands of rubber SKN  $\nu(\text{C}=\text{O}) = 1720 \text{ cm}^{-1}$ ,  $\nu(\text{C}\equiv\text{N}) = 2230 \text{ cm}^{-1}$ ]. The character of failure is cohesive by the adhesive. Therefore, this section is the place to realize ideal adhesive joint conditions, where the failure and joint strength are determined by one of the bonded materials; in this case, by the adhesive.

At the transition to the final section, the failure character alters in the same manner. In the spectrum of failure surface, the adhesive bands at 1255, 1518, 1610, 1720, and  $2230 \text{ cm}^{-1}$  and the substrate bands



**Figure 2** IR ATR spectra of failed surface on the substrate side. Radiation dose is shown in  $\text{J cm}^{-2}$ .

at  $1380 \text{ cm}^{-1}$  are observed, which correspond to the mixed character of failure.

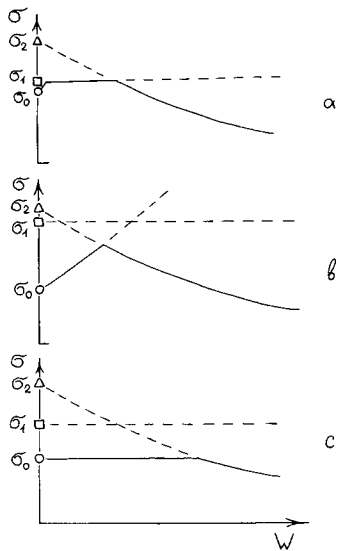
Thus the plot of joint strength dependence allows us to distinguish three sections, determined by various factors. The joint strength versus UV-treatment dependence may be written as a function:

$$\sigma = \begin{cases} \sigma_0 + K_1 W, & W < W_1 \\ \sigma_1, & W_1 < W < W_2 \\ \sigma_2 + \sigma_{20} \text{EXP}\{-K_2 W\}, & W > W_2 \end{cases} \quad (3)$$

where  $\sigma_1$  is the adhesive strength.

Based on the model suggested, one can estimate the appropriate use of UV treatment from the characteristics of the materials to be bonded. Let us consider several different situations (Fig. 3):

1. The initial strength of a joint is close to the strength of adhesive ( $\sigma_0 \approx \sigma_1$ ). There is an ideal adhesive joint without modification of the substrate surface. UV treatment can only reduce the joint strength.
2. The adhesive strength is close to that of the substrate ( $\sigma_1 \approx \sigma_2 + \sigma_{20}$ ). A particular example of this situation is autoadhesion. UV treatment somewhat increases the joint strength, but the ideal adhesive joint cannot be achieved here.
3. UV treatment does not enhance the adhesion ability of the substrate ( $K_1 = 0$ ). Accordingly, UV treatment cannot increase the joint strength.



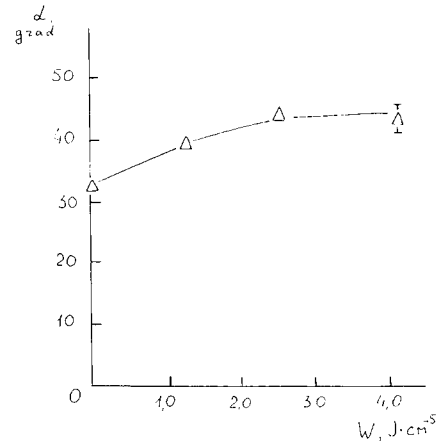
**Figure 3** Model situations of joint strength behavior during UV treatment. See explanations in text.

In cases 1 and 2, the appropriate use of UV treatment may be determined from the strength values of the bonded materials. To consider case 3, it is necessary to study the nature of interphase interaction, which determines the change in joint strength during UV treatment.

**Interface Analysis**

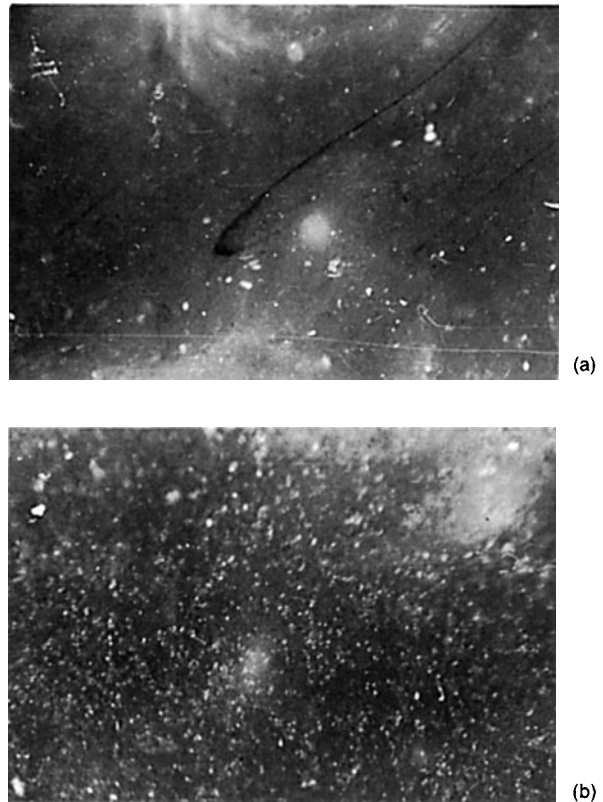
The strength of adhesive joints based on rubber-substrate EPDM-40 with epoxy adhesive is essentially determined by the presence of crosslinks of polymer networks at the interface due to the esterification reaction of epoxy groups of adhesive with carboxyl groups of EPDM-40 surface layer oxidized under the action of air and light.<sup>12</sup> But the adhesive character of unexposed substrate joint failure shows that the concentration of interface crosslinks is insufficient to obtain an ideal adhesive joint. At UV treatment, the increase in strength cannot necessarily be related to the increasing concentration of crosslinks. The modification on other structural levels and their contribution to the change in joint strength were analyzed.

The variation of substrate surface energy during UV treatment was estimated by using the wetting angle by adhesive (Fig. 4). In used UV-treatment doses, the wetting angle undergoes a little change and remains far from the good wetting conditions required for ideal adhesion. To increase the strength and to achieve an ideal adhesive joint is thus impossible in this case, due to the change in intermolecular interaction.



**Figure 4** Dependence of wetting angle of substrate 1 by adhesive on the UV treatment dose.

UV treatment of substrate also leads to a change in surface roughness (Fig. 5). As compared with the initial substrate, the surface of exposed substrate is a place of hollows and pits formed as a result of the destruction processes of rubber macromolecular chains and the removing of low-molecular-weight substances. The modifications of substrate surface



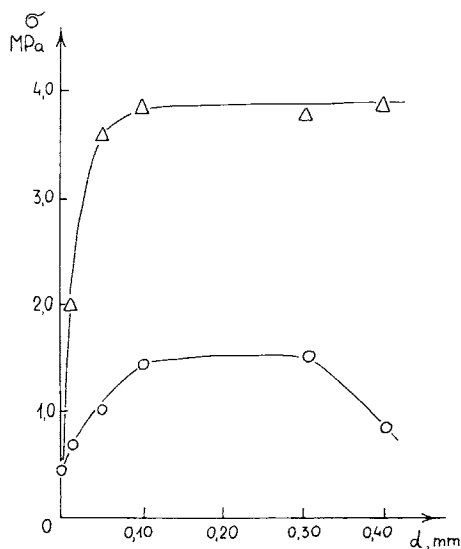
**Figure 5** Microphotographs of EPDM-40 rubber surface: (a) initial surface; (b) UV-treated surface.

morphology were modeled by roughening and shaping the substrate with abrasive paper. A nonvulcanized substrate based on the rubber SKN was used in experiments.

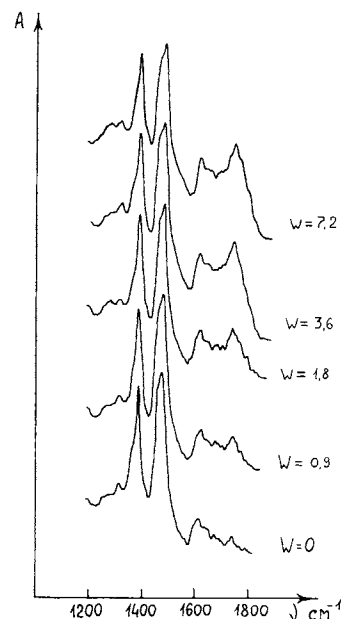
The first series of substrate samples was vulcanized using a conventional technique<sup>15</sup> between the smooth spacers and roughened with the abrasive paper of various graininess. Both surface morphology and chemical composition of the surface layer were thus modified as a result of mechanical destruction and oxidation.<sup>16</sup> The second series of samples was vulcanized between spacers of the same abrasive paper. Only the morphology of the substrate surface was assumed to be modified here.

The strength of joints with roughened substrate varies much higher than those with shaped substrate (Fig. 6), while the change in geometry in both cases is significant for this adhesive. Therefore, the change in joint strength during UV treatment due to the modification of substrate surface morphology is not significant and cannot explain the achievement of an ideal adhesive joint.

In such a case, only the effect of chemical activity of the substrate surface layer can be most important. UV treatment of rubber leads to the appearance of oxygen-containing groups in the surface layer because of radical oxidative reactions, which are manifested in IR ATR spectra (Fig. 7) by the occurrence of  $\nu(\text{OH})$  bands of hydroperoxide, hydroxyl, and carboxyl groups in the region  $3200\text{--}3600\text{ cm}^{-1}$ ;  $\nu(\text{C}=\text{O})$  bands of ketone, aldehyde, and carboxyl groups in the region  $1650\text{--}1800\text{ cm}^{-1}$ ; and  $\nu(\text{C}-\text{O})$



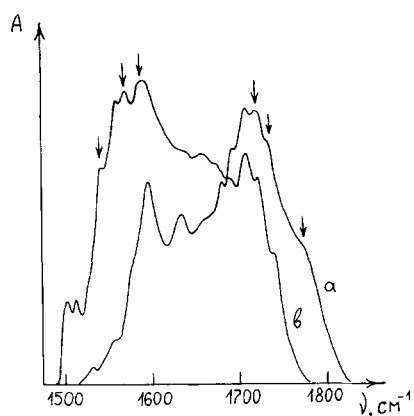
**Figure 6** Dependence of joint strength of substrate 4 and adhesive 1 on the particle sizes of abrasive paper: ( $\Delta$ ) mechanically treated samples; ( $\circ$ ) shaped samples.



**Figure 7** IR ATR spectra of EPDM-40 rubber at different doses of UV treatment. Radiation dose is shown in  $\text{J cm}^{-2}$ .

bands of ester, peroxide, and carboxyl groups in the region  $1000\text{--}1300\text{ cm}^{-1}$ . Moreover, the intensity of diene group  $\nu(\text{C}=\text{C})$  bands in the region  $1600\text{--}1650\text{ cm}^{-1}$  is increased. As was noted earlier,<sup>7,12</sup> the appearance of carboxyl groups on the polymer surface is more important for adhesion than the appearance of other groups. The quantitative measurements of carboxyl group concentrations were carried out by normalized optical density of the  $\nu(\text{C}=\text{O})$  bands because they have the largest peak extinction coefficient, which is required for measurements at small doses of UV treatment.

In order to assign the bands in the  $\nu(\text{C}=\text{C})$  region precisely, the surface of oxidized radiation-vulcanized EPDM-40 rubber was treated with 10% KOH solution in ethanol. IR ATR spectrum of rubber shows the intensity decrease in bands at  $1770$ ,  $1738$ , and  $1723\text{ cm}^{-1}$  assigned to carboxyl groups (Fig. 8). The bands that appeared at  $1597$ ,  $1580$ , and  $1560\text{ cm}^{-1}$  were attributed to  $\nu(\text{C}=\text{O})$  potassium carboxylate. The clearing of rubber surface by solutions does not change the intensity of  $\nu(\text{C}=\text{O})$  potassium carboxylate, so these bands are interpreted as  $\nu(\text{C}=\text{O})$  of groups connected with the polymer network of rubber. To calculate the concentration of carboxyl groups, a normalized peak coefficient of the  $\nu(\text{C}=\text{O})$  band was determined with the normalization of the optical density of the  $\nu(\text{CH}_2) = 1462\text{ cm}^{-1}$  band by spectra of a homological



**Figure 8** IR ATR spectra of EPDM-40 rubber at UV treatment: (a) irradiated; (b) treated with KOH.

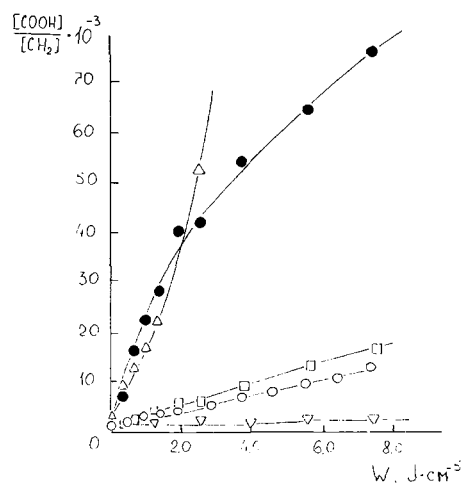
series of carboxyl acids with various lengths of methylene chain.

Figure 9 shows the dependence of carboxyl group concentration on the UV-treatment dose for different rubbers. Note that the rubbers' oxidation rates are markedly different. The application of UV sensitizer enhances the oxidation rate of rubbers.

The increase in carboxyl group concentration onto the substrate surface leads to increasing intensity of interaction between the rubber and epoxy resin. To record IR ATR spectra of the rubber surface, the epoxy resin without curing agent was applied onto the surface of radiation-vulcanized EPDM-40 rubber with various radiation doses, then exposed under curing conditions of adhesive, and the uncured resin was washed away with the solvent. Figure 10 gives the dependence of the normalized optical density of epoxy resin  $1520\text{ cm}^{-1}$  band on the UV-treatment dose of the substrate. The normalization was performed on the optical density of rubber band at  $1462\text{ cm}^{-1}$ . Increasing the dose of rubber treatment over the range studied considerably increases the amount of the epoxy resin "cross-linked" at the surface. At large radiation doses the destruction processes are involved, and the cured resin is washed away together with the oxidized and destructed rubber.

Therefore, the increase in joint strength during UV treatment and thus the  $K_1$  coefficient are associated with the increase in concentration of polymer network crosslinks at the interface. So the appropriate use of UV treatment for increasing joint strength will be determined by the need and possibility of increasing chemically active groups on the substrate surface; in this case, carboxyl groups.

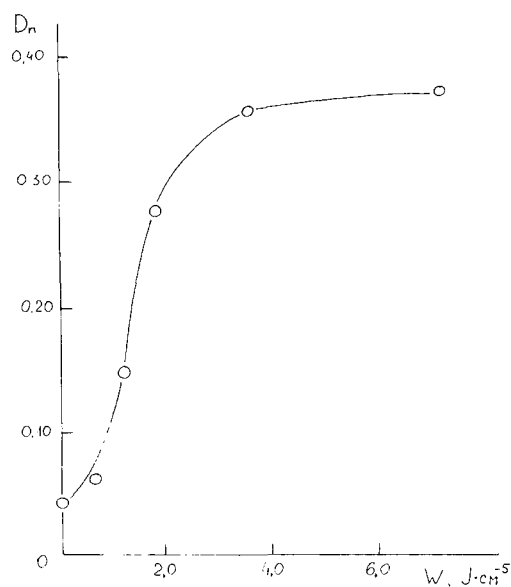
The substrate based on rubbers SKI and SKDS is characterized by a stronger oxidation under UV



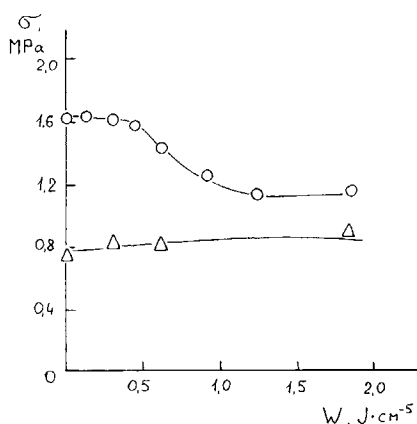
**Figure 9** Dependence of rubber surfaces' carboxyl group concentration on the treatment dose: (○) EPDM-40; (□) SKI-3; (△) SKDS; (▽) SKF-26; (●) EPDM-40 with UV sensitizer.

light and environment as compared with EPDM-40 rubber. So the joint strength of unexposed substrate is close to the strength of adhesive, and UV treatment only reduces the joint strength. This case is situation 2 and UV treatment is not appropriate (Fig. 11).

The substrate based on rubber SKF-26 is weakly oxidized under environment and is not oxidized at using radiation doses, so the joint strength is far from the adhesive strength and UV treatment can-



**Figure 10** Dependence of normalized optical density of  $1518\text{ cm}^{-1}$  band of epoxy resin in IR ATR spectra of EPDM-40 rubber on the UV treatment dose of rubber.



**Figure 11** Dependence of adhesive joint strength on the UV treatment dose of substrates with adhesive 1: (○) substrate 2; (△) substrate 3.

not increase it. This is a case of situation 3 and UV-treatment is not appropriate (Fig. 11).

Using the surface pretreatment technique of EPDM-40-based substrate, the maximum joint strength is not altered and all changes are related to the oxygen-containing group concentration. Roughening the substrate surface with abrasive paper raises only the initial joint strength due to the mechanooxidative destruction and the increase in oxygen-containing group concentration, but roughening is not sufficient to produce an ideal joint strength. When a UV sensitizer is applied onto the substrate surface prior to exposure, the kinetics of oxygen-containing group accumulation are accelerated and the maximum joint strength is achieved at lower radiation dose.

Therefore, the experiments support the suggested model of joint-strength behavior during UV modification of substrate surface.

## CONCLUSIONS

This work has suggested a model for adhesive joint behavior during the UV treatment of substrate surface in the example of vulcanized rubbers and epoxy containing rubber curable compositions. Based on this model, the possibility of predicting appropriate use of UV treatment for improving joint strength from the strength parameters and nature of bonded materials has been considered. For the materials

studied, we concluded that the main reason for increased joint strength during UV treatment is the increase in concentration of polymer network cross-links of substrate and adhesive, when the concentration of active oxygen-containing groups on the substrate surface is enhanced. This model of strength and obtained results are based on developing concepts about the question of polymer material adhesion as a problem of the effect of material structure nonuniformity in the interface region on adhesive joint strength.

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