

**Zbigniew CZECH, Magdalena WITCZAK, Agnieszka KOWALCZYK,
Jagoda KOWALSKA**

THE INFLUENCE OF RESIDUE MONOMERS ON SELECTED PROPERTIES OF ACRYLIC PRESSURE- SENSITIVE ADHESIVES

Self-adhesive materials manufactured from acrylic polymers, especially acrylic pressure-sensitive adhesives (PSA) are widely used in different industrial applications. The wide ranges of self-adhesive products comprise self-adhesive tapes which are used for the mounting of composite plates in the furniture industry. The goal of the investigations was the synthesis of solvent-based acrylic PSA used as furniture tape and the testing of the influence of free residue monomers on their properties (tack, peel adhesion, shear strength, shrinkage). The best performance for self-adhesive tapes in the form of polymeric films with 30 g/m² and 60 g/m² coating weights and containing less than 0.3 wt.% residue monomers was observed.

Keywords: adhesives, PSA, acrylics, polymer, monomers, tack, peel adhesion, shear strength, shrinkage

Introduction

Since its introduction half a century ago, pressure-sensitive acrylic adhesive has been successfully applied in many fields. PSA applications cover the mounting of decorative trims made of PCV, MDF, wood, aluminium, glass and also in buildings used for roof bow attachment and glass glazing. They are used in self-adhesive tapes, labels, sign and marking films and protective films as well as in dermal dosage systems for pharmaceutical applications and in biomedical elec-

Zbigniew CZECH, West Pomeranian University of Technology, Szczecin, Poland
e-mail: zbigniew.czech@zut.edu.pl

Magdalena WITCZAK, Wood Technology Institute, Poznań, Poland
e-mail: m_witczak@itd.poznan.pl

Agnieszka KOWALCZYK, West Pomeranian University of Technology, Szczecin, Poland
e-mail: a-butwin@tlen.pl

Jagoda KOWALSKA, West Pomeranian University of Technology, Szczecin, Poland
e-mail: jagoda.anna.kowalska@gmail.com

trodes. Pressure-sensitive adhesives based on acrylics are available on the market as solvent-based, water-borne and solvent-free systems. The difference between pressure-sensitive adhesives and other adhesives, such as contact adhesives, is in the permanent surface stickiness of the pressure-sensitive adhesives before, or after, application [Bendek 2006; Gnanou, Fontanille 2002].

The properties useful in characterizing the nature of pressure-sensitive adhesives are: tack, peel adhesion, shear strength and shrinkage. Solvent-based acrylic PSAs offer several advantages, such as: excellent aging characteristics, resistance to elevated temperatures and plasticizers, exceptional optical clarity due to the polymer compatibility, non-yellowing and excellent water resistance. Lower adhesion to non-polar substrates such as PP, PE, EPDM is caused by the polar chemistry of acrylics [Czech 2001].

Nowadays, pressure-sensitive adhesive acrylic solutions are predominantly manufactured by polymerization from a wide selection of acrylic monomers in a refluxing organic solvent in the presence of an initiator, such as organic peroxides or azo compounds. For the manufacture of acrylic pressure-sensitive adhesives, tackifying common acrylic acid esters are primarily preferred, with C4 – C8 carbon atoms in the alkyl moiety together with other comonomers. The composition of acrylic polymers that are inherently pressure-sensitive, is a combination of soft (low T_g – glass transition temperature), hard (high T_g) and functional monomers [Czech, Wesółowska 2007].

The tack and the peel properties are impacted by the soft or low glass transition temperature monomers such as 2-ethylhexyl acrylate, isooctyl acrylate or n-butyl acrylate. The harder monomers, e.g. methyl acrylate or ethyl acrylate are included to provide internal strength. The functional groups containing monomers such as acrylic acid or 2-hydroxyethyl acrylate are incorporated into the balanced monomers for specific adhesion to desired substrates and to provide sites in the form of active centres for cross-linking after coating.

After the synthesis of acrylic pressure-sensitive adhesives, the final acrylic PSA contains free residue monomers which characteristically smell and worsen the properties of coated materials such as carrier and carrier-free self-adhesive mounting tapes [Wicks et al. 2007]. Due to the very high reactivity, acrylic acid is not present, as a free monomer, in the synthesized pressure-sensitive adhesives. Residue monomers in synthesized acrylic PSA can be reduced with the addition of further radical thermal reactive polymerization starter or with post-reaction time (for medical grade of acrylic PSA often 8 h).

Self-adhesive tapes are manufactured for packing, masking, marking, construction, decoration, protection, mounting and within the field of medicine. According to their carrier material, double-sided mounting tape may be divided into nonwoven, polymeric films or foam, especially PE foam. These kinds of mounting-tapes and carrier-free tapes are used in the furniture industry for the bonding of different furniture components [Mahdavi, Taghizadeh 2005].

A variety of tapes are used in the furniture industry in the assembly of composite wood panels with veneered surfaces [Skeist, Miron 1981; Bolitsky, Hartman 2001; Spratling 2002; Pederson 2003]. Complex versions of these composite wood panels are known as “fancy face” veneered surface panels. The current practice in the furniture industry is to assemble furniture with thin wooden veneers covering a dimensionally stable but cheaper core board, such as particle board. The decorative wood species desired by consumers, such as oak, maple, cherry, and others, are expensive and thus are most commonly used in the form of thin veneers about 0.8 mm. These veneer pieces are often arranged in a side-by-side relationship and fastened together to form a composite panel or veneer surface.

The aim of the experiments carried out was to study the influence of residue monomers concentration in acrylic PSA and self-adhesives on the main properties of acrylic pressure-sensitive adhesives, such as tack, peel adhesion, shear strength and shrinkage.

Materials and methods

Synthesis of a solvent-borne acrylic pressure-sensitive adhesive

The solvent-borne acrylic pressure-sensitive adhesive was synthesized with 50 wt.% polymer content in ethyl acetate at a temperature of approx. 78°C (boiling point of polymerization medium) in the presence of a radical polymerization starter 0.1 wt.% 2,2'-azo-bis-diisobutyronitrile (AIBN) according to the amount of monomers by the use of the following mixture of monomers: 30 wt.% isooctyl acrylate (IOA), 25 wt.% 2-ethylhexyl acrylate (2-EHA), 17 wt.% butyl acrylate (BA), 10 wt.% ethyl acrylate (EA), 10 wt.% methyl acrylate (MA), 5 wt.% 2-hydroxyethyl acrylate (2-HEA) and 3 wt.% acrylic acid (AA). The polymerization was conducted in a 1 l four-necked round-bottom flask equipped with a thermometer, condenser, dropping funnel and mechanical stirrer. The polymerization reactor was charged initially with 20 wt.% of ethyl acetate/monomers mixture, and then polymerization was started at 78°C. The rest of the ethyl acetate/monomers mixture was added slowly over 2 h and the polymerization reactor was kept at 80°C for 3 h in order to pursue the polymerization in a more uniform manner. All the monomers used, the polymerization medium, ethyl acetate, and the thermal radical starter AIBN were provided by POLY-CHEM (Germany).

Evaluation of viscosity and molecular weight

The viscosity of the synthesized solvent-borne acrylic pressure-sensitive adhesive was determined with a Rheomat RM 189 from Rheometric Scientific with spindle No 3 at 23°C.

The molecular weight studies were performed in tetrahydrofuran with a liquid chromatography system LaChrom: RI Detector L-7490 and LaChrom UV Detector L-7400 from Merck-Hitachi, equipped with a PLgel 10⁶Å column from Hewlett-Packard.

Evaluation of residue monomer concentration

The residual monomers in the acrylic PSA synthesized in ethyl acetate and in dry coated self-adhesive layers were measured with a gas chromatograph Unicam 610, J&W DB-1 column, FID detector and integrator Unicam 4815. The same method for evaluation of residue monomers in acrylic PSA was used after different post-reaction times following polymerization.

Preparation of self-adhesive layers in the form of carrier-free acrylic films

For the measurement of tack, peel adhesion, shear strength and shrinkage, the synthesized PSA was cross-linked with 0.3 wt.% (according to polymer content) cross-linking agent AlACA and, after that, were coated with 30, 60, 90, 120 and 150 g/m² coat weight on a corona-treated 36 µm thick polyester film from Kalle Chemie (Germany) and dried in an oven for 10 min at 105°C. The dried acrylic films were protected with thick silicon paper (75 g/m²) from Laufenberg (Germany). Before the tests, the films were stored for 3 days at room temperature and 65% relative humidity.

Measurement of tack, peel adhesion, shear strength and shrinkage

The influence of residue acrylate monomers on pressure-sensitive adhesive properties, such as tack, peel adhesion, shear strength and shrinkage is determined by the AFERA (European Association for the Self Adhesive Tape Industry) standard.

Tack (acc. AFERA 4015). A sample of PSA-coated material 25 mm wide and 178 mm long is bonded to a vertical of clean steel test plate with at least 100 lineal mm in film contact. The vertical steel test plate is clamped in the jaws of a 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 per minute. Loop tack has the advantage of allowing for the use of wood substrates from Roholl (Germany).

Peel adhesion (acc. AFERA 4001). A sample of PSA-coated material 25 mm wide and 178 mm long is bonded to a horizontal target substrate surface of a clean steel test plate with at least 127 mm 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°. The free end is attached to the adhesion tester scale. The steel test plate is clamped in the jaws of a tensile testing machine, which is capable of moving the plate away from the scale at a constant rate of 300 mm per minute.

Shear strength (acc. AFERA 4012) is a measure at 20°C and at 70°C. Each test is conducted on an adhesive-coated strip applied to a standard stainless steel panel in such a manner that a 25 mm × 25 mm portion of the strip is in fixed contact with the panel, with one end of the strip free at a standard load of 10 N.

Shrinkage presents the percentage or millimetre change of dimensions of the PVC foil covered with PSA after PSA cross-linking, and attached to the glass after keeping it for 3 weeks at a temperature of 60°C. For acceptable application, shrinkage under 0.5% or 0.5 mm is necessary. Self-adhesive products with shrinkage greater than 0.3% or 0.3 mm are considered unacceptable or only partially acceptable in the adhesive industry.

Results and discussion

Evaluation of viscosity and molecular weight

The apparent viscosity, molecular weights (\bar{M}_w – average molecular weight, \bar{M}_n – average molecular weight number) and polydispersity (P_D) of acrylic PSA were respectively 11.3 Pa·s, and \bar{M}_w 614 000 D, \bar{M}_n 150 000, P_D 4.1. The synthesized acrylic PSA is relatively high molecular and shows a relatively small distribution of molecular weight.

Evaluation of residue monomer concentration

The residue monomer concentrations in synthesized acrylic PSA directly after polymerization are presented in table 1.

Table 1. Residue monomer concentration in synthesized acrylic PSA

Tabela 1. Stężenie nieprzereagowanych monomerów w otrzymanym poliakrylanowym kleju samoprzylepnym

Monomer <i>Monomer</i>	Concentration <i>Stężenie</i> [wt.%]	Percentage <i>Udział procentowy</i> [%]
IOA	2.9	27.4
2-EHA	2.5	23.6
BA	2.0	18.9
EA	1.6	15.1
MA	1.0	9.4
2-HEA	0.6	5.7
AA	0	0
Total <i>Suma</i>	10.6	100

The concentration of all residue monomers in the synthesized solvent-based acrylic PSA was relatively high (10.6 wt.%) and the exact concentration values of used acrylate monomers corresponded to their reactivity. Acrylic acid with an extremely high reactivity was not present in the synthesized PSA. To reduce the concentration of residue monomers after polymerization, post-reaction time was applied. The concentration of residue monomers over a 6 h post-reaction time is illustrated by fig. 1.

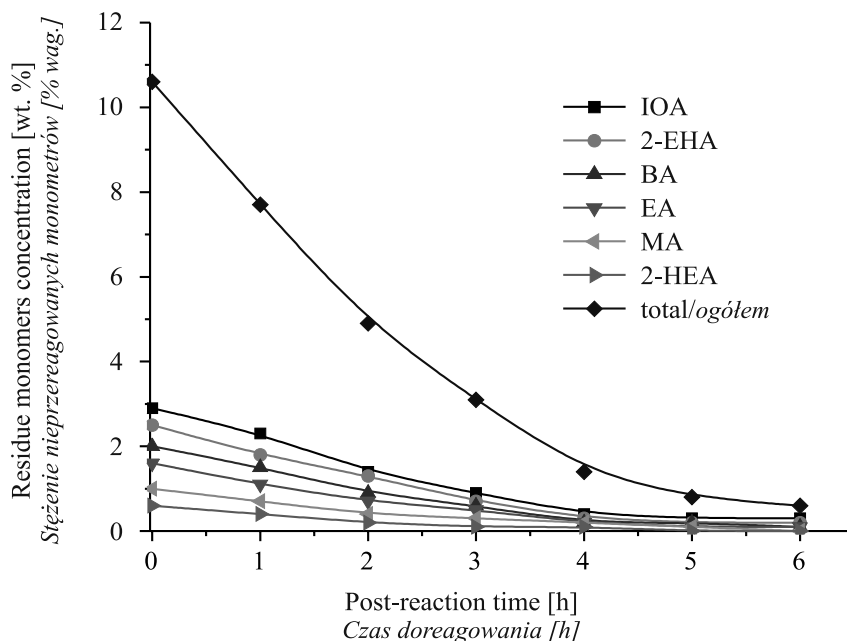


Fig. 1. Concentration of residue monomers as a function of post-reaction time
Rys. 1. Zależność stężenia nieprzereagowanych monomerów od czasu doreagowania

The post-reaction time after polymerization allows the reduction of residue monomers and improves the quality of self-adhesive products. After 1h of post-reaction time, the total measurement of residue monomers concentration attained 7.7 wt.%, after 3, 5 and 6h – 3.1, 0.8, and 0.6 wt.%, respectively. The decrease in total residue monomers concentration is dependent on the reactivity of the monomers. For example 2-hydroxyethyl-, methyl- and ethyl acrylates are more reactive than long chain butyl-, 2-ethylhexyl- and isooctylacrylates.

It was very interesting to investigate the influence of the drying time of solvent-based acrylic PSA, in the form of carrier-free self-adhesive, on the concentration of residue monomers as a function of drying time at a constant temperature and various coating weights of 30, 60, 90, 120 and 150 g/m² of the acrylic polymer films. This dependence is illustrated by fig. 2.

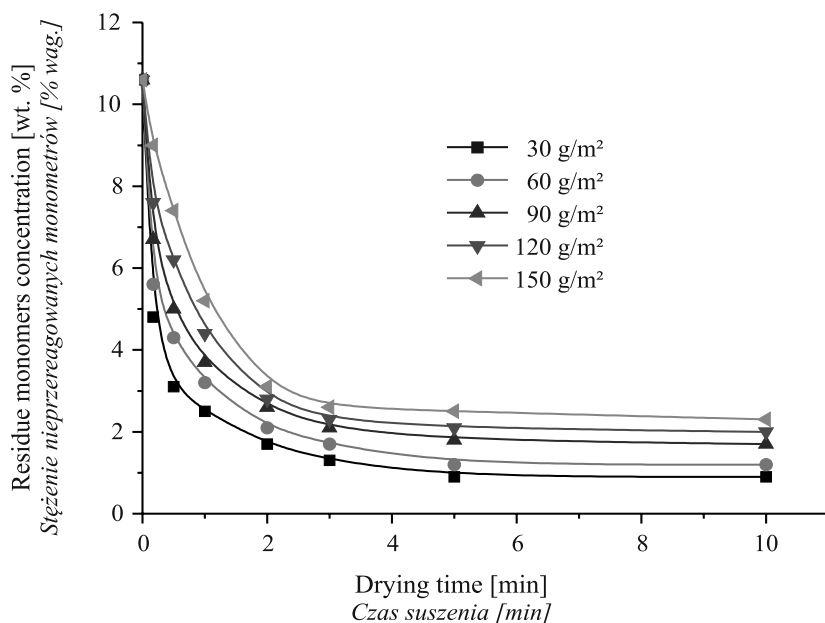


Fig. 2. Concentration of residue monomers as a function of drying time at 105°C for PSA layers with different coating weights

Rys. 2. Zależność stężenia nieprzereagowanych monomerów od czasu suszenia w temperaturze 105°C dla powłok samoprzylepnych o różnej gramaturze

The obtained results of the tested solvent-based acrylic PSA show that, at the same drying time, with an increase in the coating weight of PSA layers, the concentration of free acrylate monomers decreases. It is easier to dry thin PSA layers containing more polymerization medium and free monomers. An extension of the drying time to 10 min allows the reduction of free monomers at a relatively low level, between 0.9 wt.% for thick PSA layers with 30 g/m² and 2.3 wt.% for layers with 150 g/m² coat weight.

Influence of residue monomers on tack, peel adhesion, shear strength and shrinkage

The goal of this part of the experiment was to find the influence of free monomers concentration in acrylic pressure-sensitive layers on their main performance, such as tack, peel adhesion, shear strength and shrinkage and to find the most suitable solvent-based acrylic PSA systems, without the loss of their important properties.

The details of the investigations carried out for the tested PSA layers are presented in fig. 3–6 (the influence of free monomers on tack – fig. 3, peel adhesion – fig. 4, shear strength – fig. 5 and shrinkage – fig. 6).

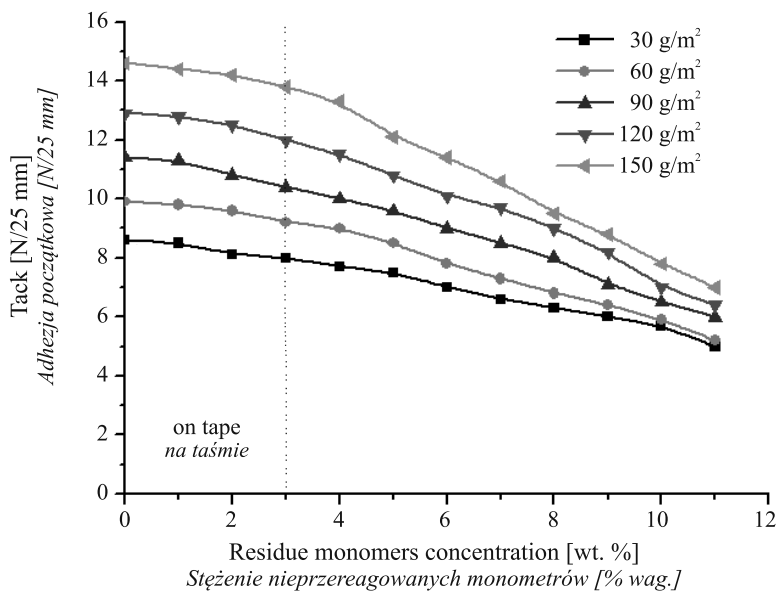


Fig. 3. Tack of self-adhesive tapes as a function of free monomers concentration

Rys. 3. Zależność adhezji początkowej samoprzylepnych taśm od stężenia wolnych monomerów

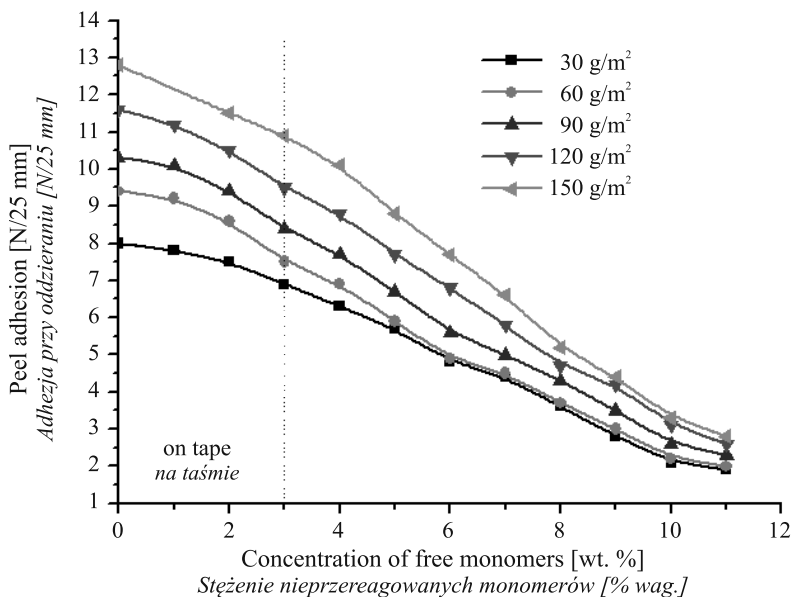


Fig. 4. Peel adhesion of self-adhesive tapes as a function of free monomers concentration

Rys. 4. Zależność adhezji przy oddzieraniu taśm samoklejących od stężenia wolnych monomerów

The best tack and peel adhesion values, dependent on the PSA layer coat weight, were observed when a 150 g/m² thick polymer layer was used. As figs. 4-5 show, the negative influence of free monomers on the tack and peel adhesion of self-adhesive tapes as a function of their thickness is more visible for tapes with a higher coat weight such as 150, 120 and 90 g/m², although in the area up to 3 wt.%, the decrease in tack is ignored and the reduction in the peel adhesion level is considered unacceptable for industrial application.

Typical shear strength resistance testing is performed with a controlled area of adhesive tape applied to a standard test surface. Because shear failure is the inability of the pressure-sensitive adhesive to resist continuous stress, any task that is a measure of stress relaxation within the adhesive gives meaningful data. A high shear resistant adhesive will maintain the stress, while a poor shear resistant adhesive will relieve the stress quite rapidly. Fig. 5 presents the shear strength of acrylic self-adhesive layers dependent on the free monomers concentration in the polymer layers.

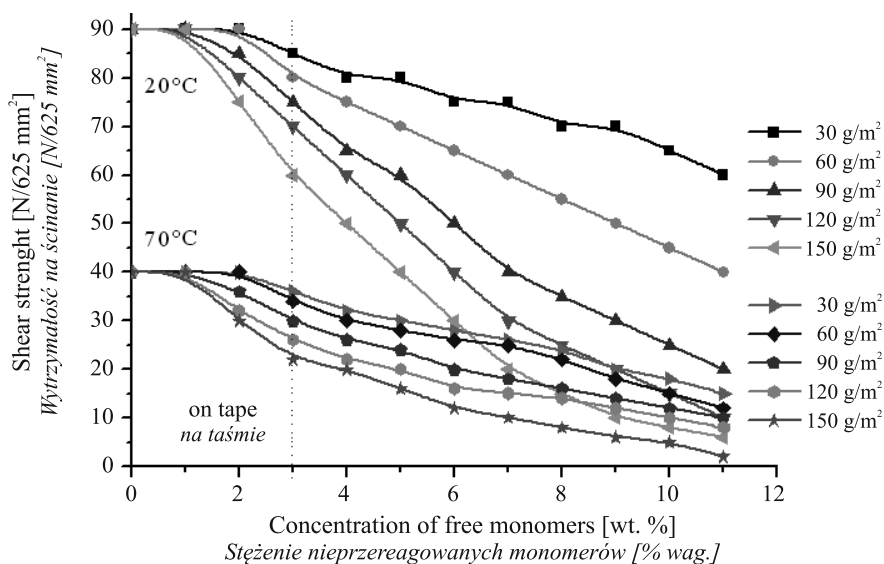


Fig. 5. Shear strength of self-adhesive tapes as a function of free monomers concentration

Rys. 5. Zależność wytrzymałości na ścinanie taśm samoprzylepnych od stężenia wolnych monomerów

As can be seen in fig. 5, the shear strength of 30 g/m² and 60 g/m² thick PSA layers tested at 20°C and 70°C stay at the same level until 2 wt.% of free monomers. Firstly, if the concentration of free monomers increases, the cohesion values are significantly reduced. Secondly, the free monomers concentration above 1 wt.% negatively influences other investigated PSA layers with 90, 120 and

150 g/m² coat weights. Among the tested PSA layers, the best shear strength level was observed for acrylic layers with a low coating weight.

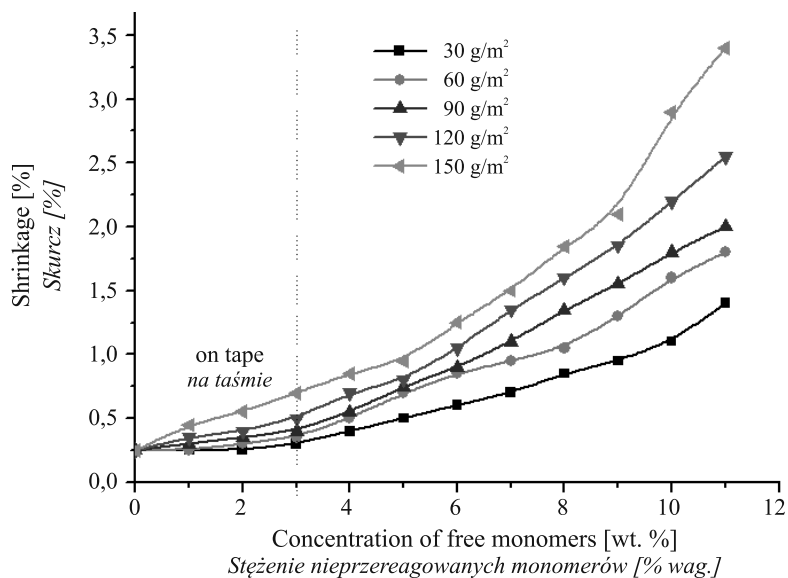


Fig. 6. Shrinkage of self-adhesive tapes as a function of free monomers concentration
Rys. 6. Zależność skurczu taśm samoprzylepnych od stężenia wolnych monomerów

Although acrylic polymers have been used successfully as pressure-sensitive adhesives in a variety of industries, a property inherent to all acrylic PSAs, which negatively impacts adhesion performance is shrinkage on different surfaces, for example wood, upon cross-linking. The shrinkage profiles of solvent-borne acrylic PSA dependent on free monomers content are shown in fig. 10. The best shrinkage results under 0.3–0.5% were achieved for self adhesive layers between 30 and 120 g/m² containing not more than approx. 2–3 wt.% of free monomers. The shrinkage run for a 150 g/m² coat weight self-adhesive layer containing more than 2 wt.% free monomers was completely unacceptable.

Conclusions

The investigations conducted concerning the synthesis of solvent-based acrylic PSA with a determination of the concentration of residue monomers (after the polymerization process, and after post-reaction time, and in prepared self-adhesive layers with different coating weights) have shown the following results:

1. The concentration of all residue monomers in synthesized acrylic PSA was relatively high, about 10.6 wt.%, and corresponded with their reactivity.

2. There is an influence of free monomers contents of solvent-based acrylic pressure-sensitive adhesives on a decrease in the mechanical properties of coated self-adhesive films such as: tack, peel adhesion, shear strength and shrinkage.
3. The use of acrylic PSA with a percentage of free monomers higher than 2-3 wt.% negatively influences all the evaluated properties of solvent-based acrylic PSA, especially the shear strength tested at 20°C and 70°C.
4. The synthesis of acrylic PSA containing less than 1 wt.% of free monomers, allows excellent tack, peel adhesion, shear strength and shrinkage performance to be reached.
5. The best results regarding the investigated properties were obtained for carrier-free films characterized by coat weights of 30 g/m² and 60 g/m² containing not more than 3 wt.% of residue monomers.
6. The unacceptable results with respect to the important evaluated properties are observed for thick PSA layers with 120 g/m² and 150 g/m² coating weights.

References

- Benedek I.** [2006]: *Developments in Pressure-Sensitive Products*, Edited by Taylor & Francis a CRC Press Book, New York, p. 126-167
- Bolitsky R. E., Hartman R. B.** [2001]: Veneer tape and method of use. Patent US 6,187,127 B1
- Czech Z.** [2001]: Solvent-based pressure-sensitive adhesives for PVC sign and marking films, *Journal of Applied Polymer Science*, 81[13]: 3212-3219
- Czech Z., Wesolowska M.** [2007]: Development of solvent-free acrylic pressure-sensitive adhesives, *European Polymer Journal*, 43 [8]: 3604-3612
- Gnanou Y., Fontanille M.** [2002]: *Organic and Physical Chemistry of Polymers*, Wiley-Interscience, New Jersey
- Mahdavi H., Taghizadeh S.M.** [2005]: The Effect of Alpha Hydroxy Acids on the Tack of Pressure-sensitive Adhesive. *Iranian Polymer Journal* 14 [4]: 379-385
- Pederson J. C.** [2003]: Adhesive measuring tape. Patent US 6,637,124 B2
- Skeist I., Miron J.** [1981]: History of Adhesives, *Journal of Macromolecular Science: Part A – Chemistry*, 15[6]:1151-1163
- Spratling M.** [2002]: Adhesive materials for flooring and methods of using same. Patent US 2002/0127374 A1
- Wicks Z. W., Jones F. N., Pappas S. P., Wicks D. A.** [2007]: *Organic Coatings*, Wiley-Interscience, New Jersey

List of standards:

AFERA 4015 Quick stick

AFERA 4001 Self Adhesive Tape. Peel adhesion of adhesive tape on stainless steel.

AFERA 4012 Self-Adhesive Tapes. Measurement of static shear adhesion

WPLYW NIEPRZEREAGOWANYCH MONOMERÓW NA WYBRANE WŁAŚCIWOŚCI POLIAKRYLANOWYCH KLEJÓW SAMOPRZYLEPNYCH

Streszczenie

Materiały samoprzylepne wytworzone na bazie polimerów akrylanowych, w tym poliakrylanowe kleje samoprzylepne (PSA) mają powszechne zastosowanie w przemyśle. Do szerokiej gamy materiałów samoprzylepnych zaliczamy taśmy samoprzylepne, stosowane przy montażu płyt kompozytowych w przemyśle meblarskim. Celem przedstawionych badań była synteza używanych w taśmach meblarskich rozpuszczalnikowych klejów samoprzylepnych na bazie poliakrylanów oraz zbadanie wpływu nieprzereagowanych monomerów na ich właściwości (kleistość, adhezja, wytrzymałość na ścinanie, skurcz). Najlepszymi właściwościami charakteryzowały się taśmy samoprzylepne w postaci filmów klejowych grubości 30g/m² oraz 60g/m², zawierających nie więcej niż 0.3% wagowych nieprzereagowanych monomerów.

Słowa kluczowe: kleje, PSA, poliakrylany, polimery, kleistość, adhezja przy oddzieraniu, wytrzymałość na ścinanie, skurcz