

ZBIGNIEW CZECH^{*)}, MONIKA KOĆMIEROWSKA

Szczecin University of Technology
Polymer Institute
ul. K. Pułaskiego 10, 70-322 Szczecin, Poland

Water-dispersible polyurethane systems used as pressure-sensitive adhesives

RAPID COMMUNICATION

Summary — Water-dispersible polyurethane systems based on anionic polyurethane aqueous dispersions were obtained. The prepolymers based on hydroxyl-terminated polybutadiene (HTPB), isophorone diisocyanate (IPDI), poly(propylene glycol) (PPG) and dimethylpropionic acid (DMPA) were synthesized in bulk. After neutralization with triethylamine (TEA) the anionomer prepolymer was dispersed in water, followed by a chain-extension reaction with ethylenediamine (EDA). The adhesive and cohesive properties of aqueous dispersions as coatings for self-adhesive articles were evaluated. It was observed that DMPA and crosslinking agent contents as well as kind of poly(propylene glycol) influenced adhesion and cohesion of polyurethane films.

Key words: pressure-sensitive adhesives, polyurethane, polybutadiene, isophorone diisocyanate, poly(propylene glycol), adhesion, cohesion.

DYSPERGOWALNE W WODZIE UKŁADY POLIURETANOWE STOSOWANE JAKO KLEJE SAMOPRZYLEPNE

Streszczenie — Otrzymano dyspergowalne w wodzie wodne systemy poliuretanowe. Zsyntetyzowano w masie prepolimery poliuretanowe na bazie hydroksylowanego polibutadienu, diizocyjanianu izofofonu, glikolu polipropylenowego oraz kwasu dimetylopropionowego (Schemat A). Zdolność anionowego prepolimeru do tworzenia dyspersji w wodzie destylowanej osiągnięto przez reakcję izocyjanianowych grup końcowych z etylenoaminą oraz poprzez neutralizację z trietyloaminą. Zbadano adhezję i kohezję usieciowanych filmów wodnych dyspersji poliuretanowych (rys. 1—3). Zaobserwowano zależność właściwości otrzymanych filmów poliuretanowych od ilości kwasu dimetylopropionowego i środka sieciującego oraz rodzaju glikolu polipropylenowego, użytych do reakcji.

Słowa kluczowe: kleje samoprzylepne, poliuretan, polibutadien, diizocyjanian izofofonu, glikol polipropylenowy, adhezja, kohezja.

The first patented pressure-sensitive adhesives (PSA) were derived from natural rubber for bandages in 1850. Recent developments in the use of polyurethane dispersions in examination gloves, to replace the natural rubber and later polyesters, polyethers and acrylics, have aroused interest in their evaluation in PSA [1, 2].

Environmental reasons are the cause of the growing research, development and production of waterborne systems, particularly those based on polyurethanes. These materials find a special application as binders for paint and coating formulations [3, 4].

Polyurethanes (PUR) make good adhesives for a number of reasons [5—10]:

— they effectively wet the surface of most substrates,

— they can interact with the surface through polar interactions (*e.g.* hydrogen bonding),

— their relatively low molecular weight allows them to permeate porous substrates (for reactive adhesives),

— they can form covalent bonds with substrates that have active hydrogen atoms (for reactive adhesives),

— through molecular composition of the adhesives their stiffness, elasticity and crosslinking can be tailored to suit specific needs.

EXPERIMENTAL

Materials

The following reagents were used without further purification in the waterborne polyurethane synthesis:

^{*)} Corresponding author; e-mail: psa_czech@wp.pl

dibutyltin dilaurate (DBTDL) and dimethylpropionic acid (DMPA supplied by Aldrich, USA), ethylenediamine (EDA) and hydroxyl-terminated polybutadiene (HTPB, $\overline{M}_w = 3500$ from Krahn Chemie, Germany), isophorone diisocyanate (IPDI delivered by Bayer, Germany), two kind of poly(propylene glycol) (PPG): Voranol 1010 ($\overline{M}_w = 1220$), Voranol 2000 ($\overline{M}_w = 2490$) purchased from Dow, USA; and triethylamine (TEA) from Aldrich, USA. We also used an emulsifier Dowfax 8390 (alkyldiphenyloxide disulfonate) supplied by Dow, USA.

Synthesis

The syntheses of the prepolymers based on HTPB, PPG, DMPA, and IPDI, catalyzed by 1 wt. % of DBTDL, was carried out in the absence of a solvent at temperature 50 °C for 2 h under nitrogen atmosphere. The prepolymer neutralization with TEA proceed at 50 °C for 1 h. After that period the temperature was reduced to 25 °C and the dispersion of the bulk in water with 1 wt. % of emulsifier was prepared using high-speed stirring. Afterwards 1.13 g of EDA was added to the dispersion that was kept at 35 °C for 1 h to complete the chain-extension reaction between the amino groups of the chain extender and -NCO end groups of the prepolymer. Scheme A shows the polyurethane aqueous dispersion synthesis scheme.

For described synthesis one of two kinds of PPG in constant amount 137 g and 46 g of IPDI were used. Amount of DMPA and HTPB together was 17 g, but in-

dividual amount of DMPA changed and was 2.5, 3.0 or 3.5 g. Finally polyurethane aqueous dispersions with a solid content of 35 ± 5 % (w/w) were obtained.

The synthesized PUR dispersion were crosslinked using IPDI in three concentrations 1, 3 or 5 wt. %.

Methods of testing

Viscosity

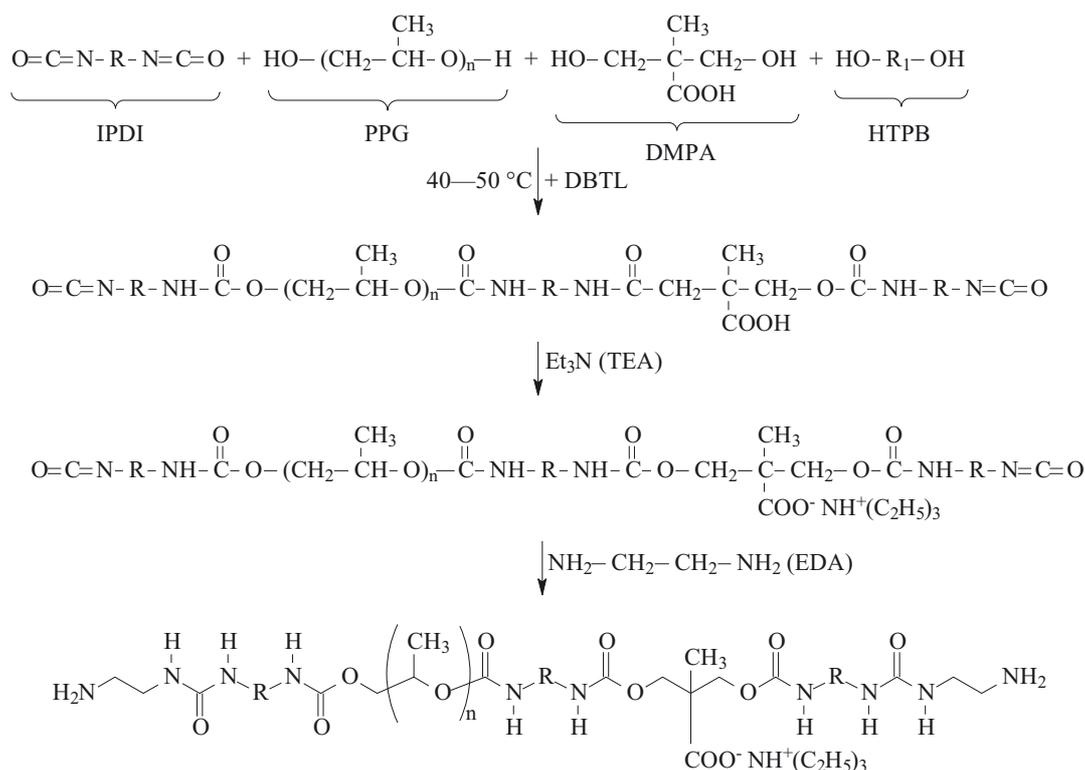
Viscosity determination was performed using rheometer RM 180 from Rheometer Scientific.

Adhesion and cohesion

The PUR dispersions were applied on the polyester film and dried for 10 min at 100 °C in conventional dryer. The coat weight of PUR-layer was about 60 g/cm².

The adhesive properties of the dispersions as coatings for wood were evaluated according to the manner described in [11] and to a standard test AFERA (Association des Fabricants Europens de Rubans Auto-Adhesifs). Exact details were found for adhesion in AFERA 4001 and for cohesion (shear strength) in AFERA 4012. The test specimens (50 × 25 mm) for peel adhesion measurements were cut from polyurethane film. A test machine, INSTRON 4206, equipped with a 1-kN load cell and pneumatic grip, was used at a crosshead speed of 50 cm/min.

Cohesion test is conducted on an adhesive-coated strip applied to a standard stainless steel panel in a manner such that a 1-inch × 1-inch (about 2.5 cm × 2.5 cm)



Scheme A. Polyurethane aqueous dispersion synthesis

portion of the strip is in fixed contact with the panel with one end of the strip being free.

RESULTS AND DISCUSSION

The viscosity of prepared aqueous dispersions varied from 16 to 17 cP, when higher molecular weight PPG was employed, and from 13 to 21 cP in those where the lower molecular weight PPG was used. Generally the dispersion viscosity decreased as the DMPA content was increased (and HTPB content was decreased).

The influence of the amount of DMPA used in the synthesis and content of crosslinking agent were investigated. As shown in Fig. 1 in the dispersions synthesized using lower molecular weight PPG (Voranol 1010) ob-

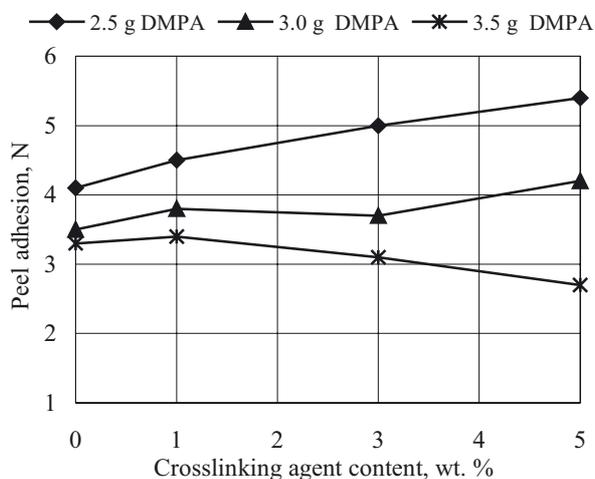


Fig. 1. Effects of content of crosslinking agent (IPDI) and amount of DMPA on peel adhesion of the film obtained from dispersion synthesized using lower molecular weight PPG (Voranol 1010)

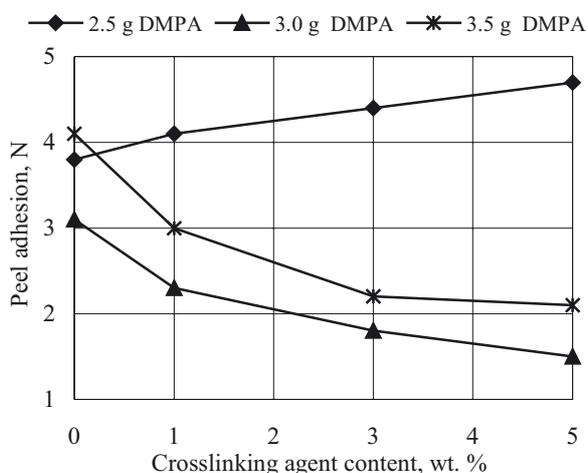


Fig. 2. Effects of content of crosslinking agent (IPDI) and amount of DMPA on peel adhesion of the film obtained from dispersion synthesized using higher molecular weight PPG (Voranol 2000)

servably lower peel adhesion was obtained for the samples obtained with higher the amount of DMPA.

Decrease in peel adhesion was larger when the content of crosslinking agent increased. Similar results, presented in Fig. 2, was obtained for the adhesives synthesized using higher molecular weight PPG (Voranol 2000), with the exception of the sample with 2.5 g of DMPA, which adhesion increased with increased IPDI concentration.

Comparison of Fig. 1 and Fig. 2 shows influence of the length of the PPG segment on peel adhesion. Higher molecular weight of PPG used in the reaction decreased the adhesion of crosslinked PUR layers.

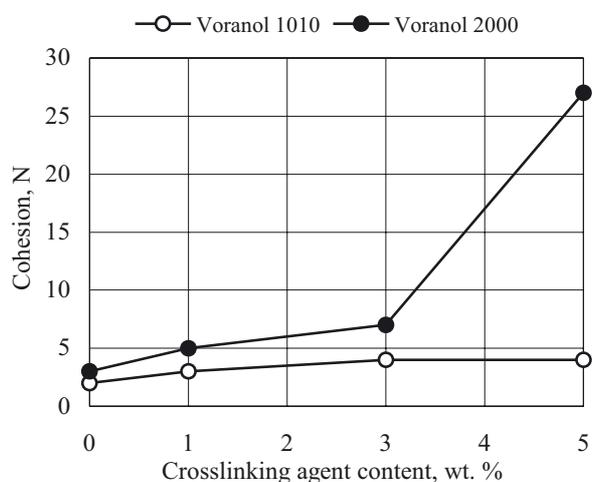


Fig. 3. Effects of content of crosslinking agent (IPDI) and kind of PPG on cohesion of the film obtained from dispersion synthesized using 2.5 g of DMPA

Opposite effect of kind of PPG was observed on cohesion, what is shown in Fig. 3. Both presented series of samples were synthesized using 2.5 g of DMPA. Independently on the content of crosslinking agent the samples exhibit higher cohesion when higher molecular weight PPG (Voranol 2000) was used, but the difference in cohesion increases with increase in concentration of crosslinking agent.

The maximum of cohesion for PUR layer obtained using Voranol 2000 and crosslinked with 5 wt. % of IPDI was observed.

CONCLUSIONS

In this study, it was shown that it is possible to develop novel water-dispersible polyurethane pressure-sensitive adhesives containing hydroxylated polybutadiene. The versatility of the chemistry provides wide technical perspectives and allows to form very soft to hard chemical architectures. The incorporation of PPG of higher molecular weight and DMPA into the polymer

backbone and the adding of isocyanate crosslinking agent improved the mechanical resistance of cast films.

REFERENCES

1. Chao H. S.: *Adhesive Age* 2002, **10**, 26.
2. Agosta M.: *Coating World* 2002, **7**, 36.
3. Lee S. Y., Lee J. S., Kim B. K.: *Polymer International* 1997, **42**, 67.
4. Noble K. L.: *Progr. Org. Coat.* 1997, **32**, 131.
5. Tharanikkarasu K., Kim B. K.: *Progr. Rubb. Plast. Technol.* 1997, **13**, 26.
6. Sciangola D. A.: *Adhesives Age* 2000, **2**, 25.
7. *US Pat.* 5 541 251 (1996).
8. Milker R., Czech Z.: *Polimery* 1987, **32**, 182.
9. Milker R., Czech Z.: *Polimery* 1990, **35**, 326.
10. Czech Z.: *Polimery* 1996, **41**, 22.
11. Czech Z., Urbala M.: *Polimery* 2004, **49**, 837.

Received 9 XII 2005.

W kolejnym zeszycie ukaza się m.in. następujące artykuły:

- Perspektywy zastosowań cieczy jonowych w chemii polimerów
- Wyjaśnienie podstaw reaktywności układów fotoinicjujących fotopolimeryzację (*j. ang.*)
- Nowe siloksanowe polimery gradientowe (*j. ang.*)
- Mikroemulsje jako źródło nanolatęksów i nanoreaktorów
- Wybrane nowe materiały z polisacharydów (*j. ang.*)
- Fotoindukowane właściwości poliestroimidów zawierających ugrupowania azobenzowe
- Hydrofilowo-hydrofobowe kompozyty gumowe o zwiększonej podatności na biodegradację (*j. ang.*)
- Degradacja wybranych syntetycznych poliestrów w warunkach naturalnych
- Hydrożelowe mikrokapsułki z udziałem naturalnych i chemicznie modyfikowanych oligochitozanów — właściwości mechaniczne i porowatość
- Modulacja współczynnika załamania światła w foliach zawierających pojedynczy i podwójny układ chromoforów (*j. ang.*)
- Wpływ budowy polimerowych katalizatorów utleniania na ich aktywność katalityczną
- Ocena mechanicznych i dynamicznych właściwości recyklatu polipropylenu napełnionego mączką drzewną (*j. ang.*)
- Wykorzystanie rozwłóknionych odpadów wielowarstwowych kartonów laminowanych do płynnej żywności jako napełniaczy polietylenu