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Development in the area of removable and repositionable polyacrylic pressure-sensitive adhesives

RAPID COMMUNICATION

Summary — The effects of the type and concentration of three multifunctional isocyanate crosslinking agents on the adhesion of titled pressure-sensitive adhesives (PSA) have been determined. Also the effects of the type and concentration of two groups of modifiers — ethoxylated amines [Formula (I)] and *n*-octylphenoxy derivatives of polyethylene oxide [Formula (II)] on PSA adhesion have been investigated. Both groups of modifiers decrease peel adhesion and cause PSA moving to the removable and repositionable area. The influence of ageing on the adhesion of PSA, modified with mentioned polyethylene oxide derivative, to various surfaces has been estimated.
Key words: removable and repositionable acrylic pressure-sensitive adhesives, isocyanate crosslinking agents, modifiers of removability, ethoxylated amines, *n*-octylphenoxy derivatives of polyethylene oxide.

Present work is a continuation of our earlier investigations on pressure-sensitive adhesives (PSA) [1] and concerns the removable and repositionable PSA.

Removable PSA are those, which predictably adhere yet remain repeatedly peelable from the various substrates over a long period of time without damaging the substrate. They have many commercial applications; for example in masking tapes, removable labels or office notes, protective films and medical tapes, which must quickly adhere to the metal, paper, plastics, glass, wood or skin, but must also peel smoothly away from these various substrates without leaving any adhesive residue on or damaging the surface of a particular substrate [2, 3].

Repositionable PSA are those, which allow to place an article containing such an adhesive onto a receptor in an exact position, because the article can be adjusted to the receptor after initial placement [4]. In some cases, the adhesive can be designated repositionable or repeatedly reusable. Such adhesives show aggressive tack but low peel adhesion properties, thus allowing repeated reuse. Commercial products such as 3M Post-it^{TM} show such adhesive characteristics. Repositionable adhesive systems, however, as used herein, generally show high peel adhesion and increased shear strength after placement in position.

Ideally, depending on the substrate, the removable PSA must reveal sufficient tack to quickly fix the adhesive to the desired substrate, adequate peel strength to prevent damage of the surface when the adhesives is removed, and show the appropriate cohesive strength to control the transfer of adhesive to the substrate [5].

The term "removable and repositionable" is intended to refer not only to the products, which can be temporarily adhered to, removed from, and repositioned on diverse substrate sheets but also to the products to which substrate sheets can be temporarily adhered, removed, and repositioned [6].

Classification of PSA in respect of peel adhesion properties presented in Table 1.

Table 1. Classification of PSA according to peel adhesion

Kind of PSA	Peel adhesion of PSA, N/2.5 cm (180° peel adhesion)
Excellent permanent	>14
Permanent	10—14
Semi-removable	6—8
Removable and repositionable	2—4
Excellent removable	<1

The aim of this work was to study the influence of amount of isocyanate crosslinking agents, as well as ethoxylated amines and polyalkylene oxides used as

modifiers on removability (peel adhesion) of acrylic PSA from diverse substrates.

EXPERIMENTAL

Materials

Materials used were as follows:

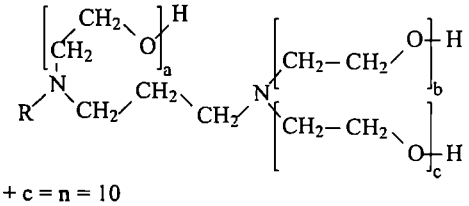
— 2-ethylhexyl acrylate and acrylic acid (BASF);

— ethyl acetate, acetone, 2,2'-azo-diisobutyronitrile (AIBN) and aluminum acetylacetonate (AlACA) (Merck);

— isophorone diisocyanate (IPDI) and toluene 2,4-diisocyanate (TDI) (Degussa);

— 4,4-diisocyanatediphenyl methane with trade name Basonat A 270 (BASF);

— ethoxylated amine Rewopal TPD 100 [Formula (I)] (Witco),

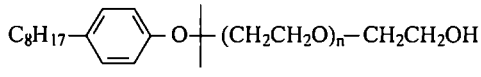


(I)

a + b + c = n = 10
R - talgpropylene group

— polyoxyethylene-(15)-oleylamine and polyoxyethylene-(50)-tallowamine (Akzo);

— polyalkylene oxides derivatives Antarox CA [Formula (II)] (GAF).



(II)

hydrophobic hydrophilic

Synthesis of PSA

The solvent based PSA was synthesized at temperature *ca.* 78°C from 80 wt. % of 2-ethylhexylacrylate and 20 wt. % of acrylic acid in a mixture of 70 wt. % ethyl acetate + 30 wt. % acetone as a solvent and in the presence of 0.1 wt. % AIBN as initiator. Solid content was about 50%. The monomers containing AIBN were added to the stirred solvent during the dosage time 3 h. The product contained 50 wt. % of a solid substance.

Crosslinking and modification of PSA

The synthesized PSA were crosslinked with investigated multifunctional isocyanates (IPDI, TDI and Basonat A 270) at concentration levels from 0.1 to 1.0 phr*).

*) Here and in the further text we use the shortening "phr" meaning parts per hundred of a resin.

Because the crosslinking reaction proceeds at room temperature, the isocyanate must be added and mixed just before the coating with 30 g/m^2 on polyester film. The film of PSA solution on the polyester base was heated in an oven at 105°C for 10 minutes. The solvent-based PSA contained crosslinking agent and modifer (ethoxylated amines or polyalkylene oxides) were cast with knife coater with 60 g/m^2 on polyester film and dried for 10 min at 105°C. This modified PSA were crosslinked not with isocyanates but with 0.3 phr of AlACA.

Methods of testing of removable PSA

180° Peel adhesion

PSA are considered removable if they are removed cleanly from a test substrate without causing any damage of the test substrate over a range of peel rates and varied periods of being kept at room temperature.

Criterion of removability valuation is 180° peel adhesion measurement (2—4 N/2.5 cm — see Table 1) realized the following way. The sample to be tested consists of a base laminated to or coated with PSA. A stainless steel test panel at least 5 cm times 25 cm is used as the substrate from which the sample is peeled. The last 2.5 cm of the length of the panel is covered with masking tape. Strips of tape samples 2.5 cm times 25 cm are adhered by PSA to one major surface on the stainless steel test panel this way that the end of the sample overlies the masking tape. The sample of tape is rolled twice with 4.5 kg roller to firmly bond it to the test panel. The major surface of the test panel not bearing the tape sample is adhered to the surface of peel adhesion tester by means of a double-coated tape. One end of the test sample is separated from the masking tape by hand and peeled at a rate of 305 mm/min through a distance of 25 cm at a peel angle of 180 grades. The initial 2.5 cm of peel data is ignored. The average peel force measured over the remaining peel length is recorded.

Ageing

The ageing consisted in keeping of PSA samples, modified with 80 phr of Antarox CA-890, for the periods of 3 days, 3 weeks and 3 months. 180° peels adhesion measurements were done after those periods.

RESULTS AND DISCUSSION

Influence of the kind and amount of multifunctional isocyanate crosslinking agents on peel adhesion of acrylic PSA

The effect of the kind and amount of crosslinking agents on the peel adhesion is shown in Fig. 1. The increase in multifunctional isocyanate concentration from 0.1 to 1.0 phr decreases the peel adhesion. The most favourable amount of isocyanate, with respect to remov-

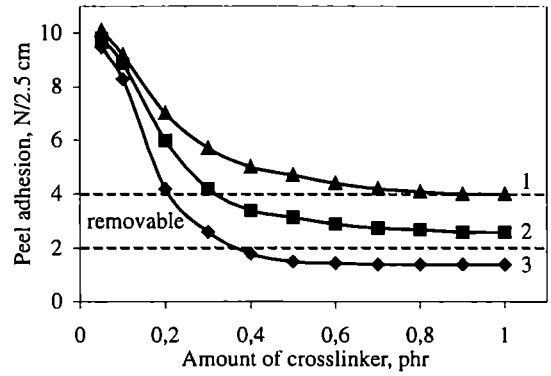


Fig. 1. Effect of the kind and amount of multifunctional isocyanates on peel adhesion of PSA; crosslinking agent: 1 — IPDI, 2 — TDI, 3 — Basonat A 270

ability of PSA, depends on the type of isocyanate used. Multifunctional isocyanate Bosonat A 270 shows the lowest effective concentration (0.2 phr) causing removability occurring.

Influence of the kind and amount of ethoxylated amines on peel adhesion of acrylic PSA

The synthesized PSA were modified with ethoxylated amines, which were chosen on the base of Hydrophilic-Lipophilic Balance (HLB) value. The relative hydrophilicities of the ethoxylated amines are indicated on the scale from 0 to 20 HLB. Higher HLB values correspond with stronger hydrophilic character of the ethoxylated amines. Ethoxylated amines with HLB values over 15 are favoured for applications for removable PSA containing carboxylic groups. The greatest attention in this development area was paid to ethoxylated amines Rewopal TPD 100 (HLB = 15), polyoxyethylene-(15)-oleylamine (HLB = 19) and polyoxyethylene-(50)-tallowamine (HLB = 20). They were used at concentration

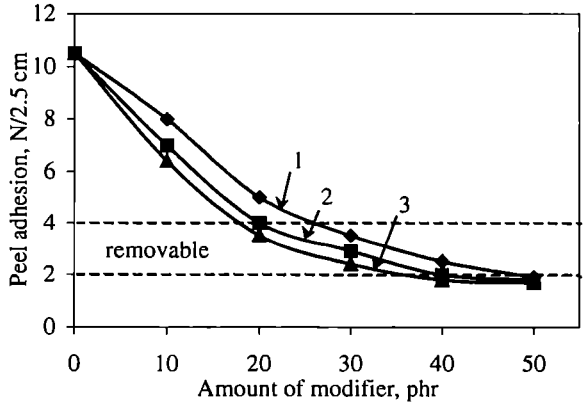


Fig. 2. Effect of the kind and amount of ethoxylated amines on peel adhesion of PSA; 1 — Rewopal TPD 100, 2 — polyoxyethylene-(15)-oleylamine, 3 — polyoxyethylene-(50)--tallowamine

levels from 10 to 50 phr. Influence of the kind and concentration of these ethoxylated amines on peel adhesion of modified PSA is presented in Fig. 2.

Increase in ethoxylated amines content decreases the peel adhesion

In respect of removability, the sufficient peel adhesion decrease can be reached for over ~20 phr of either polyoxyethylene-(15)-oleylamine or polyoxyethylene-(50)-tallowamine while Rewopal TPD 100 concentration must be at least about 30 phr.

Influence of the kind and amount polyalkylene oxides on peel adhesion of acrylic PSA

Polyoxyethylene derivatives important in respect of PSA removability are selected similarly as ethoxylated amines using the HLB value. Polyalkylene oxides derivatives showing HLB values between 12 and 18 are most suitable as modifiers of PSA removability.

40 to 120 phr of Antarox CA-620 (HLB = 12.0), Antarox CA-720 (HLB = 14.6) or Antarox CA-890 (HLB = 18.0) were added to the adhesive compositions. The effect of the type and amount Antarox CA compounds on peel adhesion of PSA are presented in Fig. 3.

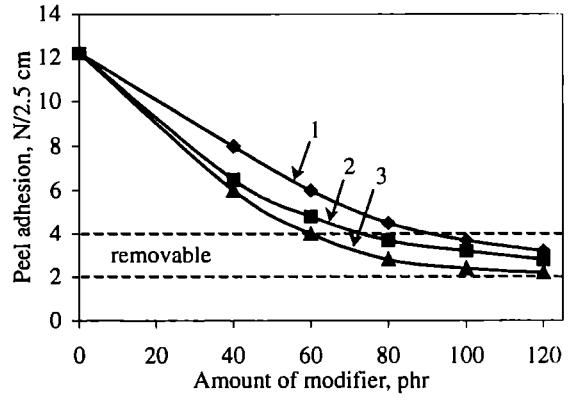


Fig. 3. Effect of the type and amount of Antarox CA compounds on peel adhesion of PSA; 1 — Antarox CA-620, 2 — Antarox CA-720, 3 — Antarox CA-890

As expected, the increase in the amount of Antarox CA affects positively the removability of acrylic PSA. As it results from Fig. 3, Antarox CA-890 shows the widest range of useful concentration (60—120 phr).

Ageing test of removable PSA containing Antarox CA-890

The effect of ageing on modified PSA removability has been investigated. Peel adhesion of PSA, modified with 80 phr of Antarox CA-890, to the steel, aluminum

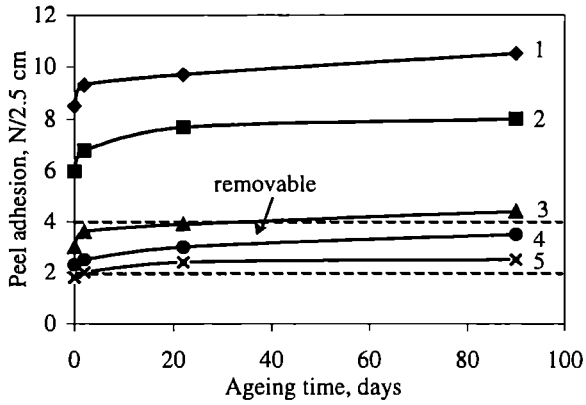


Fig. 4. Peel adhesion PSA modified with Antarox CA-890 to various surfaces versus ageing time; 1 — steel, 2 — Al, 3 — glass, 4 — PP, 5 — PE

(Al), glass, polypropylene (PP) and polyethylene (PE) was determined. The results are presented in Fig. 4. As it is seen, peel adhesion, in all cases, increases a bit during first couple of days and then seems to be constant.

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