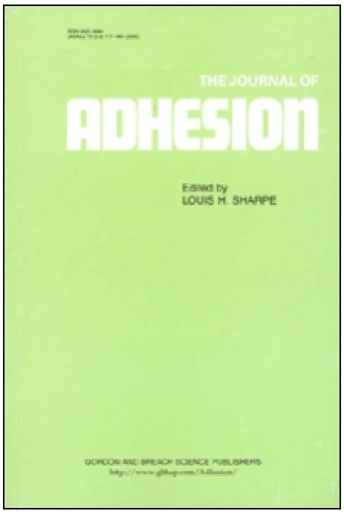

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Alexey Kondyurin[a]; Svetlana Imankulova[b]
[a] Institute for Polymer Research, Dresden, Germany [b] Institute of Technical Chemistry, Russian Academy of Sciences, Perm, Russia

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ADHESION OF QUINONE ADHESIVE TO RUBBERS

Alexey Kondyurin
Institute for Polymer Research, Dresden, Germany

Svetlana Imankulova
Institute of Technical Chemistry, Russian Academy of Sciences,
Perm, Russia

Adhesion joints based on ethylene-propylene EPDM-40, butadiene-nitrile SKN-40, and fluorinated SKF-26 rubbers with an adhesive based on SKI-NL isoprene rubber, ED-20 epoxy resin, and EH-10 quinone ether were studied. The results obtained indicate that quinone ether is involved in the formation of interchain links between substrate and adhesive networks. It was also found that, in the case of fluorinated rubber, active unsaturated carbon-carbon groups occur on the substrate surface subjected to additional treatment (roughening) prior to adhesive formation. These groups, active to quinone ether, are capable of forming networks in the interface region.

Keywords: Adhesion; Rubber; Quinone; IR ATR spectroscopy

INTRODUCTION

The strength of adhesion joints of multicomponent polymer materials is ascribed to different physical and chemical processes observed in the interface region on curing the joining adhesives. In many cases, the most essential processes influencing the adhesion strength can be revealed. In particular, for rubbers with high concentration of plasticizers, the formation of a joint network between the adhesive and substrate networks in the interface region is a basic factor defining the adhesion strength [1, 2]. Based on the results of investigation of the network formation in these adhesion joints, one can

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Address correpondence to Alexey Kondyurin, Institute for Polymer Research, Dresden 01059, Germany. E-mail: kond@mailcity.com

predict the behavior of the adhesion strength of rubbers depending on their composition, prehistory, the manner of joint formation, etc.

The study of the adhesion joints of rubbers with adhesives based on polyisoprene rubber, epoxy resin, and quinone ether is a challenge. The analysis of the interface interaction in the adhesion joints of rubbers and adhesives based on epoxy resin showed that the chemical bonds in the interface region can be formed by the reaction of epoxy groups with oxygen-containing groups of the surface layer of rubber. These oxygen-containing groups appear in the surface layer of rubber due to destructive processes caused by environmental conditions [3]. However, in the case of nitrile rubber, diffusion of epoxy resin can significantly change the stoichiometry in the boundary layer of the adhesive and lead to the formation of a weak adhesive layer at the interface. Thus, in general, the strength of the adhesion joint decreases [4]. The analysis of the interface interaction in the adhesion joint of fluorinated rubber and epoxide adhesive revealed that the epoxy groups cannot react with the active groups of the surface layer of rubber and provide adequate strength to such adhesion joints [4].

Introduction of quinone ether into the adhesive changes the chemical activity of this adhesive. Therefore, we can suppose that the formation of chemical bonds in the interface region is provided by the chemical reaction of quinone ether with active groups of the rubber. In the present work, we have analyzed the interface interaction in the adhesion joint with an adhesive containing quinone ether.

EXPERIMENTAL

Four types of vulcanized rubbers were used as substrates: the first substrate was based on ethylenepropylene rubber, EPDM-40; the second substrate was based on butadiene-nitrile rubber, SKN-40M; the third was based on fluorinated rubber of low molecular mass, SKF-26; and the 4th substrate was based on SKF-26 rubber of high molecular mass. A composition of polyisoprene rubber (SKI-NL) epoxy resin (ED-20) and quinone ether (EH-10) was used as the adhesive. Formulas (recipes) for the substrates and the adhesive are given in Table 1. The adhesive was cured in an oven at 80°C for 7 days. All components were industrially cleaned and studied by IR spectroscopy. For the 3rd and 4th substrates, rubbers with roughened and non-roughened surfaces were used. The rubbers were roughened using an abrasive disk with a particle size of 500 μm. The abrasive disk was spun at slow speed to avoid overheating the rubber surface.

The strength of adhesion joints was determined using fracture techniques described in Klyachkin et al. [3]. Substrate plates with a thickness

TABLE 1 Adhesive and Substrate Compositions

Sample	Components	Mass parts
Adhesive		
	SKI-NL rubber	7.9
	ED-20 resin	0.3
	EH-10	0.5
Substrate 1		
	EPDM-40 rubber	100.0
	Sulfur	2.0
	2-mercapto-benzothiazole	2.0
	Stearic acid	1.0
Substrate 2		
	SKN-40M rubber	100.0
	Phenol-formaldehyde resin	100.0
	2-mercapto-benzothiazole	1.0
	Dithiomorpholine	3.0
	Tetramethylene thiuramdisulphide	2.0
	Stearic acid	2.0
	ZnO	5.0
Substrate 3		
	SKF-26 rubber	50.0
	MgO	10.0
	N,N-bis(furalident)-1,6-hexamethylenediamine	3.0
Substrate 4		
	SKF-26 rubber	50.0
	MgO	10.0
	N,N-bis(furalident)-1,6-hexamethylenediamine	3.0

of 2.5 mm were bonded to metal cylinders with a diameter of 25 mm and a length of 30 mm. The adhesive mixture was poured into the gap between the substrate plates and then cured. The thickness of the adhesive was 1 mm. The joints were tested on an 2099 R-5 tensile machine (Russia) with a loading rate of 100 mm/min at a temperature of 293 °K.

IR and IR ATR spectra were recorded on UR-20 and Specord M-82 spectrometers (Carl Zeiss Jena, Germany) with an ATR accessory based on a KRS-5 crystal (number of reflections, 19; angle of reflection, 45°).

RESULTS AND DISCUSSION

The results achieved in the adhesion strength tests are presented Table 2. A high strength was observed for all joints. Although the character of destruction was mixed (adhesive and cohesive), in most cases it was adhesive. The adhesion strength and the character of destruction showed that the adhesion in all joints is high.

TABLE 2 Strength of Adhesion Joint

Substrate	Character of destruction	Adhesion strength, MPa
1	Adhesion-cohesion	1.546
2	Adhesion-cohesion	1.467
3	Adhesion-cohesion	1.242
4	Adhesion-cohesion	1.277

As is known [5], adhesion can be realized both by physical and chemical bonds. However, at high temperature or in a swelling solvent or solvent mixture, the physical bonds in the interface region can be destroyed, and in this case adhesion is realized only by chemical bonds. Therefore, the investigation of adhesion in a swelling solvent is useful in analyzing for chemical bonds at the interface. Qualitative results for chemical bonds in adhesion joints can be obtained by this method. Thus, the adhesion joint was immersed in a solvent with good penetration ability and then tested. At good adhesion, the joint remained unchanged in the solvent. At weak adhesion, with physical bonds only, the adhesion joint was destroyed. In the case of different adhesive and substrate nature, the solvent diffusion ability is different as well. The substrate and the adhesive swell to different volumes, and tangential stress appears on the interface boundary. The tangential stress can be high enough to destroy the adhesive joint even with chemical bonds in the interface region. To exclude differential swelling of the substrate and adhesive, mixtures of solvents were used in which the substrate and adhesive swell to equal extent and no tangential stress appears. To find the proper mixture, substrate and adhesive samples were each swelled to maximal volume in various mixtures of swelling solvents. For example, the swelling dependence of substrate **4** and adhesive in toluene-dimethylformamide mixtures is presented in Figure 1. Where the two curves intersect is taken as the mixture which equally swells the substrate adhesive.

It should be noted that a network in the interface region is not taken into account because the interface network layer is sufficiently thin and thus the swelling ability cannot result in a high stress in the adhesion joint. This approximation is based on the low Young's modulus and the small dimension of the interface region. In the general case, the swelling ability of the interface layer must be taken into account as well.

The results of the experiments presented in Table 3 showed that all adhesion joints were unchanged in solution except for the sample of fluorinated rubber without roughening. It was, therefore concluded

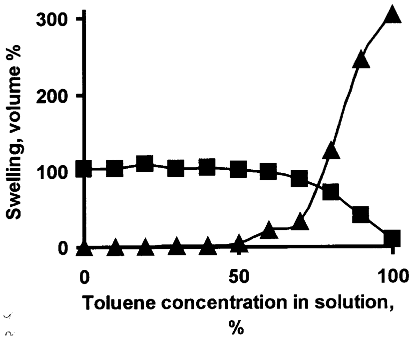


FIGURE 1 Maximal swelling of substrate **4** (squares) and adhesive (triangles) in toluene—dimethylformamide mixture.

that on the interface boundary of all adhesion joints there were chemical bonds. To determine the type of these chemical bonds, the chemical reactions that initiated the network formation in the interface region were studied [3, 6]. The analysis covered all possible chemical reactions between adhesive and substrate components in the interface region on curing the adhesive. For example, consideration was given to the chemical reaction encountered in substrate vulcanization and activation of its surface by the environment. The analysis implies the choice of reactions that would lead to the network formation or inhibit it in the interface region. In addition, some real experiments were performed with model mixtures of active components under adhesive curing conditions. The analysis of chemical interactions was made by the IR spectral method. The network formation was determined by the solvent method.

For the first adhesion joint, the model mixtures are the following: EPDM-40 rubber and quinone ether EH-10, and SKI-NL rubber and

TABLE 3 Swelling of Adhesion Joints in Mixture of Solvents

Adhesion joint	Mixture of solvents	Joint in solvent
1	CCl_4 : toluene (85 : 15)	Safe
2	CCl_4 : acetone (55 : 45)	Safe
3 (not roughened)	toluene : DMFA (80 : 20)	Destroyed
4 (not roughened)	toluene : DMFA (80 : 20)	Destroyed
3 (roughened)	toluene : DMFA (80 : 20)	Safe
4 (roughened)	toluene : DMFA (80 : 20)	Safe

DMFA, dimethylformamide.

sulfur. The percentage content of quinone ether and sulfur did not exceed 5%. Samples were cured at 80°C for 7 days.

The model mixture of SKI-NL and sulfur exhibited no changes and was soluble in CCl_4. It is evident that this reaction cannot influence the interface network. After thermal treatment, the mixture of EPDM-40 rubber and quinone ether becomes insoluble in CCl_4 and swells up to 3840%.

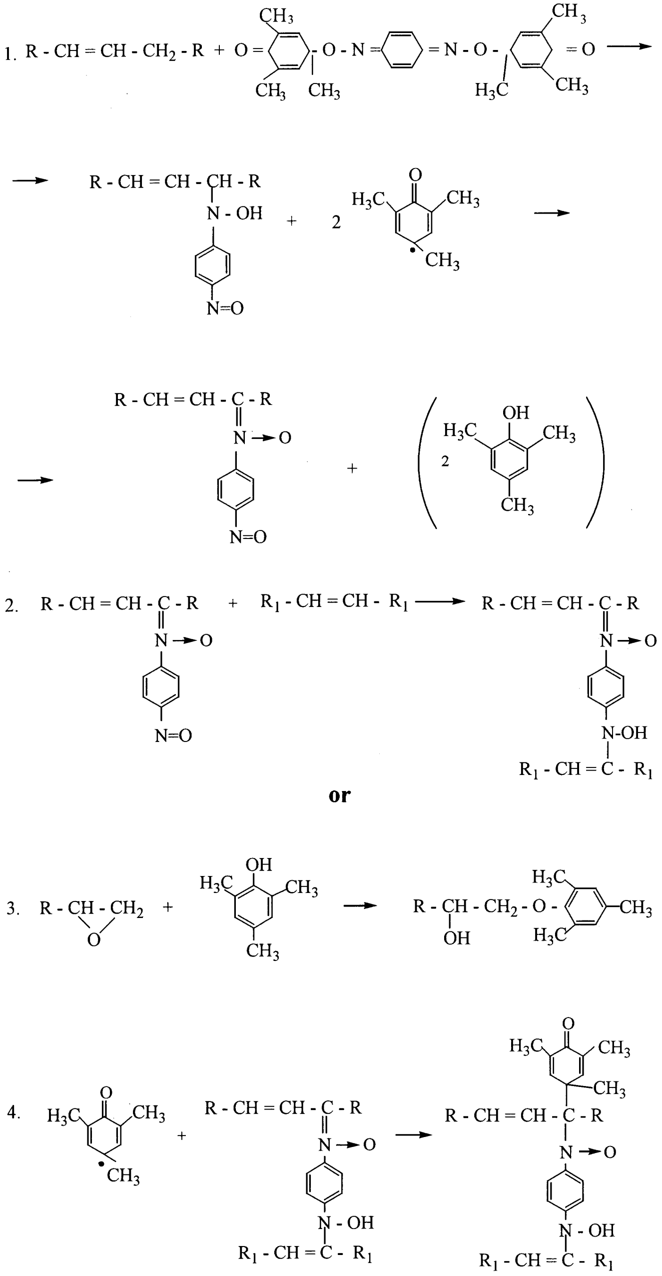
For the second adhesion joint, the model mixture is SKN-40 and quinone ether. After thermal treatment, the mixture swells up to 360% in toluene.

The adhesion joint of fluorinated rubber remained unchanged after drying and roughening. When the rubber was only dried, without roughening, the adhesion joint was destroyed in solvent. We can suppose that the mechanical treatment of fluorinated rubber leads to the formation of active groups on the surface. These new groups react with active groups of the adhesive (oxygen-containing and unsaturated carbon-carbon groups). For this adhesion joint, mixtures of SKF-26 with quinone ether, SKF-26 rubber with epoxide resin ED-20, and SKF-26 rubber with SKI-NL rubber were made on a roll mill. After thermal treatment, the mixture of SKI-NL rubber became soluble, the mixture of epoxy resin was transformed to a gel in solution, and the mixture of quinone ether swelled in dimethylformamide. Therefore, a network in the interface region of this adhesion joint can be formed by the chemical reaction of the substrate rubber with components of the adhesive-epoxy resin and quinone ether.

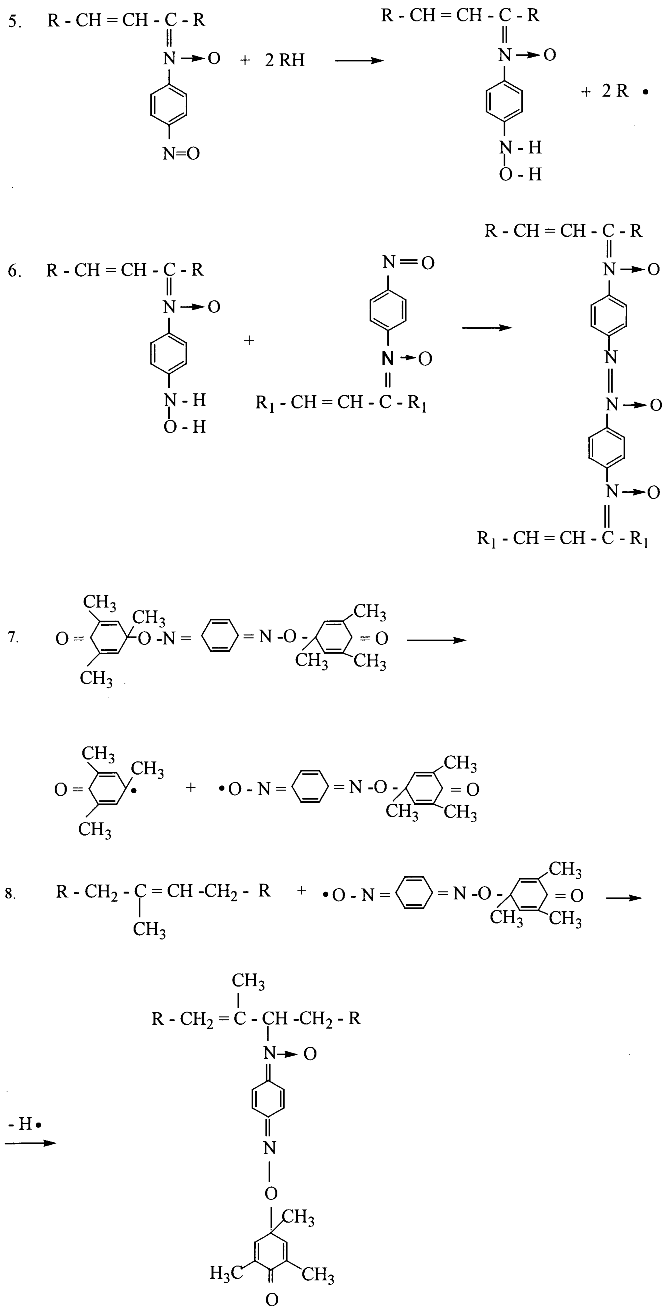
The course of the reaction of rubbers and epoxy resin has been discussed in Klyachkin et al. [3]. The chemical reaction of epoxy groups of resin with oxygen-containing groups of environmentally-degraded rubber has been observed.

The interaction of quinone ether with rubbers is more complicated and involves three courses of the reaction. The most probable interaction of quinone ether with rubbers goes by unsaturated carbon-carbon bonds [7, 8] and is followed by the formation of 2,4,6-trimethylphenol groups **1** and subsequent formation of interchain bonds **2**. The products of reaction can react with epoxy groups of the adhesive **3**. Next is the interaction by the radical mechanism **4**, **5** and **6**. The third is as described by formula **7** and **8** (see Scheme 1).

To define the course of reaction at the interface, the IR spectra of model mixtures of SKI-NL with EH-10, EPDM-40 with EH-10, and SKN-40M with EH-10 were recorded. The spectra of thermally-treated mixtures reflected the disintegration of quinone ether molecules. For example, the spectrum of the EPDM-40/EH-10 mixture



SCHEME 1



SCHEME 1 *(continued)*

after thermal treatment is compared with the spectrum of EH-10 in Figure 2. The presence of chemical reactions was revealed by observing the decrease in the intensity of the 1665 cm^{-1} peak interpreted as carbonyl group vibration, the 1645 cm^{-1} peak interpreted as amide group vibration, the 970 and 840 cm^{-1} peaks interpreted as nitrile group vibration, the 1610 and 1520 cm^{-1} peaks interpreted as aromatic ring vibrations, and the 1240 cm^{-1} peak interpreted as N-O vibration. The same changes were observed in the spectra of other mixtures and in the spectra of the cured adhesive. These changes accord with the first type of quinone ether reaction. The peaks for N=N vibrations were not observed, and the peaks for aromatic ring resonance were not kept (if these peaks were unchanged, then this situation would correspond to the second and

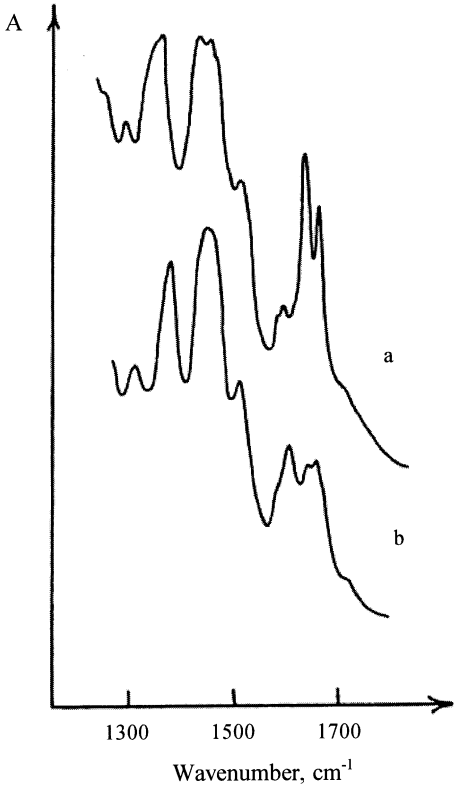


FIGURE 2 IR spectra of initial EH-10 quinone ether in Nujol (a) and IR spectra of the model mixture of EPDM-40 rubber and EH-10 quinone ether after thermal treatment (b).

third types of reactions). The IR spectra of fluorinated rubber with quinone ether did not show similar changes corresponding to the chemical reaction.

The analysis of the chemical interaction of the adhesive with fluorinated rubber was made by IR ATR spectra for the destroyed adhesion joint (Figure 3). For the smooth substrate, in the spectra of the rubber side the weak peaks at 1615 and 1520 cm^{-1} for the aromatic ring of conjugated quinone ether were observed. For the

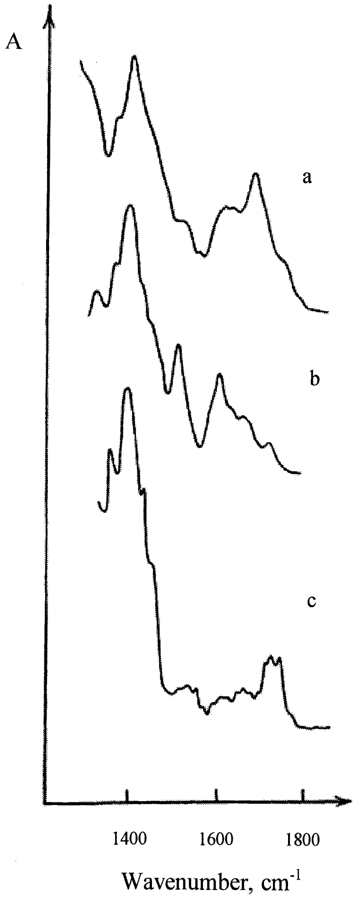


FIGURE 3 IR ATR spectra of the surface of the destroyed adhesion joint. Substrate is SKF-26 rubber: (a) substrate was not roughened before joint formation; (b) substrate was roughened before joint formation; (c) initial SKF-26 substrate surface.

roughened substrate, spectral peaks at 1615 and 1520 cm^{-1} with higher intensity were observed. This phenomenon, related to the destruction processes encountered in roughening, can lead to the formation of unsaturated groups in the surface layer of the substrate. The obtained groups can react with the active groups of quinone ether according to the first type of reaction. However, in the spectra there are no peaks of the SKI-NL rubber-like adhesive, which corresponds to the destructive loss of adhesion. Thus, the interchain links of the network of adhesive and substrate are formed by the chemical reaction of quinone ether and active groups of the substrate, yet the concentration of these links is not sufficient for good adhesion. This fact explains the low adhesion strength of the third and fourth joints.

CONCLUSION

The obtained results allow us to conclude that quinone ether can react with active groups of the substrate in the interface region of adhesion joints with ethylene-propylene, butadiene-nitrile, and fluorinated rubbers. In the adhesion joint with fluorinated rubber, good adhesion is achieved by increasing the concentration of unsaturated groups in the substrate surface layer, for example by roughening the substrate surface before the formation of joints.

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