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Properties of pressure-sensitive adhesives based on styrene copolymers

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Pressure-sensitive adhesives (PSA) represent a specific kind of adhesives which are able to form adhesive joints practically solely owing to physical interaction between adhesive and adherent. PSA must possess apparently conflicting properties. As the formation of an adhesive joint necessitates perfect contact at the molecular level, the mobility of adhesive molecules has to be sufficiently high, i.e., the adhesive must possess adequate viscoelastic properties. On the other hand, it is valid in general that the cohesive strength of the joint decreases with diminishing viscosity of adhesive.

The perfect contact between adhesive and adherent is not only dependent on the viscoelastic properties of the adhesive but also on its ability to wet the surface of the adherent which is connected with interfacial tension at the boundary of the adhesive joint. It is therefore advisable for the adhesive to have the highest possible value of surface free energy.

While the used rubber or elastomeric copolymer has decisive influence on elastic properties of PSA, the low-molecular tackifier resins or tacky admixtures significantly influence the viscoelastic properties of PSA and its ability to wet the surface of adherent.

The block copolymers of elastomers with styrene, natural rubber, random polymer butadiene-styrene rubber, butyl rubber or polyacrylate are polymers most widely used as PSA [1–3].

Besides polymer, further components of PSA are tackifiers, softeners and stabilizer [4–6]. As for these admixtures, the utilization properties of PSA are significantly affected by tackifiers, which have decisive influence on its adhesive properties. A good tackifier resin must have the following basic properties. It must be sufficiently compatible with fundamental polymer and have very low molecular weight when compared with the used elastomer, and its glass transition point must be higher than that of the polymer used [7].

The majority of applied tackifiers have the glass transition point T_g in the temperature region between +30 °C and +60 °C. There are two fundamental groups of tackifier's resins that are most frequently used for the preparation of PSA, i.e., derivatives of colophony or aliphatic hydrocarbon resins.

In this study we used the PSA modified by colophony resins and derivatives (Union Camp Chemicals, England; Spolchemie, Czech Republic) as well as hydrogenated poly (cyclopentadiene) Escorez 530 D (Shell, USA).

The softeners differ from tackifiers, in particular, by the low value of their T_g. In this line we used polybutene oligomers (British Chemicals, England), polypropylene oligomers (Slovnaft, Slovak Republik).

Butadiene-styrene (BS) rubber Kralex 1507 (Kaučuk Kralupy, Czech Republic) and carboxylated butadiene-styrene rubber LBSK 70-48 (Zaklady Chemiczne, Poland) were used as base for PSA and statistical (styrene-2-ethyl hexyl acrylate) (St–EHA) copolymer containing 14 mass% of styrene (Synpo, Czech Republic) was used as a PSA modifier.

The adhesive mixtures were prepared in a mixer at 413 K. The mixture (100 g) was agitated for 30 min. The mechanical work of adhesion [8] was measured by peeling the adhesive joint at 90 ° angle on a universal testing machine Instron 4301 by means of an aluminum-peeling ring. The measurements were carried out at a cross head speed of 50 mm/min. The tack adhesion was measured on a prototype device by the Probetack method by which the tractive force perpendicular to the bonded joint necessary for its disconnection was measured. The adhesive joint was formed by short and light touch—0.2 s; 2 kPa.

The surface free energy of the polymers was measured by a goniometric method on a Contact Angle Meter Zeiss (Zeiss, Germany) by determining the contact angles of a set of testing liquids deposited on the polymeric surface or on the surface of the substrate. The interfacial tensions were calculated from the values of polar and dispersion component of surface free energy of the polymers [9, 10].

The results of measurement of adhesive properties of PSA on the base of BS copolymers are presented in Figs 1–5.

Fig. 1 represents the dependence of tack adhesion of BS copolymer (Kralex 1507) on content of oligomeric high-viscosity polybutene Hyvis 200. The tack adhesion of the mixture of BS copolymer with oligomer modifier increases with butene concentration from 5 to 75 kPa which corresponds to 20 mass% of oligomer in the mixture with BS copolymer. After reaching the maximum at the presence of 21 mass% of oligomer in the mixture its tack adhesion decreased with further increase of polybutene content because of decreasing cohesive strength of the BS copolymer/polybutene mixture.

The investigation of the relationship between tack adhesion and concentration of softeners in the mixture with BS copolymer (Fig. 2) led to equal conclusion. In these experiments naftenic oil, polypropylene oligomer and polybutene Napvis 3 were used as modifiers. The increase in tackiness with increasing

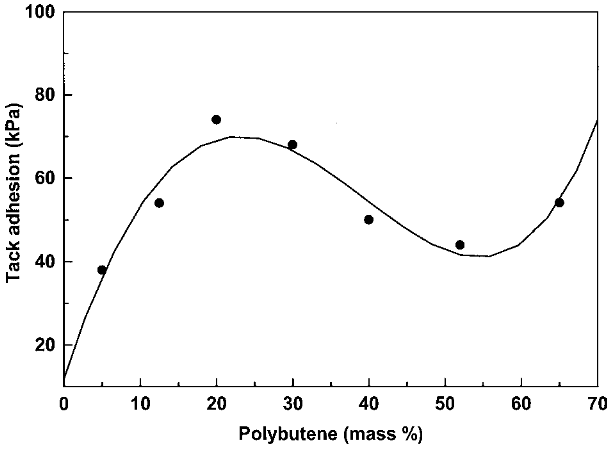

Figure 1 Variation of adhesion of BS rubber (Kralex 1507) with content of polybutene (Hyvis 200).

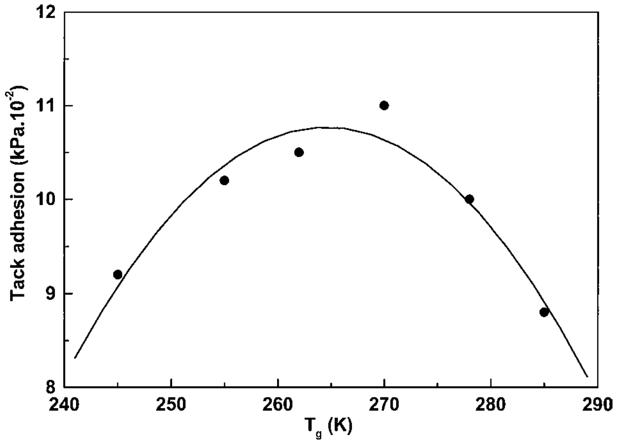

Figure 3 Tack adhesion of mixtures of the carboxylated BS rubber as a function of content of Abiester 100 modifying T_g of the mixture.

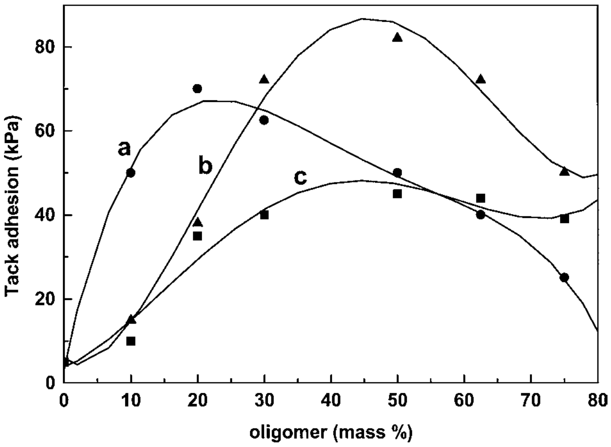

Figure 2 Variation of tack adhesion of BS rubber (Kralex 1507) with content of oligomer: (a) naphtenic oil, (b) Napvis 3, and (c) PP oil Z-800.

concentration of applied oligomers in mixtures with BS copolymer was found for all investigated agents. The highest value of tack adhesion (85 kPa) was obtained with 50 mass% of polybutene Napvis 3 and the lowest value of tack adhesion was attained with 50 mass% of polypropylene oligomer in the mixture. As for the mixture of BS copolymer and naphtenic oil, the maximum of tack adhesion (70 kPa) was obtained with 20 mass% of oligomer in the mixture.

In contrast to softeners, tackifiers exhibit high values of T_g and thus raise the temperature of the glass transition of the whole polymer mixture, which shifts into a convenient region.

Fig. 3 represents the dependence of tack adhesion on the glass transition temperature (T_g) for the mixture of carboxylated BS rubber and resin Abiester 100 based upon glycerol ester of abietic acid (glycerol triabietate). According to Fig. 3 the tack adhesion of the investigated mixtures increases with T_g from 245 K up to the maximum of tackiness at 270 K and afterwards the tack adhesion of the mixture of carboxylated BS modified by resin decreased with further increase in T_g. Impaired wetting of the surface of substrate causes a decrease in tack adhesion of the mixture of BS copolymer after reaching the maximum with PSA mixture in connection with increasing resin concentration. The carboxylated BS rubber exhibited compatibility with resin Abiester 100 in the whole investigated concentration range. The influence of other resins on tack adhesion of carboxylated BS copolymer is described in Fig. 3.

It is of great interest to investigate the long-term tack adhesion of BS rubber modified by different tackifiers in terms of their type and concentration (Fig. 4). The mixture of BS rubber with poly(cyclopentadiene) Escorez 530 D reached the highest stability of tack adhesion. Its value amounted to 95 kPa and did not practically vary in the course of 100 days. Tack admixtures on the base of esters of glycerol and abietic acid (Abiester 90) and natural colophony exhibited permanent decrease in tack adhesion. Its value fell from ca 80 to 60 kPa (Abiester 90) or 45 kPa (colophony) (Fig. 4).

The judgment on suitability for using different oligomer admixture in BS rubber to prepare PSA mixtures showing high tack adhesion necessitates knowledge of the interfacial tension which is formed between substrate surface and deposited PSA system. This interfacial tension characterizes the surface wettability of PSA substrate and is inversely proportional to tack adhesion of the PSA mixture. Fig. 5 depicts the decrease in interfacial tension due to concentration increase of ST–EHA oligomer mixed with BS rubber. The dependence of interfacial tension in the aluminum—PSA system

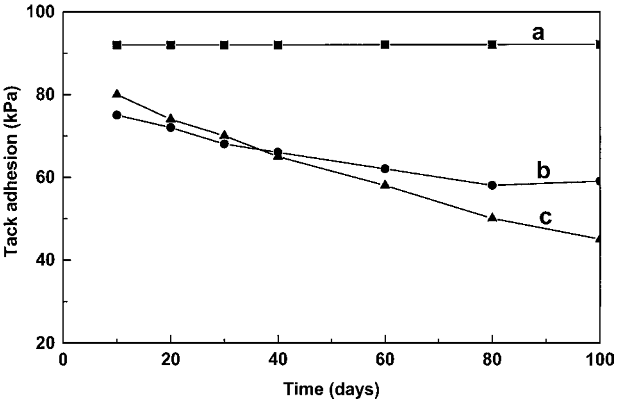

Figure 4 Dependence of long-term stability of tack adhesion of PSA on type of the applied tackifier: (a) Escorez 530 D, (b) colophony, and (c) Abiester 90.

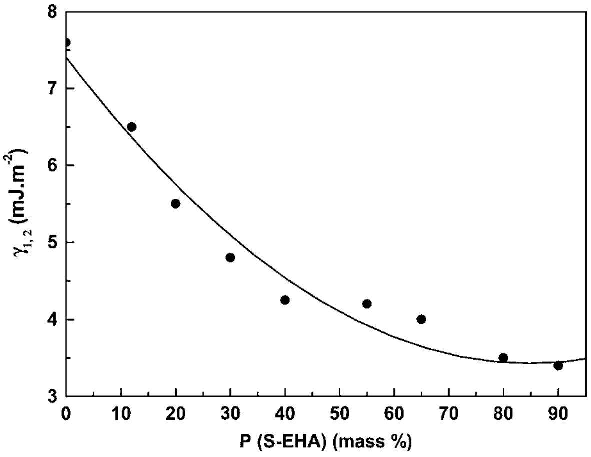

Figure 5 Interfacial tension between BS rubber modified by (St–EHA) copolymer and aluminum as a function of oligomer content in the mixture.

exponentially decreases with increasing concentration of polar oligomer in the mixture from 7.4 mJ · m^{-2} for additive-free BS rubber to 3.4 mJ · m^{-2} for PSA mixture containing 85 mass% of oligomer. As a result of the thermodynamic condition of high adhesion, the adhesive properties of PSA mixtures on the base of BS rubber grow with decreasing interfacial tension owing to better or more complete wetting of the surface of the metal substrate by a film of PSA mixture.

The obtained results have confirmed that the tackiness of PSA proportionally increases with oligomer content and tackifier content in BS copolymer. The investigated relations go through a maximum, which is, as a rule, attained, at a certain concentration which is lower the higher is the tackifier T_g. The compatibility of a given resin with polymer frequently has essential and decisive influence. The carboxylated BS rubber widely exhibited better compatibility with resins. The long-term stability of adhesive properties of open PSA films was also investigated. In this line, the best results for tackiness of PSA based on BS rubber were obtained by using hydrogenated derivatives of synthetic resin. The dependence of interfacial tension in the aluminum—PSA system on concentration of polar EHA oligomer in mixtures with BS rubber correlates with adhesive properties of the mixture. The adhesion of PSA increases with decreasing interfacial tension.

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References

1. D. SATAS, in “Handbook of Pressure-Sensitive Adhesive Technology,” edited by D. Satas (VNR, New York, 1989).
2. E. H. ANDREWS and T. A. KHAN, *J. Appl. Polym. Sci.* **41** (1990) 595.
3. F. L. MAGNUS and G. R. HAMED, *Rub. Chem. Technol.* **64** (1991) 66.
4. C. D. HAN, S. KIM and D. M. BAEK, *J. Adhesion* **36** (1998) 85.
5. K. NAKAAME and T. SATO, *ibid.* **36** (1998) 85.
6. K. NAKAAME, T. SATO, G. R. ZHOU and T. MATSUMOTO, *ibid.* **36** (1998) 97.
7. N. NAKAJIMA, R. BABNOWITZ and E. R. HARRELL, *J. Appl. Polym. Sci.* **44** (1992) 1437.
8. Š. FLORIÁN and I. NOVÁK, *Angew. Makromol. Chem.* **239** (1996) 55.
9. I. NOVÁK and I. CHODÁK, *J. Mater. Sci. Lett.* **18** (1999) 1131.
10. I. NOVÁK and Š. FLORIÁN, *Polym. Intern.* **50** (2001) 49.

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