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Synthesis in extruder of UV-crosslinkable solvent-free acrylic pressure-sensitive adhesives

The present report is related to a process for producing the solvent-free acrylic pressure-sensitive adhesives (PSA) in the twin-screw extruder. New applications and technical specifications stimulate the continuous development of new methods of radical polymerization of solvent-free acrylics. New synthesis of 100% acrylic PSA includes polymerization in the extruder and production of pressure-sensitive adhesive tapes comprises a carrier layer having a thickness between 0.03 mm (30 g/m²) and 2.0 mm (2000 g/m²) and comprising of UV-crosslinked pressure-sensitive adhesive layers characterized by good performance.

Key words: acrylic PSA, solvent-free adhesives, polymerization, extruder, UV-crosslinking, tack, adhesion, cohesion

Synteza sieciowanych UV bezrozzpuszczalnych poliakrylanowych klejów samoprzylepnych w wyltaczarce

Przedstawiony raport opisuje proces wytwarzania bezrozzpuszczalnych poliakrylanowych klejów samoprzylepnych (PSA) w wyltaczarce dwuślimakowej. Nowa metoda otrzymywania bezrozzpuszczalnych poliakrylanowych klejów samoprzylepnych z wykorzystaniem procesu polimeryzacji radikalowej stwarza nowe możliwości zastosowania tego typu klejów. Syntezowane w dwuślimakowej wyltaczarce 100-proc. kleje samoprzylepne umożliwiają produkcję transferowych taśm samoprzylepnych o grubości pomiędzy 0,03 mm (30 g/m²) a 2,0 mm (2000 g/m²), które po usieciowaniu promieniowaniem UV charakteryzują się zespołem bardzo dobrych właściwości.

Słowa kluczowe: bezrozzpuszczalne samoprzylepne kleje poliakrylanowe, polimeryzacja, wyltaczarka, sieciowanie UV, tack, adhezja, kohezja

1. Introduction

Pressure-sensitive adhesives are being used for various products represented by adhesive tape, labels, protective and decorative foils [1]. Their functional characteristics like instantaneous adhesiveness, repeated adhesiveness, tackiness, etc. as well as their ease of adhesive work, and the applications are spreading in various directions. Together with the expanding applications for PSA, the capabilities required for PSA also are widening, and various types of PSA have been developed.

The desire to use PSA without having to deal with organic solvent has been with us almost as long as self-adhesive products have been in mass production [2]. The hot-melt types, dispersion types, and other technologies for non-solvent types PSA are being realised for a part of the applications for PSA. However, technologies for substitute solvent-free types of PSA in sectors requiring high performance in regard to weather

resistance or heat resistance have not been completed, and acrylic PSA of the solvent type continue to be used widely [3].

Hot-melt PSA, however, only achieved real practical significance in the 70 s with the appearance of thermoplastic rubber, the styrene-butadiene (SBS) and styrene-isoprene (SIS) block copolymers [4]. These thermally reversible or physically crosslinking products allow the formulation of hot-melt PSA with good processing performance. For this reason they represent an apparently promising advance in substitutes for rubber solutions. This order of magnitude is surprising as the qualitative demands on the adhesive can only be satisfied to a limited degree. There is no need here to describe in detail the typical disadvantages such as unacceptable temperature resistance or poor resistance to plasticizers.

The adhesives must frequently be subjected to the exigencies of the process in order to achieve the melt characteristics required. It is principally for this reason that hot-melt PSA based on SBS/SIS block copolymers



Figure 1. Twin-screw extruder qualified for polymerization process

Rysunek 1. Wylączarka dwuślimakowa użyta w procesie polimeryzacji

have not achieved the performance expected of them and are only able to substitute for rubber solutions in a limited field of application. According to BASF [5], they achieve a relatively small, but stable, market share.

Acrylics with self-adhesive properties have been well established among solvent-free pressure-sensitive adhesives (PSA) for long time because of their excellent properties and their aging stability. As an additional variation to the classical hotmelts, research and development in the PSA industry increasingly involves radiation-curable, hotmelt pressure-sensitive adhesives (HMPSA).

Photoinduced UV-crosslinking in polymer technology is a rapidly expanding technology on PSA area resulting from its main advantages such as solvent-free process, efficient and economical energy used new properties and quality of chemical crosslinking bonding [6-8].

From the three different manufacture processes:

- polymerization in the extruder with subsequent UV station for UV-crosslinking of PSA layer
- polymerization in the reactor with removal of the solvent and UV-crosslinking of the solvent-free PSA layer
- polymerization of syrup-kind PSA directly on the carrier

were tested in experiment polymerization in mass in the twin-screw extruder, available from SHJ-78H/high Performance Twin Screw Extruder with ZAMBELLO's GEAR-BOX/Italy (Fig. 1).

2. Experimental

The experiments were performed in order to study the diverse parameter such as acrylic acid content, radical starter concentration and the screw speed during the polymerization in the extruder, the viscosity, molecular mass, tack, adhesion, cohesion of PSA and on other important properties of polymerization process of acrylate monomers such as polymer yield and polymerization conversion.

During the UV-crosslinking process the conducted experiments have shown the relation between the UV-crosslinking time with constant irradiation strength and the conversion ratio for a fixed added of unsaturated photoinitiator, the relation between the thermal starter concentration and the conversion ratio under the various conditions, the screw speed according to performance of UV-crosslinked acrylics based on UV-crosslinkable solvent-free acrylic from extruder in form of PSA layer.

The main properties of crosslinked PSA layers such as tack, peel adhesion (adhesion) and shear strength (cohesion) of acrylic pressure-sensitive adhesives synthesised in extruder were tested according to international norm A.F.E.R.A. 4015 (tack), 4001 (adhesion) and 4012 (cohesion). Shrinkage of PSA layers after UV-crosslinking presents the percentage (S) or millimeter (l_p) change of dimensions of the foil covered with PSA and attached to the glass after keeping it 1 week in temperature of 70°C . The greatest attention was attached to the shrinkage parameter. With shrinkage greater than 0.5%, other properties were neglected.

3. Twin-screw extruder design

The twin-screw extruder is the most important mechanical element of a screw extruder. Its design directly determines the conveying, heating, melting, plasticizing, mixing, homogenizing, devolatilization, venting, degassing, dispersing, pressure development, and polymerization of the acrylate monomers to pressure-sensitive adhesive acrylics. Several types of twin-screw extruder are available for polymer processing. Each type presents unique requirements for screw design. According to the direction of screw rotation, twin-screw extruders are divided into corotating (both screws turn in the same direction) and counterrotating (screws turn in opposite directions, either into each other at the top or away from each other at the top). Twin-screw extruders are also used for bulk reactions of vinyl or acrylic monomers, various condensation and addition reactions [9-14].

4. Polymerization in the twin-screw extruder with subsequent UV-crosslinking

The objective of polymerization in the extruder is to produce solvent-free crosslinkable PSA acrylics, having a conversion rate above 97 to 98 % (residual monomer content < 2 to 3%), a mean molar mass $M_w >$

250 000 g/mol and a perfect optical quality (free of gel particles).

The first development work on using the extruder as the chemical reactor for polymerization was carried out some 60 years ago. A patent publication [15] describes a continuous process for the polymerization of acrylate monomers in a single or double screw extruder. A degree of transformation of 93 to 99% is achieved by suitable screw geometry and adjusting the temperature of the various zones of the extruder. The example given, however, does not cover a pressure-sensitive adhesive, the glass transition temperature (T_g) of the extrusion polymerizate being approximately 29°C.

European patent [16] describes continuous radical polymerization in a special reactor. An isooctyl acrylate/acrylic acid combination is mentioned in the description and in the examples.

It was proposed feeding the acrylate monomers into an extruder together with a starter and polymerizing it *in situ*. This would mean the viscose polymer being delivered from the extruder by way of a gear-wheel pump into a wide-slot nozzle, applied to a web and being cured by UV radiation. An elegant solution at first glance, but, as we soon discovered, also the solution with the most chemical and process-engineering traps.

5. Bulk polymerization in extruder and influence of technical parameters like screw speed

The experiment was carried out in a double-screw extruder available from SHJ-78H/high Performance Twin Screw Extruder with ZAMBELLO's GEAR-BOX/Italy with eight heatable zones including a degassing zone, with it being possible to adjust the speed of the screws and the temperatures in the various zones in a wide range. The polymerization process was carried out with a monomers mixture selected of 79.0 parts 2-ethylhexyl acrylate (2-EHA), 15.0 parts methyl acrylate (MA) 5.0 parts acrylic acid (AA), 1.0 part 4-acryloyloxyethoxy benzophenone (AEBP) and 0.5 part of thermal initiator 2,2'-azo-diisobutyronitrile (AIBN) as the basic recipe.

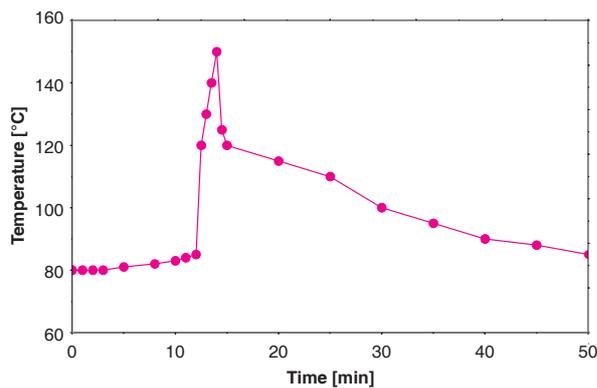


Figure 2. Curve of an uncontrolled substance acrylate polymerization

Rysunek 2. Krzywa niekontrolowanej polimeryzacji substancji akrylanowej

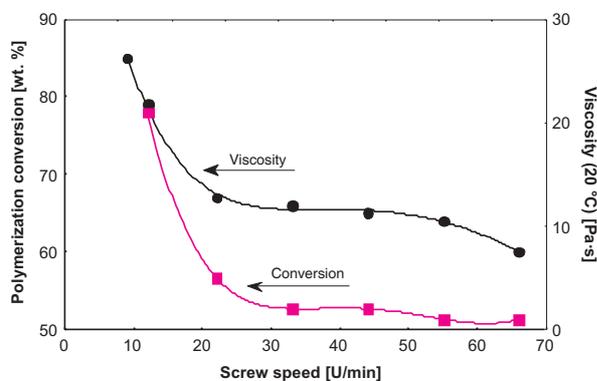


Figure 3. Polymerization conversion and viscosity dependence on screw speed

Rysunek 3. Zależność przebiegu polimeryzacji i lepkości od prędkości ślimaka

In the case of substance polymerization, acrylate monomers are polymerized without solvents (Fig. 2).

Despite several polymerization techniques, the dissipation of the emitted polymerization heat from a technical point of view is extremely difficult. An uncontrolled heat build-up can occur due to a gel effect. The local overheating during polymerization leads to extreme cases to degradation or eventually to discolouration of the polymers.

The variable technical parameters are screw speed and the length of the extruder zone. As was to be anticipated, the polymerization yield and the viscosity of the

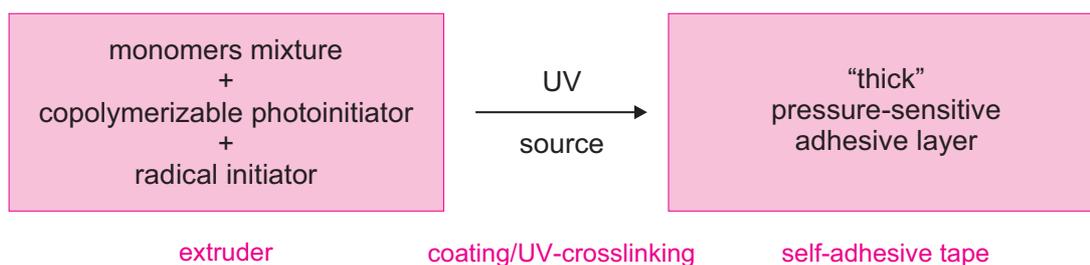


Figure 4. Components and factors to manufacturing "thick" pressure-sensitive adhesives

Rysunek 4. Materiały i czynniki prowadzące do otrzymania klejów samoprzylepnych

PSA produced declines with increasing screw speed as the reaction time actually available decreases (Fig. 3).

Shortening the extruder by two zones and higher zone temperatures has no significant effect on the polymerization yield. It remained in the range from 70 to 80%. The best results of the polymerization yield and viscosity of PSA were achieved with the screw speed of 5 rpm. The greatest weakness in the system was the degassing zone which did not permit the greatest possible removal of the residual monomers.

An interesting variation to manufacture thick PSA layers between 30 and 2000 g/cm² is a process by which the extruder pressure-sensitive adhesive bulk reaches its final cohesion under UV light (Fig. 4).

5.1. Influence of the acrylic acid amount and the starter concentration

They are investigated the effect of acrylic acid and thermal initiator AIBN amount of polymerization conversion, viscosity, and molecular mass of synthesized PSA acrylics.

Starting from this basis the acrylic acid content has been varied and so the quantity of starter, with the temperatures of the various zones and the screw speed being set as follows:

- Temperatures from zone 1 to zone 8: 90/90/90/100/100/110/120/120°C
- Screw speed: 5 rpm

The influence of starter AIBN and acrylic acid content on the mentioned properties such as polymerization conversion and viscosity are presented in Figs. 5 and 6.

As expected, the increase of AIBN content affects positively the polymerization conversion. The viscosity shows a maximum for about 0.4 wt % of AIBN.

The increase of acrylic acid content generally has a positive influence on shrinkage. The value of polymerization yield stayed on the same level.

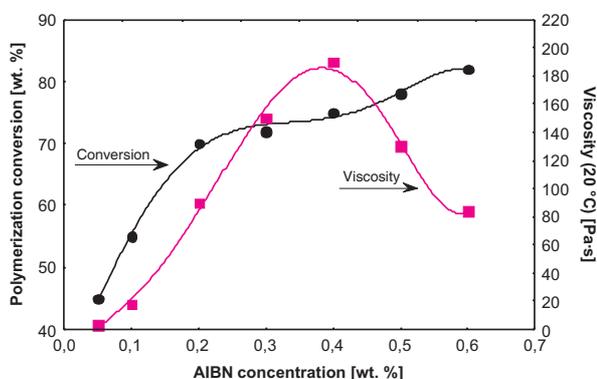


Figure 5. Effect of AIBN amount on polymerization yield and viscosity
Rysunek 5. Wpływ ilości AIBN na wydajność polimeryzacji i lepkość otrzymanego produktu

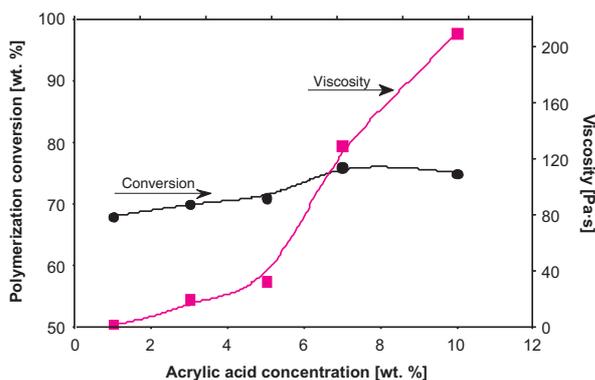


Figure 6. Effect of acrylic acid amount on polymerization yield and viscosity
Rysunek 6. Wpływ ilości kwasu akrylowego na wydajność polimeryzacji i lepkość otrzymanego produktu

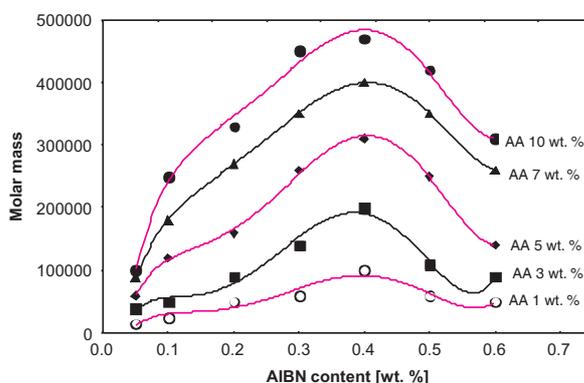


Figure 7. Influence of AIBN and acrylic acid concentration on molecular mass of PSA
Rysunek 7. Wpływ stężenia AIBN i kwasu akrylowego na masę cząsteczkową PSA

The effect of AIBN and acrylic acid amount on molecular mass of polymerized in extruder PSA was showed in Fig. 7.

The increase of acrylic acid content and increase of initiator AIBN content has a beneficial effect on molecular mass of synthesized PSA acrylics. The PSA with high molecular mass were polymerized with 10 wt. % of acrylic acid and about of 0.4 wt % of AIBN.

5.2. UV-crosslinking of extruder polymerizates

Industrial applications of UV crosslinkable materials have grown tremendously over the past decade. An entire industry has evolved based on the existence of chemicals which respond to UV light. The growing success of UV crosslinking technologies in a wide variety of industrial products and processes can be attributed to the productivity and environmental benefits that result from such technologies.

As basic model acrylic polymer a polymerizate has been selected with the highest molar mass ($M_w = 476\ 000$ g/mol) determined during the series of experi-

ments. Although it was possible to crosslink this material 60 g/m^2 thick with UV radiation with UV lamp AKTIPRINT-mini 18-2 from Technigraf (Germany) with UV-A wavelength between 315 do 400 nm and a constant UV dose of 600 mJ/cm^2 between 30 s and 2.5 minutes, especially 3 minutes UV-crosslinking time. The UV-exposure can be measured using an integrating radiometer Dynachem™ Model 500, available from Dynachem Corporation, 2631 Michelle Drive, Tustin, CA 92680.

The result was far from being an acceptable coat of pressure-sensitive adhesive. The odour of residual monomers and the unacceptable ultimate elongation, which can be attributed to the embrittlement of the adhesive coat as a consequence of excessive UV curing, contributed to this.

The results of tested tack, adhesion and cohesion are presented in Figs. 8 and 9.

The crosslinked PSA with high molecular mass and high viscosity gives the PSA the high level of cohesion performance after UV-crosslinking.

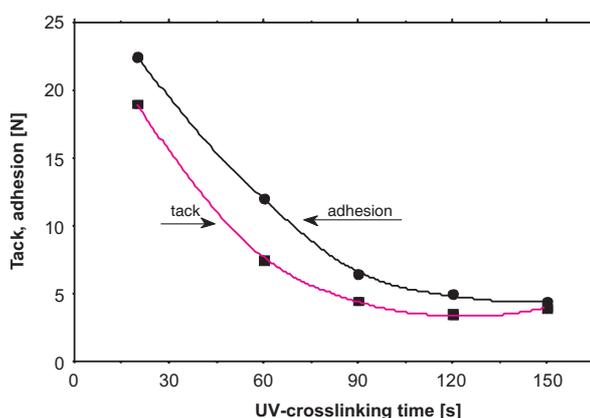


Figure 8. Tack and cohesion of UV-crosslinked extruded acrylic PSA

Rysunek 8. Tack i kohezja sieciowanych UV wytłaczanych poliakrylanowych PSA

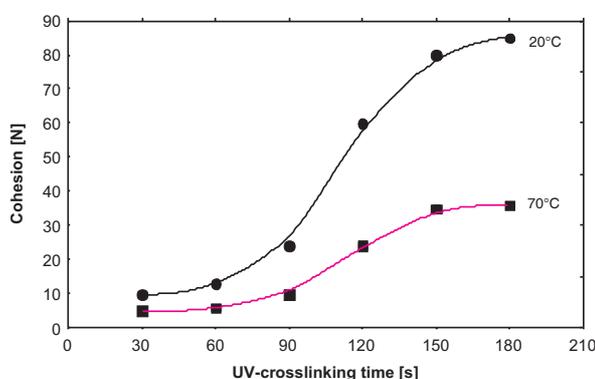


Figure 9. Cohesion of UV-crosslinked extruded acrylic PSA

Rysunek 9. Kohezja sieciowanych UV wytłaczanych poliakrylanowych PSA

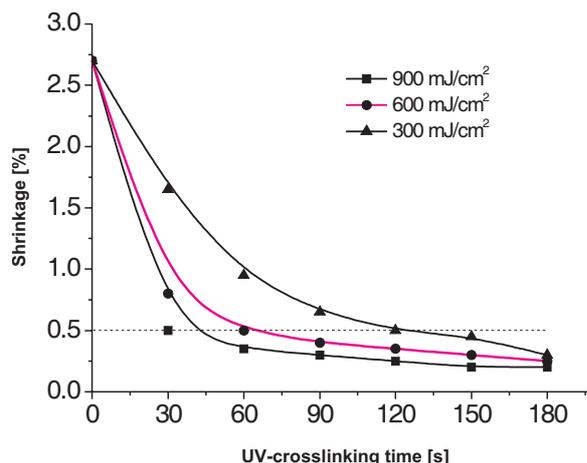


Figure 10. Shrinkage of UV-crosslinked extruded acrylic PSAs as function of UV-crosslinking time and UV-dose

Rysunek 10. Skurcz sieciowanych UV wytłaczanych klejów akrylowych w funkcji czasu sieciowania i dawki UV

The photoreactive UV-crosslinkable solvent-free acrylic PSA synthesized in extruder were cast with a knife coater on the siliconized paper with 60 g/m^2 dry adhesive coat weight. The coated PSA layer on siliconized paper was UV-crosslinked using UV lamp emitted UV-dose of 300, 600 and 900 mJ/cm^2 and after crosslinking applied on to the PVC film. The influence of the UV-crosslinking time on shrinkage of the synthesized solvent-free acrylic PSA layers is described in Fig. 10.

As expected, the increase of the UV-crosslinking time and UV-dose corresponds with the decrease of shrinkage of investigated acrylic PSAs.

Up to 30 s crosslinking time by 900 mJ/cm^2 and up to 60 s crosslinking time by 600 mJ/cm^2 the shrinkage values of 0.5 % was observed. By the UV-dose 300 mJ/cm^2 for UV-crosslinking time of 120 s the shrinkage level dropped under 0.5 %.

6. Outlook

There are numerous examples of competing systems in nature not necessarily implying the extinction of one variant. The candle, for instance, still retains its niche despite the invention of the electric bulb. We cannot, therefore, expect, and nor would it be practicable or reasonable, that acrylate hot-melt pressure-sensitive adhesives decline into “old junk” as established raw material and/or production process. Producers of adhesive tape are also subject to the second principle of thermodynamics, the law of entropy, and other laws of Nature. And they will modify the, initially so promising, progress of new raw materials or innovative methods to a marginal improvement, or sometimes no improvement at all.

UV crosslinkable acrylate adhesives are certainly an alternative worth considering for companies having no machinery of their own for coating adhesives con-

taining solvents. They would be up-to-date, almost by the back door route, with pseudo-solvent acrylate pressure-sensitive adhesives, as long as the chemistry is correct.

UV polymerized, thick acrylate hot-melt pressure-sensitive adhesive coatings crosslinked on the substrate are generating excitement about their properties, the only problem being that the market for them is characterized by a high barrier to entry. In addition, the company would be looking at a risky and expensive development, including a production plant which is yet to be designed. Small and medium sized adhesive tape companies will be overstretched by this.

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