ZBIGNIEW CZECH

Szczecin University of Technology
Institute of Chemical Organic Technology
ul. K. Pułaskiego 10, 70-322 Szczecin, Poland
e-mail: psa_czech@wp.pl

Crosslinking of the acrylic pressure-sensitive adhesives using polycarbodiimides

RAPID COMMUNICATION

Summary — The crosslinking of polyacrylic pressure-sensitive adhesives (PSAs) is an interesting method of modification of their physicochemical and mechanical properties. The syntheses and crosslinking of polyacrylic PSA, used for the manufacturing of pressure-sensitive protective films, have become recently of a special importance. In the paper the basic properties of polyacrylic PSA crosslinked with polycarbodiimides, such as tack, adhesion and cohesion, were determined. The tack was measured at temp. 20 °C while the other properties mentioned were determined at 20 and 70 °C. Taking into account the obtained values of tack, adhesion and cohesion one can find that the adhesives investigated are useful for the production of a wide variety of pressure-sensitive protective films.

Key words: polycarbodiimides, acrylic pressure-sensitive adhesive, crosslinking, tack, adhesion, cohesion.

SIECIOWANIE POLIAKRYLANOWYCH KLEJÓW SAMOPRZYLEPNYCH ZA POMOCĄ POLIKARBODIIMIDÓW

Streszczenie — Sieciowanie samoprzylepnych klejów (PSA) poliakrylanowych stanowi interesującą metodę modyfikacji ich właściwości fizykochemicznych i mechanicznych. Szczególnego znaczenia nabrały w ostatnim czasie synteza i sieciowanie poliakrylanowych PSA stosowanych do produkcji samoprzylepnych folii ochronnych. W pracy określono podstawowe właściwości poliakrylanowego PSA sieciowanego polikarbodiimidami, takie jak lepność (tack), adhezję oraz kohezję. Lepność mierzono w 20 °C, a pozostałe wymienione wyżej właściwości zarówno w 20 jak i w 70 °C. Uwzględniając otrzymane wartości lepności, adhezji oraz kohezji można stwierdzić, że badane kleje nadają się do produkcji szerokiego asortymentu samoprzylepnych folii ochronnych.

Słowa kluczowe: polikarbodiimidy, samoprzylepny klej poliakrylanowy, sieciowanie, lepność, adhezja, kohezja.

Crosslinking is one of the most interesting processes, attractive for the chemist, informative for the physicist and helpful for the user in the joint development of tailored solvent-borne acrylic pressure-sensitive adhesives (PSAs). In general acrylic PSAs are used increasingly for coating of labels, tapes, decorative films and similar self-adhesive articles. The PSAs must have defined properties. Besides a good surface adhesion, the PSAs should have good stability against light, oxygen, moisture and plasticizers, and the adhesion characteristics should be constant in very large temperature range [1, 2].

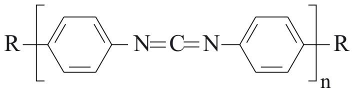
The crosslinking of acrylic PSAs is a useful process in the repertoire of general procedures going through many of the applications of PSAs. In the nomenclature, „crosslinking" is a correlation of a network which relates to a net of interconnected chains. Polymeric networks or crosslinked systems consist of interconnected macromolecules, which extend into all three dimensions [3, 4]. Therefore, the parts of lower molecular weight are those, which preferably remain without ties to the network when low crosslinking degree applies, because the polydispersal characteristics of polymers is usually normal.

The physicochemical and mechanical properties (tack, adhesion and cohesion) of acrylic self-adhesives are determined largely by the type and amount of crosslinking agent added to the copolymer. It is known that an acrylate copolymer, which has no crosslinking or is crosslinked only by hydrogen bonds, has no sufficient thermal and mechanical stability and is practically useless as a PSA [5].

The crosslinking can be considered as a critical factor in the formulation of a PSA in the application stage [6].

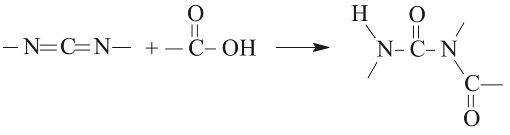
The generated crosslinked connections inhibit extensively the mobility of the polymer molecules by chemical bondings in the network of the polymeric PSA. A crosslinked PSA therefore cannot melt any more. Perhaps it becomes somewhat softer at increased temperature, but does not melt. It undergoes rather the decomposition above a certain temperature.

A new crosslinking agent's group — polycarbodiimides was come onto the market in 1994 by Rohm and Haas Company [7]. The aromatic polycarbodiimides


(I)

having the structure shown by formula (I) render the reaction with nucleophilic carboxyl groups of a polymer possible.

Several grades of multifunctional carbodiimides have been used in the coating industry, normally supplying the product as 50 % of active solids in ethyl acetate miscible solvents (*e.g.* glycol ether acetates). The crosslinking reaction involves the addition of the carboxylic acid group across the carbodiimide to form an *N*-acylurea:


(1)

EXPERIMENTAL

Materials

The monomers 2-ethylhexyl acrylate, methyl acrylate and acrylic acid were available from BASF (Germany). 2,2'-Azo-diisobutyronitrile (AIBN) was purchased from TCI (Japan). Ethyl acetate was supplied by Shell (The Netherlands).

The investigated polycarbodiimides: Permutex XR-5551 and Permutex XR-5580 delivered by Stahl (The Netherlands) contained 50 wt. % of solid phase. Producer recommended the use of this crosslinking agents in a concentration of 3—10 wt. % and specified pot life for 24 h. The chemical structure of both polycarbodiimide crosslinkers is not presented in the commercial data sheets.

Synthesis of solvent-borne acrylic PSA

For the crosslinking trials the investigated solvent-borne PSAs were synthesized using a mixture containing: 65 wt. % of 2-ethylhexyl acrylate, 30 wt. % of methyl acrylate and 5 wt. % of acrylic acid. The polymerization was performed 4 hours in the presence of 0.1 wt. % of AIBN in a boiling organic solvent (ethyl acetate) at 50 wt. % of acrylic polymer amount [8].

Coating of solvent-borne acrylic PSA

The synthesized solvent-borne acrylic self-adhesives containing tested polycarbodiimides Permutex were cast with knife coater with about 60 g/m^2 on 25 μm polyester film Hostaphan RN from Hoechst (Germany) and dried for 10 min at 105 ^oC.

Method of testing of UV-crosslinked acrylic layers

Tack (Quick stick)

Quick stick method measures the instantaneous adhesion of a loop of adhesive-coated material using no external pressure to secure contact. According to another definition the quick stick tack value is the force required to separate at a specific rate a loop of material, which was brought into contact with a standard surface. The quick stick method according to standard AFERA 4015 (AFERA is abbreviations of Association des Fabricants Europeens de Rubans Auto-Adhesifs) is relatively simple and may be carried out using common tensile strength test machines. A sample of PSA-coated material 1 inch (about 2.5 cm) wide and about 7 inch (about 17.5 cm) long is bonded to a vertical clean steel test plate at least 10 lineal cm in firm contact. The vertical steel test plate is clamped in the jaws of a Zwick tensile testing machine. The scale reading in Newtons is recorded as the tape is peeled from the steel surface with a constant rate of 100 mm. Quick stick has the advantage of allowing tack to be measured on a wide range of substrates, such as stainless steel, glass, polyethylene and paper.

Adhesion

There are two meanings of the term adhesion. On the one hand, adhesion is understood as the process through which two bodies are attached to each other when brought together. In this sense adhesion characterizes the sum of all intermolecular and electrostatic forces acting across the interface. On the other hand, we may examine the process of breaking the already adhesive in contact. In this case adhesion is the force, or the energy, required to separate the two bodies, often called „practical adhesion" or „adherence".

A sample of PSA-coated material 1 inch (about 2.5 cm) wide and about 5 inch (about 12.7 cm) long is bonded to a horizontal target substrate surface of a clean steel test plate at least 12.7 cm in firm contact. A 2 kg hard rubber roller is used to apply the strip. The free end of the coated strip is doubled back nearly touching itself so the angle of removal will be 180^o. The free end is attached to the adhesion tester scale. The steel test plate is clamped in the jaws of a tensile testing machine Zwick

1445, which is capable of moving the plate away from the scale at a constant rate of 300 mm/min.

Cohesion

According to AFERA standard definitions of cohesion include: „The propensity of a single substance to adhere to itself, the internal attraction of molecules towards each other; the ability to resist partition from the mass; internal adhesion; the force holding a single substance together".

The cohesion, measured as shear strength is a measure of the cohesiveness or internal strength of an adhesive. It is based upon the value of force required to pull an adhesive strip from a standard flat surface in a direction parallel to the surface to which it has been affixed with a definite pressure, according to standard AFERA 4012, at 20 and at 70 °C. It is measured in Newtons for 4 h load times. Each test is conducted for two adhesive-coated strips applied to a standard stainless steel panel in a manner such that a 2.5 × 2.5 cm portion of the strip is in fixed contact with the panel with one end of the strip being free.

RESULTS AND DISCUSSION

This section discusses the influence of the polycarbodiimides: Permutex XR-5551 and Permutex XR-5580 on the important properties of solvent-borne acrylic PSAs as tack at 20 °C, adhesion and cohesion at 20 °C and 70 °C.

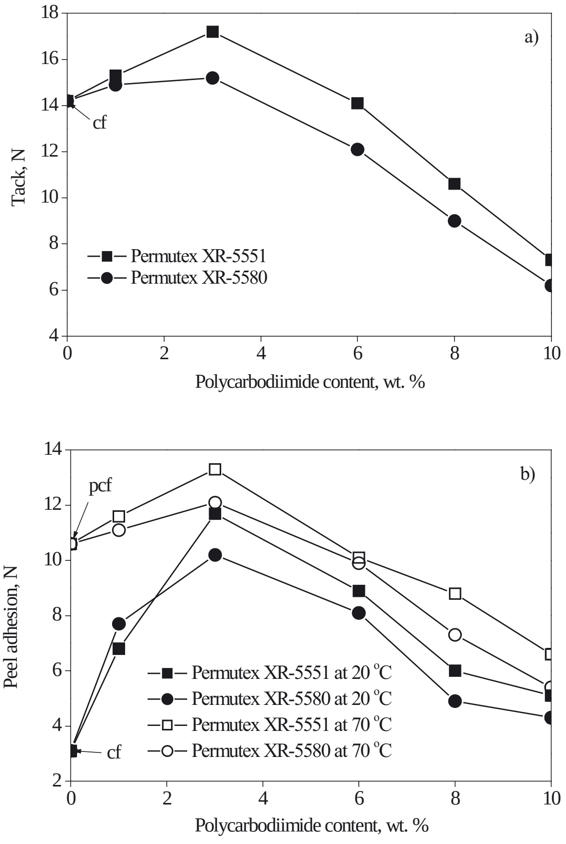


Fig. 1. Effect of kind and amount of crosslinking agent on: a) tack at 20 °C, b) adhesion

As it was shown in Figure 1 the uncrosslinked solvent-borne acrylic PSA shows low values of tack and adhesion along with cohesive failure (cf). After addition of a small amount of polycarbodiimide (Permutex XR-5551 or Permutex XR-5580) the acrylic PSA begins to crosslink. The PSA structure is now compact, tack and adhesion increase and an amelioration of the properties, like tack (Fig. 1a) and adhesion (Fig. 1b), was observed. The maxima of tack and adhesion are achieved for 3 wt. % of either polycarbodiimide. PSA layers crosslinked with polycarbodiimides are highly tacky. After exceeding a threshold of 3 wt. % of polycarbodiimide, the tack and adhesion levels decrease.

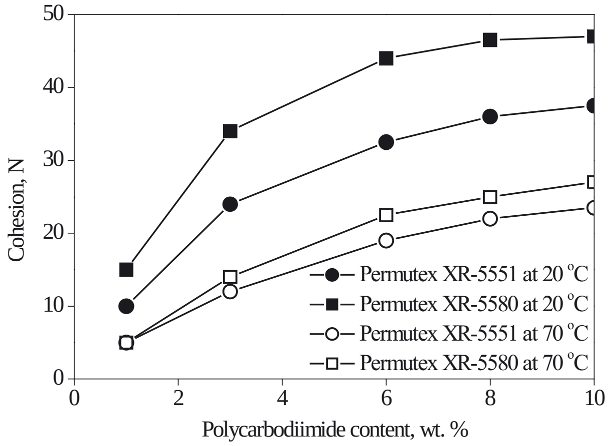
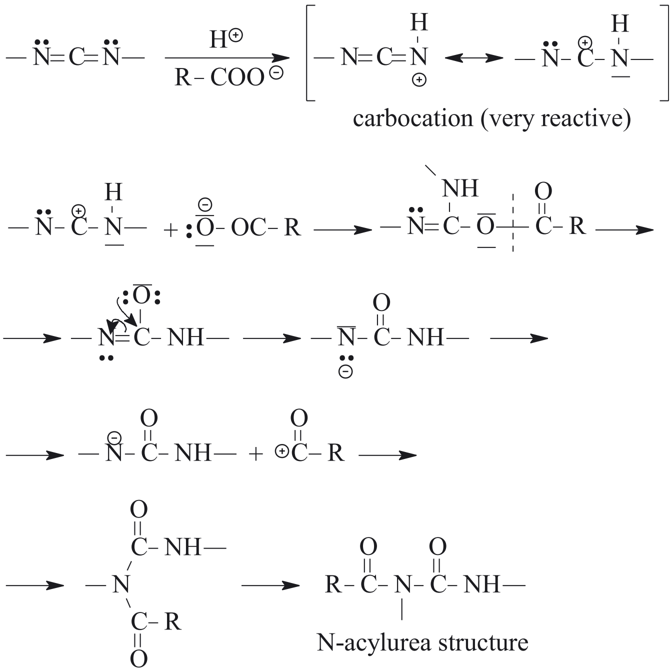


Fig. 2. Effect of kind and amount of crosslinking agent on the acrylic PSA cohesion

The results presented in Figure 2 show that the polycarbodiimides differ in their ability to improve the cohesion of the crosslinked basic acrylic PSA. Permutex XR-5580 is a better crosslinking agent than Permutex XR-5551. In order to reach the cohesion of 45 N at temp. 20 °C and 25 N at 70 °C it is necessary to use about 9 wt. % polycarbodiimide crosslinking agent Permutex XR-5580.

Taking into consideration the relatively high concentration of polycarbodiimides used and their price level, they seem not to be competitive compared to the other commercial crosslinking agents. The pot life of acrylic PSAs containing multifunctional polycarbodiimides is limited to about 24 h. Using an alcohol stabilizer the pot life can be prolonged, even to a few months.

The medium PSAs performance achieved with the application of polycarbodiimides have shown this crosslinking agents' group is useful for acrylic PSAs suitable for protective foils.



Scheme A. Mechanism of the reaction between carboxylic groups and polycarbodiimides during crosslinking of acrylic PSAs

Polycarbodiimides actions as crosslinking agents consist in the formation of very reactive carbocations which react with carboxylic groups of polymers forming *N*-acylurea structures. The reaction mechanism between the carboxylic groups of the acrylic polymer chain and polycarbodiimide is shown in Scheme A (according to [7]).

CONCLUSIONS

Multifunctional polycarbodiimides are good crosslinking agents for self-adhesive articles with low tack, low adhesion and moderate cohesion for a wide range of applications in the protective films area. The short pot life of 24 hours can be prolonged by addition of an alcohol, preferably isopropanol, which enables to achieve a pot life of days or months.

REFERENCES

1. Czech Z.: *Polym. Int. Sci.* 2003, **52**, 347.
2. Czech Z.: *Polimery* 2005, **50**, 831.
3. Milker R., Czech Z.: *Polimery* 1987, **32**, 182.
4. Czech Z., Loclair H.: *Polimery* 2005, **50**, 64.
5. Czech Z.: „Vernetzung von Haftklebstoffen auf Polyacrylatbasis", Ed. Technical University Szczecin, Szczecin 1999.
6. Milker R., Czech Z.: *Adhäsion* 1989, **33**, 20.
7. „Polycarbodiimides", Rohm and Has Company, USA 1994.
8. Czech Z.: *Polimery* 2006, **51**, 754.

Received 18 IV 2006.