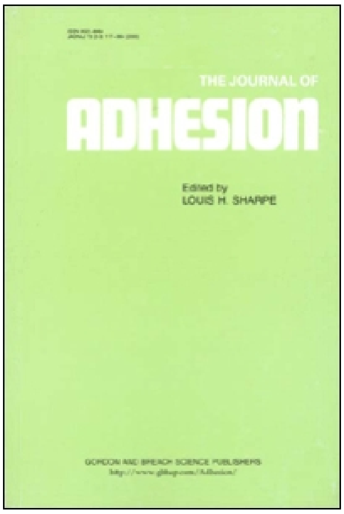


The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Adhesion Studies on Piperylene-Styrene Copolymer Modified Polychloroprene Adhesive: Phase Morphology and Surface Composition

Kristina Žukienė[a]; Virginija Jankauskaitė[a]; Kazys Vytautas Mickus[a]
[a] Department of Clothing and Polymer Products Technology, Kaunas University of Technology, Kaunas, Lithuania

To cite this Article Žukienė, Kristina , Jankauskaitė, Virginija and Mickus, Kazys Vytautas(2008) 'Adhesion Studies on Piperylene-Styrene Copolymer Modified Polychloroprene Adhesive: Phase Morphology and Surface Composition', The Journal of Adhesion, 84: 7, 601 — 618

To link to this Article: DOI: 10.1080/00218460802255491

URL: http://dx.doi.org/10.1080/00218460802255491

The Journal of Adhesion, 84:601–618, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 0021-8464 print/1545-5823 online
DOI: 10.1080/00218460802255491

Taylor & Francis
Taylor & Francis Group

Adhesion Studies on Piperylene-Styrene Copolymer Modified Polychloroprene Adhesive: Phase Morphology and Surface Composition

Kristina Žukienė, Virginija Jankauskaitė,
and Kazys Vytautas Mickus
Department of Clothing and Polymer Products Technology, Kaunas
University of Technology, Kaunas, Lithuania

The effect of piperylene-styrene copolymer (PSC) content on the bulk and surface properties of polychloroprene (CR) adhesive was investigated by different methods. Addition of PSC improves adhesion and strength properties of CR. PSC slightly deteriorates thermal stability of CR. X-ray diffraction, UV, and IR spectroscopies studies showed that no chemical interaction between CR and PSC phases occurs. Distinct bulk and surface structure of modified adhesive is caused by the high surface energy difference between CR and PSC phases. By AFM force-distance curve measurements it was deduced that the differences between pull-off force values of modified CR film surfaces in contact with air and backing was related to the enrichment of the higher surface energy component at the backing/film interface. The properties and structure of boundary layers of adhesive modified by high surface energy polymeric additive are essential for the adhesion behavior.

Keywords: Adhesion; Morphology; Piperylene-styrene copolymer; Polychloroprene adhesive; Surface properties

INTRODUCTION

Rubber-based adhesives systems, also called elastomeric adhesive systems, offer the greatest variety of properties of any generic class of adhesives. These systems typically offer higher adhesion, shear, and flexibility properties in comparison with other adhesive systems [1]. The elastomer provides the backbone of the adhesive; therefore, the main performance of the adhesive is provided by the rubber

Received 18 January 2008; in final form 10 April 2008.

Address correspondence to Kristina Žukienė, Department of Clothing and Polymer Products Technology, Kaunas University of Technology, Studentu 56, LT-51424 Kaunas, Lithuania. E-mail: kristina.zukiene@ktu.lt

properties. Several elastomers can be used in rubber-based adhesives and one of them is polychloroprene [1].

Chloroprene rubber (CR), also known as Neoprene, is a chlorine-containing elastomer. Over 30 different types of CR are manufactured. It provides a very useful all-round balance of properties: good mechanical strength; high ozone, ageing, and weather resistance; low flammability; good resistance towards chemicals; high adhesion to many substrates, which have led to CR use for general purposes; and also as a raw material for adhesives.

CR-based adhesives enjoy a pre-eminent position as elastomeric binders. The immediate strength of CR films from solvent solutions, their tack, and autoadhesion lead to a strong dominance of rubber-based adhesive systems. CR adhesive exhibits excellent adhesion to many substrates including rubber, glass, plastics, and painted metals. These properties have promoted adhesive use in the shoe, furniture, automotive, and construction industries [1,2].

It is common to incorporate modifying additives (tackifiers, plasticizers, reinforcing resins, fillers) in CR adhesive formulations for the enhancing of properties. The chemical and physical properties of elastomeric adhesives can be improved by modifying rubbers *via* grafting and blending. Extensive investigations have been performed on modification of CR by graft polymerization of different acrylate monomers: methyl methacrylate, cyclohexyl methacrylate, n-butyl methacrylate, and butyl acrylate [3–6]. The obtained graft copolymers show higher permeability to different hydrous solutes, and higher mechanical and adhesion properties.

In order to improve its performance properties, CR can be blended with rubbers or other polymeric materials [7–12]. The incorporation of polybutadiene rubber (BR) improves CR low temperature properties, abrasion resistance, and heat ageing characteristics [8]. Blends of CR and styrene butadiene rubber (SBR) show higher crystallization resistance, lower brittleness temperature, and higher resistance to sunlight discoloration [9]. Blends of CR/BR/SBR are characterized by higher mechanical properties [10]. In order to improve thermal properties it is imperative to blend CR with polyethylene vinyl acetate [11], while thermal conductivity can be improved by blending with polyaniline [12].

Styrene derivatives can be used in CR compositions as adhesion promoters. The properties of CR adhesive modified by styrene derivatives are described in [13]. It was shown that poly-α-methylstyrene resin improves the adhesion properties of CR adhesive to a wide variety of thermoplastic rubbers. The influence of styrene derivatives on CR adhesive properties has also been examined in [14–17]. It was shown that piperylene-styrene copolymer (PSC) blended with CR leads to the improvement of the adhesion, mechanical, and rheological properties.

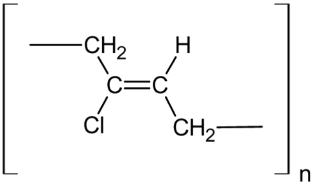
However, neither morphology nor the detailed phase structure of modified CR have been reported. The aim of the present work is to get a deeper insight into the morphology and phase structure of PSC-modified CR by IR spectroscopy, X-ray diffraction, UV absorption spectra, thermal analysis (T_g and DTA), and AFM, providing a correlation between the adhesion properties and structure of the modified adhesive films.

EXPERIMENTAL

Materials

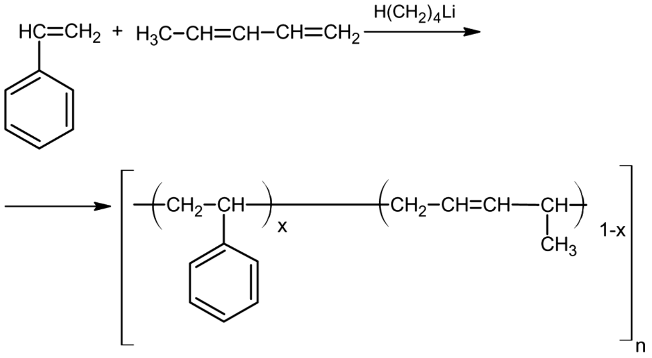
Polychloroprene, named Baypren 330, was manufactured by Bayer AG (Leverkusen, Germany) with a molecular weight of $M_w = 300{,}000$ and glass transition temperature of $T_g = -45°C$. Baypren 330 is a mercaptan-modified chloroprene elastomer. It is rapidly crystallizing polymer for contact adhesives formulations, with rapid strength development.

Polychloroprene is prepared by free radical initiated emulsion polymerization of 2-chloro-1,3-butadiene, which is obtained by the chlorination of butadiene or isoprene. The high amount of 1,4-trans units in the polymer (about 90%) leads to the polychloroprene adhesive, which has a high degree of crystallinity:



1,4 – trans polychloroprene

Piperylene-styrene copolymer was obtained from the Institute of Physical Organic Chemistry (Minsk, Belarus). The copolymer was synthesized by radical polymerization [14]:



The PSC molecular weight is $M_w = 35{,}000$ and its glass transition temperature is $T_g = 55°C$. The IR spectrum of the copolymer film shows a double bond is found in position 2,3 of the piperylene chains. However, in some chains it is possible to find a double bond in positions 1,2 or 3,4.

The nature of reactants, their stoichiometry, and copolymerization conditions determine PSC structure and its ultimate properties. PSC exhibits excellent compatibility with a variety of polymers, plasticizers, and oligomeric resins. It can be fully dissolved in aromatic and chlorinated hydrocarbons.

Preparation of Adhesive Films

CR and PSC were prepared by dissolving each polymer in a 2:1 mixture (by volume) of ethyl acetate (Penta, Prague, Czech Republic) and *n*-hexane (OBR PR, Plock, Poland) in a laboratory mixer EURO-ST P CV (Ika-Werke GMBH & Co., Staufen, Germany) (150 rpm for 4 h) by mixing the homopolymer solutions in the noted proportions. The solid content of both solutions was 20 wt. %. The homogeneous polymer mixture was obtained by stirring at 20 ± 2°C for 300 s.

Polymer films for mechanical and AFM testing were prepared by solution casting on an inert Teflon® panel (backing) and dried for more than 72 h. The residual solvent from the polymer films was evaporated under mechanically created vacuum in a vacuum chamber SPT-2000 (Unitra Inc., Stafford, Texas, USA) at 50°C for 4 h by weighing of samples up to constant weight. The thickness of the dried films was 0.3–0.4 mm.

Peel Strength Measurements

The adhesion properties of modified CR adhesive were determined using a T-peel test (LST EN 1392)* on joints of the styrene-butadiene-styrene thermoplastic rubbers [Raplan 2899 NL/1 Grigio 4599 (TR1) and Raplan 3296 NLE Bianko 125 (TR2) (API S.p.A. Mussolente, Italy)] and canvas (dimension of strips was 100 × 30 mm) using a universal testing machine H25KT (Tinius Olsen, Redhill, England) with a load cell of 5 kN capacity at a cross-head speed of 100 ± 10 mm/min. The rubber surface was roughened (in a scouring machine at 2800 rpm using an abrasive sheet with aluminum oxide

---

*LST EN 1392 is the Lithuanian version of standard EN 1392 "*Adhesives for leather and footwear materials–Solvent-based and dispersion adhesives–Test methods for measuring the bond strength under specified conditions*."

grains of size 60) to remove the surface layer. The adhesive was applied by a brush. It was coated the surfaces of on twice both rubber and canva strips and allowed to dry for 30 and 60 min, respectively. An adhesive layer of 0.25 ± 0.05 mm thickness was obtained. The dry adhesive film was heat reactivated at 85 ± 5°C under IR radiation. The rubber and canvas specimens were immediately placed into contact and a pressure of 0.4 MPa was applied for 30 s to achieve suitable bond strength. Afterwards, the TR/canvas joints were kept at 20 ± 2°C for 24 h before the T-peel test was carried out. All reported values are averages of results for at least six specimens.

Mechanical Properties

The mechanical properties of the adhesive films were obtained from a uniaxial tensile test using a universal testing machine, H25KT, with a load cell of 5 kN capacity (Tinius Olsen, Redhill, England). A cross-head speed of 100 mm/min was used for this study. A dumb-bell specimen was used to determine the tensile stress–strain properties. Measurements were performed at room temperature with specimens having a gage area of 10 × 10 mm and a thickness of 0.3 ± 0.05 mm. The tensile strength at break, elongation at break, and Young's modulus were determined from the load–displacement curves. Six film specimens were tested for each set of samples and the mean values were calculated.

AFM Measurements

The adhesive film surface properties in contact with air and backing were measured by an atomic force microscope NT–206 (Microtest-machines Co., Gomel, Belarus) and scanning probe microcopy (SPM) processing software *SurfaceView*.

A V-shaped Si cantilever with a spring constant of 0.35 N/m was used in contact mode in the AFM. The cantilever was 200 μm long, 40 μm wide, and 1.0 μm thick. The tip curvature radius was 10.0 nm and cone angle was 20° (values provided by MicroMash, San Jose, CA, USA). A sample area of 12 × 16 μm was scanned. The measurements were performed in air at room temperature.

All measurements were performed with the instrument mounted in a vibration isolation system. Adhesion forces were determined from force-distance (loading-unloading) curves. A force-distance curve was obtained by the monitoring of the vertical displacement of either the cantilever probe or the sample. In the present case the sample is fixed to the piezoelectric ceramic that monitors the cyclic vertical displacement. Since the cantilever stiffness is markedly lower than that of the sample, the cantilever deflection is almost equal to the vertical piezoelectric displacement. Therefore, the pull-off force is proportional to the vertical piezoelectric displacement required to unstick the tip from the surface. The pull-off force is given by:

$$F_{adh} = k_{tip} \Delta z_p, \tag{1}$$

where k_{tip} is the cantilever stiffness and Δz_p is the magnitude of the vertical displacement to unstick the tip.

Blend Structure Characterization

X-ray diffraction was performed on a DRON-3 diffractometer (Bourevestnik, Saint Petersburg, Russia) using Cu K_α radiation.

Differential thermal analysis (DTA) and thermogravimetry (TG) were carried out using the Paulic-Paulic-Erday system derivatograph Mod. 1500 (MOM, Budapest, Hungary) in an air atmosphere at temperatures up to 300°C and at a heating rate of 2.5°C/min. The mass of each sample was 0.1 g.

Infrared spectra were obtained in transmission on an IR spectrometer, Model 983 (Perkin Elmer, Waltham, Mass., USA), at ambient temperature and reported as wave numbers.

Ultraviolet absorption spectra of 2% polymer solutions in chloroform were recorded at ambient temperature with a DU650 UV spectrophotometer (Beckman Coulter, Inc., Fullerton, CA, USA) over the range of 200–300 nm.

RESULTS AND DISCUSSION

Adhesion Studies

It has been determined that PSC shows high adhesion and mechanical properties, which depend on the ratio of piperylene to styrene [14]. Increasing amounts of styrene improve adhesion properties of the copolymer. As can be seen from Figure 1, the maximal peel strength is achieved at 70 wt. % of styrene (11.8 kN/m). In this case, the loci of failure of the adhesive joints, determined by visual inspection of the debonded rubber test samples, were cohesive in the TR1. However, the joints produced with higher styrene content (80 wt. %) exhibit cohesive failure of the adhesive and a decrease in peel strength that

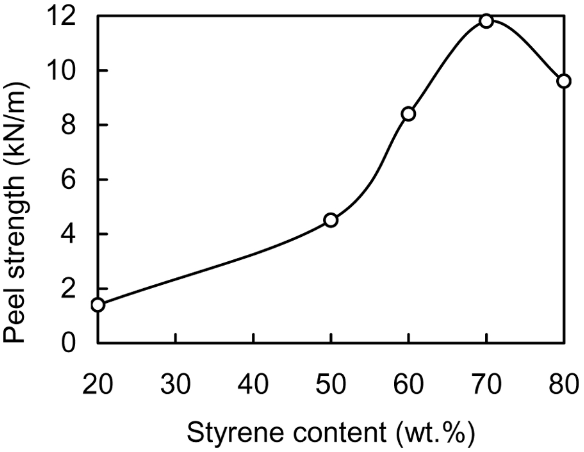


FIGURE 1 Effect of styrene content on the peel strength of TR to canvas joints.

can be attributed to the decrease in chain flexibility. Therefore, the increase of styrene content in the copolymer reduces the plasticity of the copolymer films. Brittleness of the PSC-based adhesive limits its use for the bonding of elastomers in dynamic applications [14].

The low surface energy of TR rubber is responsible for poor adhesion; therefore, a surface halogenation treatment is needed. However, it was found [14] that addition of PSC with high styrene content (70wt. %) makes unfilled CR compositions suitable for TR bonding without a surface treatment procedure. Figure 2 shows the peel strength of TR and canvas joints as a function of PSC (70 wt. % of styrene) content in CR adhesive compositions. The peel strength increasess by more than a factor of two when 25 or 30 wt. % of PSC is added. Cohesive failure is characteristic for these joints.

The mechanical properties of the adhesive varied widely depending on PSC content (Table 1). Young's modulus increases from 28 MPa up to 72 MPa as the PSC content increases. The tensile strength of adhesive films does not change up to 25 wt. % of PSC. However, further increase of PSC content up to 40 wt. % decreases the tensile strength of CR films (from 17.5 MPa down to 11.0 MPa). In this case, the elongation at break decreases from 600% down to 200%. This is related to the lower mechanical strength of the copolymer compared with that of CR (Table 1). Therefore, further investigations were performed with the adhesive composition of CR/PSC 75/25 wt. %, which shows high adhesion and mechanical properties.

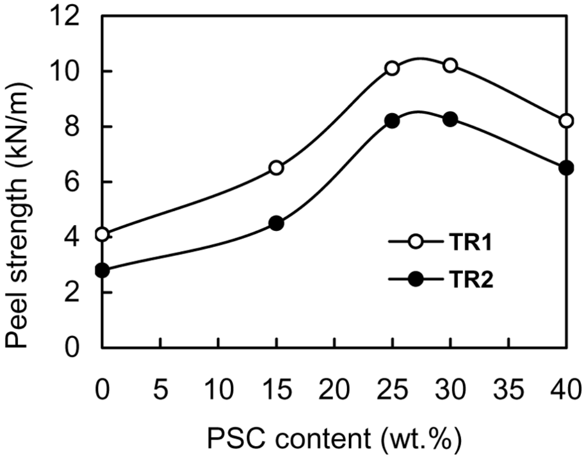


FIGURE 2 Effect of PSC (70 wt. % of styrene) content on the peel strength for TR to canvas joints. Reprinted from Žukienė, K. and Jankauskaitė, V., *J. Adhesion Science and Technology* **19** (No. 8), p. 633 (2005), with permission of the publisher, Koninklijke Brill NV.

Structural Characterization of Adhesive

The influence of PSC on the thermal characteristics of CR was investigated by DTA and TG methods. TG curves for CR, PSC homopolymer, and their 75/25 wt. % blend are presented in Figure 3. The thermal degradation of the materials was investigated up to 300°C. It can be seen that degradation of CR occurs at 180°C with weight being gradually lost, which is closely related to the reported value for that type of rubber [18,19]. CR degradation occurs predominantly in a two stage process: it starts as early as 200°C with the loss of HCl, whilst the second stage of degradation, which occurs in the range

TABLE 1 Mechanical Properties of CR and PSC (70 wt. % of Styrene) and its blend

			CR/PSC, wt. %			
Properties	PSC	CR	85/15	75/25	70/30	60/40
Tensile strength, MPa	8.6	17.5	17.5	17.0	14.5	11.0
Young's modulus, MPa	106	28	29	44	63	72
Elongation at break, %	10	600	530	350	250	200

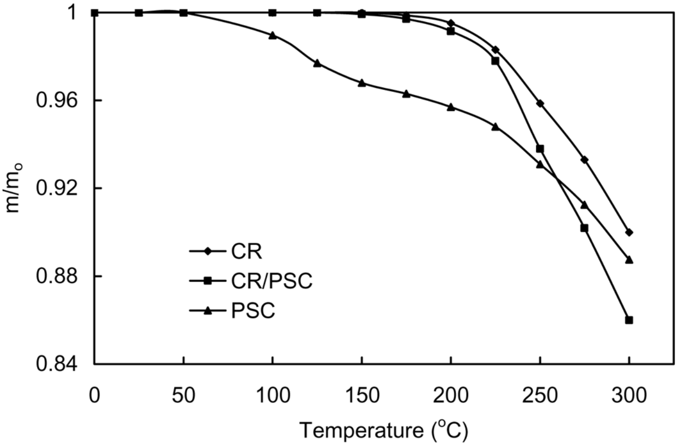


FIGURE 3 TG curves for CR, PSC, and CR/PSC 75/25 wt. % blend.

of 400–550°C, involves the production of volative hydrocarbons through chain scission [18].

The thermal degradation curve of PSC at the investigated temperature range is very similar to that of CR. Two weight loss steps can also be observed in this case. The first weight loss step (5%) at 80°C can be attributed to the evaporation of surface adsorbed water. The second one, at a temperature of 200°C, leads to a weight loss of about 15% and represents the degradation of copolymer.

As can be seen from Figure 3, the addition of PSC to CR slightly worsens its thermal stability. The initial degradation temperature of the adhesive decreases from 180°C down to 150°C, when 25 wt. % of PSC is added.

The DTA curves of CR, PSC homopolymers, and an adhesive composition of 75/25 wt. % CR/PSC are presented in Figure 4. They reveal the appearance of two peaks in all cases of the investigated materials—endothermic peaks at low temperature range and large exothermic peaks at temperatures higher than 200°C. Low temperature endothermic peaks can be assigned to the phase transition of the polymers, 40°C to the melting of crystalline phase of CR in the curves of CR and CR/PSC, while the peak at 63.0°C in the PSC curve can be assigned to the glass transition temperature of the copolymer.

The exothermic peaks in the DTA curves in the temperature range of 200–300°C are due to the decomposition of the investigated materials. A large exothermic peak at 287.2°C can be seen in the case of PSC, while the observed peak at 222.5°C of CR is in good agreement with

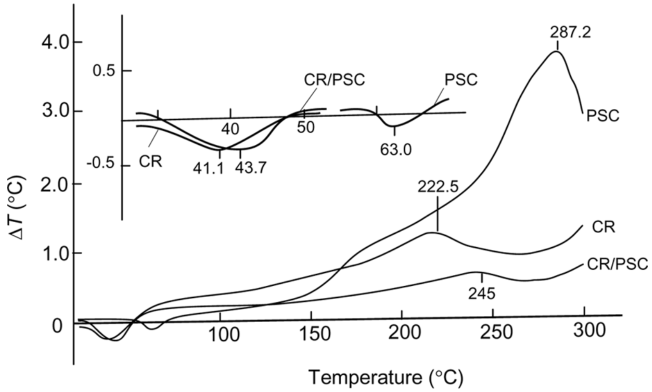


FIGURE 4 DTA thermograms of CR, PSC, and CR/PSC 75/25 wt. % blend.

the weight loss observed in the TG curve. The peak that is due to the decomposition of 75/25 wt. % CR/PSC is slightly shifted to higher temperature (up to 245.0°C). Thus, the addition of PSC increases the decomposition reaction temperature of the adhesive blend.

In order to examine the influence of PSC content on the structural characteristics of CR, X-ray diffraction studies have been performed. X-ray diffractograms in the range of diffraction angle $2\theta = 10.0$–40.0° for CR, PSC, and the adhesive composition of 75/25 wt. % CR/PSC are shown in Figure 5. A broad peak in the diffraction angle curves of PSC at $2\theta = 23.0^\circ$ is observed. For CR sharp peaks at $2\theta = 19.0^\circ$, 21.5°, and 25.0° were detected. As can be seen from Figure 5, the typical peaks of CR were detected in the adhesion composition of 75/25 wt. % CR/PSC. However, PSC does not change the intensities of peaks in the adhesive diffractograms. Thus, X-ray diffraction analysis reveals that the addition of PSC do not change the unit cell parameters (regularity of structure) of CR.

IR spectroscopy is a useful tool to elucidate possible interactions between polymers. IR spectra of CR, PSC, and the adhesive composition of 75/25 wt. % CR/PSC are presented in Figure 6. CR spectrum shows some of the characteristic features expected for polychloroprene, *i.e.*, C–H stretching band at 2900 cm^{-1}, C=C band at 1659 cm^{-1} [20]. The well established deformation vibrations $\delta(CH_2)$ give rise to absorption in the 1500–1400 cm^{-1} region. The C-Cl stretching region between 800 and 600 cm^{-1} is well known for its resonance specific to the configuration structures of trans-1,4-polychloroprene. Therefore, the strong band at 669 cm^{-1} observed in this spectrum can be attributed to C-Cl stretching.

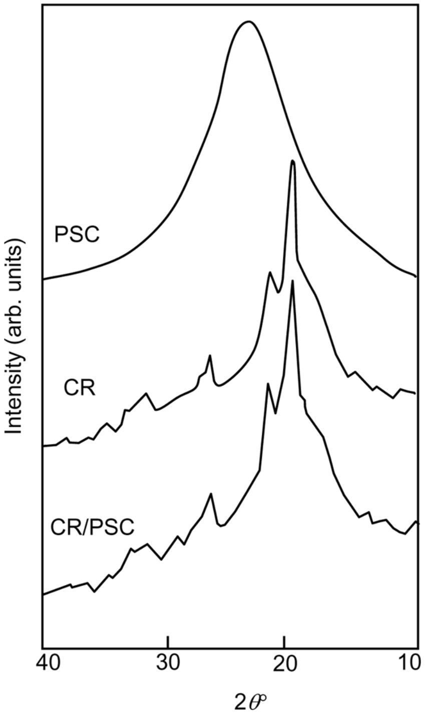


FIGURE 5 X-ray diffraction diagrams of CR, PSC, and CR/PSC 75/25 wt. % blend.

The typical bands of the styrene units are detected in the PSC spectrum. A triplet at 3084, 3060, and 3024 cm^{-1} are due to the C-H stretching vibrations; bands at 1600, 1494, and 1452 cm^{-1} are due to the skeletal stretching modes of the semi-unsaturated C-C bonds; and strong bands at 752 and 700 cm^{-1}, produced by the out-of plane C-H bending vibrations of the hydrogen atoms remaining on the aromatic ring, are observed.

The spectrum of PSC-modified CR adhesive film still has the characteristic absorbance peaks of CR and PSC.

UV spectroscopy was used to study the interaction between modified adhesive components. From the UV absorption spectrums, displayed in Figure 7, it can be observed that PSC shows a strong absorption of radiation between 250 and 269 nm due to the presence of styrene units. The absorption spectrum of CR exhibits the absorption band at 238 nm. Decreased in intensity absorption peaks of

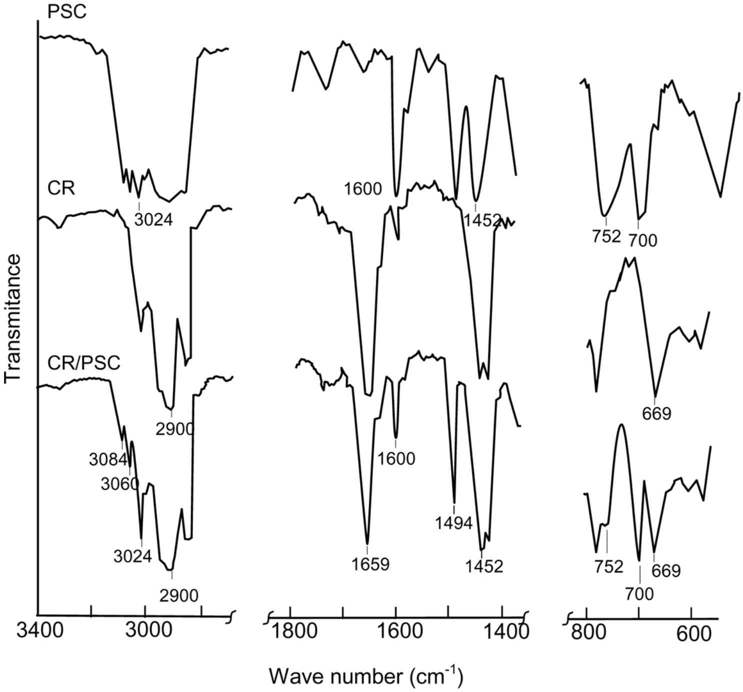


FIGURE 6 IR spectra of CR, PSC, and CR/PSC 75/25 wt. % blend.

PSC-modified adhesive are located at 238 nm, 270 nm, and 269.5 nm and correspond to the homopolymers.

Thus, the blending of PSC and CR does not cause chemical changes in the composition and only physical blends of CR/PSC are formed. It can be supposed that changes of adhesion properties of PSC-modified CR can be related to the surface morphology.

Surface Analysis

Polymer blends usually exhibit different bulk morphology compared with that of the surface due to the tendency for one of the homopolymers to be enriched at the surface in preference to the other. In general, the component with lower surface free energy is enriched at the surface in order to minimize polymer–air surface energy [21]. The driving force for the surface enrichment process may be incompatibility, molecular weight, bulk composition, and surface energy difference of blend components.

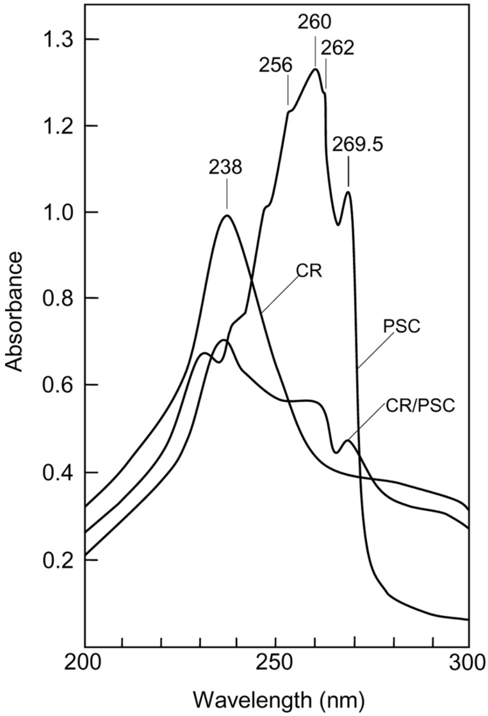


FIGURE 7 UV spectra of CR, PSC, and CR/PSC 75/25 wt. % blend.

The surface free energy of adhesive components can be estimated theoretically from the relationship between the surface energy and the parachor:

$$\gamma = \left(\frac{P}{V}\right)^4, \tag{2}$$

where γ is the surface tension, V is the molar volume, and P is the Sugden Parachor for a repeating unit, the values of which are listed by Van Krevelen in [22]. The group contributions of CR and PSC to molar volume and parachor are presented in Table 2.

From the surface energy data estimated from Eq. (2) it is evident that the γ of CR is lower than that of PSC, *i.e.*, 38.9 mN/m and 42.5 mN/m, respectively. It may be supposed that high differences in surface free energy values between CR and PSC will favor surface enrichment by the lower surface energy component.

In previous studies [23,24] AFM topographical and compositional mapping and further mathematical roughness analysis showed that

TABLE 2 The Group Contributions of CR and PSC to Molar Volume and Parachor [22]

Polymer	Group	Number of group	V (cm^2/mol)	P ((cm^3/mol) $\times$ (mJ/m^2)$^{1/4}$)
CR	Cl	1	20.0	54.3
	$-CH_2-$	2	34.0	78.0
	C	1	8.0	16.4
	$=CH-$	1	13.0	33.5
	Σ		75.0	182.2
PSC	$-CH_2-$	2	20.5	78.0
	$-CH<$	2	13.5	43.8
	$-CH_3$	1	13.7	56.1
	$=CH-$	2	16.9	33.5
	$-C_6H_5$	1	45.8	190.0
	Σ		110.5	434.9

PSC-modified CR adhesive films have a segregated surface structure. The changes of relative homopolymer proportion in this adhesive composition changes the surface morphology. The adhesive containing 15 wt. % of PSC has a two-phase structure, when PSC forms dispersive phase domains distributed in the CR matrix. In the case of 25 wt. % or higher PSC content the top and bottom of CR/PSC films have different structures, because CR enriches the top of film, while PSC is located at the bottom [23]. It was supposed that the increase in the adhesion strength of TR joints is related to the increase of compatibility between the TR and the modified adhesive due to the bottom layer enrichment by PSC [15,23,24].

Further AFM investigations were performed to prove this proposition. The compositional changes in the surface structure can be deduced by measuring the interaction (adhesion) forces between the AFM tip and the polymer surface, which contains chemical and viscoelastic information about the sample, by monitoring the pull-on and pull-off forces from the force-distance curves. The obtained pull-off force, *i.e.*, the force required to return the tip to its equilibrium position, provides information on the interaction forces, resulting from the long-and short-range force of molecular interactions [25–28].

The force-distance curves for CR and PSC films cast on a Teflon panel (backing) are shown in Figure 8. It is clear that PSC leads to the higher tip-sample interaction of both pull-on and pull-off forces than CR. Regardless of whether the tip was positioned—on the top or on the bottom of the homopolymer films—the same value of tip-sample pull-off forces were observed. The average of the adhesion pull-off forces are 12.8 and 21.1 nN for CR and PSC films, respectively (Figure 8).

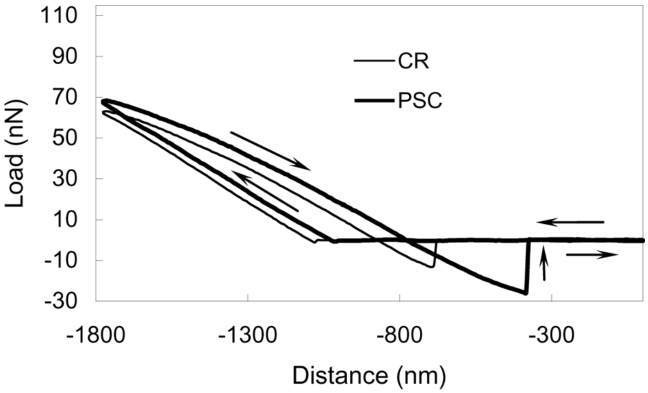


FIGURE 8 Force-distance curves obtained on the top of CR and PSC films.

It can be noted that for these measurements the manufacturer's value for the cantilever spring constant was assumed. While it may not be entirely accurate, the relative values of the measured adhesion forces must be correct since all measurements were taken with the same cantilever. Besides, the reproducibility of the changes in the adhesion forces was determined by measuring a number of force-distance curves at different locations.

Using the same tip and experimental conditions, force–distance curves were determined for CR adhesive films modified by various contents of PSC. Figure 9 shows average values of the pull-off force for the adhesive film of top and bottom. As was mentioned previously [17,23,24], the existence of two-phase structure with different surface properties independently of the film side was observed in a adhesive composition with 15 wt. % of PSC. The notable differences in obtained

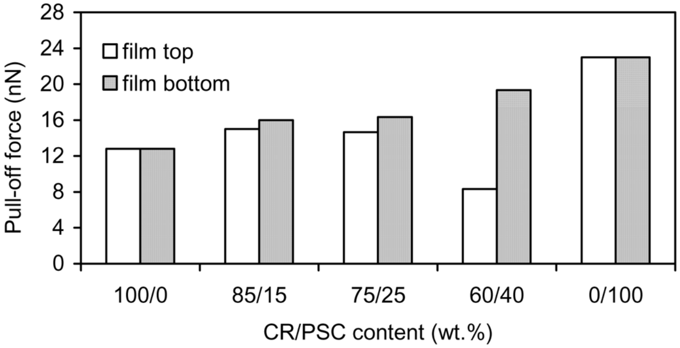


FIGURE 9 Dependence of pull-off force on the adhesive composition.

pull-off force values can be determined in different regimes. It was observed that some pull-off forces have a value of approximately 12 nN, while the other is significantly higher—about 20 nN. The different pull-off force values are characteristic of those of CR and PSC regions. Therefore, it can be supposed that two different pull-off force values correspond to the two-phase structure of the compositions.

Up to 25 wt. % of PSC, the pull-off force values on the film top and bottom are similar. However, a significant difference between the pull-off force values was obtained on the top and bottom of 40 wt. % PSC-modified CR film (Figure 9). The average pull-off force on the top of film is 8.3 nN, while on the bottom it is markedly higher—19.3 nN. It was found that the average pull-off force of the adhesive film top is very close to that of CR, while on the film bottom its value is very close to that of PSC. This is in good agreement with our previous observations [17,23,24], where it was proposed that the top of adhesive films with higher that 25 wt. % copolymer content exhibit the same surface structure as CR film, while the bottom was the same as PSC.

The obtained data allow us to confirm that the modification of CR adhesive by PSC causes the increase of adhesion strength of TR joints due to the increase of compatibility between TR and adhesive film. During the adhesive drying and film forming, CR enriches the film surface, simultaneously increasing PSC concentration at the film bottom (Figure 10). It may be supposed that PSC acts as a primer and intensifies the PCP adhesive film interaction at the interface with rubber.

Therefore, in a further investigation an attempt to use PSC as a primer for bonding TR with unmodified CR was made. In this case, a PSC layer was first formed on the TR surface and after drying it a CR layer was applied. Meanwhile, on the canvas strips two layers of CR were applied. It was found that such TR and canvas joints also show enhanced adhesion properties (Figure 11). As can be seen, the peel strength of TR/canvas joints increases by 20–40% compared with that obtained with only unmodified CR adhesive.

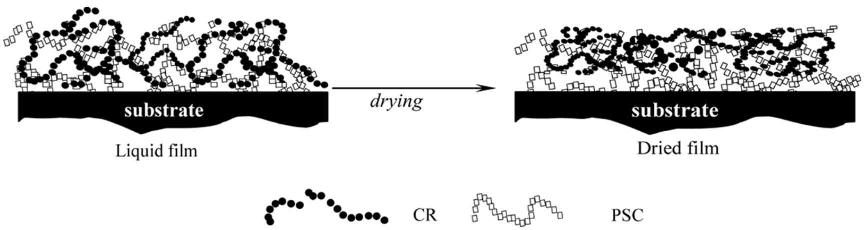


FIGURE 10 Scheme of modified adhesive film formation on TR surface.

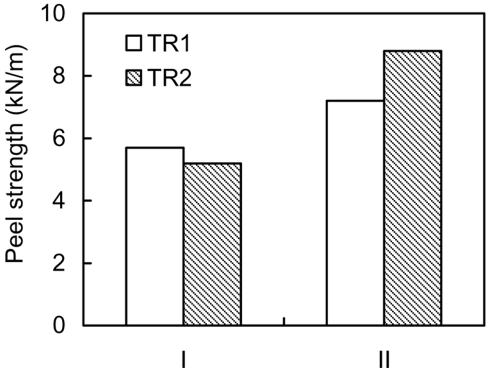


FIGURE 11 Dependence of peel strength for TR to canvas joints on the adhesive layer on TR surface formation method: I–two layers of CR, II–first layer of PSC, second layer of CR.

Thus, the properties and structure of boundary layers of adhesive modified by high surface energy polymeric additives are essential for the adhesion behavior.

CONCLUSIONS

The high adhesion properties of CR adhesive to thermoplastic rubber (TR) can be achieved by modifying it *via* blending with PSC. Addition of 25–30 wt. % of PSC in a CR composition results in the improvement of the mechanical and adhesion properties of the adhesive. However, IR and UV spectroscopies and X-ray diffraction studies do not show chemical changes in the modified CR composition. The adhesion behavior of PSC-modified adhesive greatly depends on the surface morphology.

The surface structure of PSC-modified CR adhesive is different from that of the bulk due to the tendency for one of the homopolymers to be enriched at the surface in preference to the other. The surface free energy difference between CR and PSC is suggested as one of the possible reasons for the segregated surface structure of a CR/PSC blend. AFM pull-off force values on 60/40 wt. % CR/PSC adhesive film top and bottom surfaces are similar to those of the homopolymers, *i.e.*, pull-off force values on the top of the adhesive film are close to that for CR film, while on the bottom are close to that for PSC. This indicates enhancement of PSC content at the interface of the adhesive film and the thermoplastic rubber surface.

REFERENCES

[1] Adams, R. D., (Ed.) *Adhesive Bonding: Science, Technology and Applications*, (Woodhead Publishing Limited, Cambridge, 2005), Ch. 18.3, pp. 433–436.

[2] Packham, D. E., *Handbook of Adhesion*, (John Wiley & Sons, Chichester, England, 2005), 2nd ed, pp. 430–438.

[3] Itoyama, K., Dohi, M., and Ichikawa, K., *J. Adhes. Soc. Jpn.* **20**, 34–41 (1984).

[4] Srinivasan, K. S. V., Radhakrishnan, N., and Kuttalam Pillai, M., *J. Appl. Polym. Sci.* **37**, 1551–1558 (1989).

[5] Chun, X., *J. Appl. Polym. Sci.* **64**, 1733–1737 (1997).

[6] Ahmed, S., Radhakrishnan, N., Srinivasan, K. S. V., and Sanjeevi, R. *Adv. Polym. Technol.* **23**, 103–110 (2004).

[7] Gorelova, M. M., Pertsin, A. J. I., Volkov, O., Filimonova, V., and Obolonkova, E. S., *J. Appl. Polym. Sci.* **60**, 363–370 (1996).

[8] Menon, A. R. R. and Viskonte, L. L. Y., *J. Appl. Polym. Sci.* **102**, 3195–3200 (2006).

[9] Das, A. and Basu, D. K., *J. Appl. Polym. Sci.* **96**, 1492–1504 (2005).

[10] Mingyi, L., Hua, Z., and Jianfeng, L., *J. Appl. Polym. Sci.* **71**, 215–220 (1999).

[11] Kundu, P. P., Choudhury, R. N. P., and Tripathy, D. K., *J. Appl. Polym. Sci.* **71**, 551–556 (1999).

[12] Pinho, M. S., Gorelova, M. M., Dezzoti, M., Soares, B. G., and Pertsin, A. J., *J. Appl. Polym. Sci.* **70**, 1543–1549 (1998).

[13] Piorkowski, C. E., *European Adhesives and Sealants* **1**, 22–23 (1988).

[14] Jankauskaitė, V. and Barkauskas, R., *Pigment & Resin Technology* **26**, 75–82 (1999).

[15] Žukienė, K. and Jankauskaitė, V., *J. Adhesion Sci. Technol.* **19**, 627–638 (2005).

[16] Barkauskas, R., Jankauskaitė, V., Mickus, K. V., and Žukienė, K., *Mater. Sci. (Medžiagotyra)* **3**, 22–27 (1999).

[17] Jankauskaitė, V., Žukienė, K., and Mickus, K. V., *Mater. Sci. (Medžiagotyra)* **11**, 239–247 (2005).

[18] Dick, C. M., Liggat, J. J., and Snape, C. E., *Polym. Degrad. Stab.* **74**, 397–405 (2001).

[19] Gardner, D. L. and McNeill, I. C., *Eur. Polym. J.* **7**, 569–591 (1971).

[20] Wallen, P. J., *Spectrochim. Acta, Part A: Mol. Spectrosc.* **47**, 1321–1326 (1991).

[21] Gabasi, F., Morra, M., and Occhiello, E., *Polymer Surfaces from Physics to Technology*, (John Wiley & Sons, New York, 1998) Ch. 8, pp. 289–313.

[22] Van Krevelen, D. W., *Properties of Polymers*, (Elsevier, New York, 1990), 3rd ed., Part VII, pp. 816–823.

[23] Žukienė, K., Jankauskaitė, V., and Petraitienė, S., *Appl. Surf. Sci.* **253**, 966–973 (2006).

[24] Jankauskaitė, V., Žukienė, K., and Petraitienė, S., *Polym. Eng. Sci.* **47**, 824–829 (2007).

[25] Paige, M. F., *Polymer* **44**, 6345–6352 (2003).

[26] Raghavan, D., Gu, X., Nguyen, T., VanLandingham, M., and Karim, A., *Macromolecules* **33**, 2573–2583 (2000).

[27] Raghavan, D., VanLandingham, M., Gu, X., and Nguyen, T., *Langmuir* **16**, 9448–9459 (2000).

[28] Kikkawa, Y., Suzuki, T., Tsuge, T., Kanesato, M., Doi, Y., and Abe, H., *Biomacromolecules* **7**, 1921–1928 (2006).