Manufacturing of solvent-free acrylic pressure-sensitive adhesives in form of self-adhesive layers

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ABSTRACT

The present publication is related to a process for producing the non-solvent acrylic pressure-sensitive adhesive (PSA). New applications and technical specifications stimulate the continuous development of new methods of polymerization of solvent-free acrylics. New synthesis of solvent-free acrylics includes polymerization in the reactor with removal of the solvent and polymerization of the carrier. The polymerization process is connected with UV-crosslinking.

Keywords: pressure-sensitive adhesive; acrylics; polymerization; solvent-free; UV-crosslinking

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 including 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 realized 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, 14-17].

Thermoplastic 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. There is no need here to describe in detail the typical disadvantages such as unacceptable temperature resistance or poor resistance to plasticizers [5].

The ideal would be to link the proven good PSA properties of acrylic PSA produced or formulated in solvents (including water) with solvent-free acrylic adhesive systems. Acrylic pressure-sensitive adhesives which are UV-crosslinked or which are polymerizable on the carrier suggest them here.

Photoinduced UV-crosslinking 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 [6-10].

Three different manufacture processes were tested in experiment like polymerization in the extruder with subsequent UV-crosslinking, polymerization in the reactor with removal of the solvent and UV-crosslinking of the solvent-free PSA or polymerization of syrup-type PSA directly on the carrier.

The first development work on using the extruder as the chemical reactor for polymerization was carried out some 60 years ago. A patent publication [11] 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 [12] describes continuous radical polymerization in a special reactor. An isooctyl acrylate/acrylic acid combination is mentioned in the description and in the examples.

2. EXPERIMENTAL

The following experiments were conducted in order to study the diverse parameter such as acrylic acid content, radical starter concentration and 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 such as polymer yield and polymerization conversion.

In the case of polymerization in the reactor with removal of the solvent the conducted trials have shown comparison of various acrylic hot-melt PSA, influence on web speed at 40 and 120 g/m². The UV-crosslinking of hot-melt PSA were compared with a conventional acrylic dispersion.

During the polymerization process on carrier the conducted experiments have shown the relation between the UV energy with various irradiation strength and the conversion ratio for a fixed added amount of photoinitiator, the relation between the number of UV irradiation passes and the conversion ratio under the various conditions, the web speed vs. coat weight and coating efficiency of UV-crosslinked acrylics based on UV polymerizable syrup.

2-Ethylhexyl acrylate, acrylic acid and 2,2'-azo-diisobutyronitrile are available from BASF (Germany), the unsaturated photoinitiator 4-acryloyloxy benzophenone (ABP) is available from Chemtec Company (Germany).

The viscosity of synthesized in extruder PSA was measured with viscometer RM 180 Rheomat from Rheometric Scientific Company. Their molecular mass was determined with HPLC-System with Isocratic Pump & DRI-Detector from HP Company.

Tack, adhesion and cohesion of investigated acrylic pressure-sensitive adhesives were tested according to A.F/E.R.A. 4015 (tack), 4001 (adhesion) and 4012 (cohesion).

2. 1. Polymerization in the extruder with subsequent UV-crosslinking

The objective of polymerization in the extruder is to produce solvent-free crosslinkable acrylic PSA, having a conversion rate above 97-98 wt. % with residual monomer content lower than 2-3 wt. %, characterized by molecular mass $M_w > 250\,000$ Dalton.

Influence of technical parameters like screw speed

The experiment was carried out in a double-screw extruder from the Leistritz Company (Nürnberg) 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 94.0 parts 2-ethylhexyl acrylate (2-EHA), 5 parts acrylic acid (AA), 0.5 parts 4-acryloyloxy benzophenone (ABP) and 0.5 parts of thermal initiator 2,2'-azo-diisobutyronitrile (AIBN) as the basic recipe.

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 PSA produced declines with increasing screw speed as the reaction time actually available decreases (Fig. 1).

Fig. 1. Polymerization conversion and viscosity dependence of screw speed.

Changing the extruder by two zones and higher zone temperatures has no significant effect on the polymerization yield. It remained in the range from 70-80wt.%. 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.

Influence of the acrylic acid amount and the starter concentration

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:

- Temperature of zones 1-8: 90/90/90/100/100/110/120/120 °C

- Screw speed: 5 rpm

The influence of starter AIBN and acrylic acid content on the investigated properties such as polymerization conversion and viscosity are presented in Figs. 2-3.

Fig. 2. Effect of AIBN amount on polymerization yield and viscosity.

As expected, the increase of AIBN concentration affects positively the polymerization conversion. The viscosity shows a maximum for about 0.4 wt % of AIBN (Fig. 2).

Fig. 3. Effect of acrylic acid amount on viscosity and polymerization yield.

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

The effect of AIBN and acrylic acid amount on molecular mass of polymerized in extruder PSA was showed in Fig. 4.

Fig. 4. Influence of AIBN and acrylic acid concentration on molecular mass of PSA.

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.

UV-crosslinking of extruder polymerizates

As a suitable model polymer the polymerizate has been selected with the highest molecular mass ($M_w = 476\,000$ Dalton) determined during the series of experiments. Although it was possible to crosslink this material 1000 μm thick with UV radiation with UV lamp U 350 M-I-DL from IST Company with UV-A wavelength between 315 do 400 nm and a constant UV dose of 800 mJ/cm^2 between 30 s and 3 minutes.

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. 5-6

Fig. 5. Tack and cohesion of UV-crosslinked extruded acrylics PSA.

Fig. 6. Cohesion of UV-crosslinked extruded acrylics PSA.

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

Evaluation of the results

We were not able to obtain a useable, polyacrylate-based pressure-sensitive adhesive by mass polymerization in the extruder, which would satisfy the normal requirements for a pressure-sensitive adhesive tape. The substantial drawbacks were as follows:

Gel particle content

Because of the significant heat of the reaction in mass polymerization of the acrylate, it is almost impossible to adjust the temperature precisely, or at least this can only be done with difficulty, which leads to the formation of gels and products of degradation.

Residual monomer content

The holding time, expressed by the speed of the screw, in the extruder can only be adapted to the polymerization process with some difficulty. De facto this means too short a reaction space and hence an unacceptable reaction time. On the other hand, extending the extruder does not guarantee the secondary reaction and thus the reduction of the amount of residual monomer. The integrated degassing zone also ensures that removal of the residual monomers is incomplete.

2. 2. Polymerization in the reactor with removal of the solvent

Polymerization takes place in the organic solvent (e.g. ethyl acetate, petrol, acetone, toluene), with a covalent photoinitiator being incorporated into the polymer chain during polymerization. The polymerization medium is then removed under a vacuum. The resultant polymerizate is then, in a manner similar to a classical hot melt, coated at high temperature and crosslinked in seconds or minutes with UV radiation. This concept is based on tried and tested techniques and comes with the least risks. However, it is built on a pseudo-hot melt pressure-sensitive adhesive, since solvents are indeed used. The significant point is that there is the advantage that, by contrast to the mild, slow drying process in adhesive tape coating, large quantities of solvent are rapidly driven from the adhesive material, which can then be processed like a hot melt. The solvent removed, naturally, be used again for the polymerization process [13].

As a standard, a pressure sensitive adhesive acrylic has been polymerized with the following composition:

2-Ethylhexyl acrylate (2-EHA)	- 94 wt. %
Acrylic acid (AA)	- 5 wt. %
Thermal starter (AIBN)	- 0.5 wt. %
Unsaturated photoinitiator (ABP)	- 0.5 wt. %

in ethyl acetate with 50 wt. % polymer content.

Once ethyl acetate is removed, there remains a non-volatile, solvent-free highly viscous material, which can be processed on a hot-melt coating machine at temperatures of between 100 and 120 °C.

The procedure is as follows in order to obtain useful values on the performance of such adhesives:

- single-sided coating of polyester film (8 µm) in the range of 40-120 g/m² with constant UV radiation and varying coating rates
- production of a typical double-sided adhesive tape (with paper substrate) for medium-weight use at varying coating rates and constant radiation dose.

Working conditions: Extruder
Wide slot nozzle
UV radiation lamp from IST Company

An initial screening revealed that apart from the own polymerizate (HM1) and the hot-melt pressure-sensitive adhesives from a manufacturer of adhesive raw materials well-known in the market-place (HM 2) were worthy of further examination (Tab. 1).

Working process: Wide slot nozzle
 Backing: 12 pm PETP-fail
 Liner: siliconized paper
 Coat weight: 60 g/m²
 Web speed: 5 m/min

Table 1. Comparison of various acrylate hot-melt pressure-sensitive adhesives

Type	Tack [N]	Adhesion [N]		Cohesion [N]	
		20 °C	70 °C	20 °C	70 °C
HM 1	11.5	12.5	5.5	8.0	2.0
HM 2	12.0	11.5	5.0	6.0	2.0
HM 3	6.0	8.0	4.0	10.0	1.0
HM 4	3.5	7.0	3.0	1.0	5.0
HM 5	2.0	7.0	2.5	7.0	5.0

The limits of the bond-coat weights were determined and the crosslinking rates using the own synthesized Products HM 1. These were 60 g/m² and 120 g/m² and between 5 and 20 m/min (Fig. 7). Adhesion at 20 °C and cohesion at 70 °C for UV-crosslinked hot-melt PSA acrylics were tested.

Fig. 7. Influence of web speed at 60 g/m² and 120 g/m² coat weight on adhesion and cohesion.

It was determined that, within the various test groups (mass application/coating rate) the adhesive power at 20 °C with increasing coating rate and the cohesion decreases with increasing of web speed on the coating machine.

The performance at higher temperatures however showed typical weaknesses of a hot-melt. The UV-crosslinking was not able to make any improvement in this.

The adhesion properties of a double-sided adhesive tape, coated with a UV crosslinked acrylate hot-melt pressure-sensitive adhesive are respectable and encouraging by comparison with a conventional adhesive tape, as the Table 2 shows.

Table 2. Adhesion properties of UV-crosslinked hot-melt pressure-sensitive adhesive

Tape	Web speed [m/min]	Tack [N]	Adhesion [N]		Cohesion [N]	
			20 °C	70 °C	20 °C	70 °C
A	10	12.5	26.5	16.5	60	25
B	10	11.5	28.0	14.5	45	<5

CH – Cohesive failure

A Experimental product
 $2 \times 60 \text{ g/m}^2$ UV crosslinked
 12 g/m^2 paper substrate
 90 g/m^2 silicon paper liner

B Standard adhesive tape
 $2 \times 60 \text{ g/m}^2$ UV crosslinked
 12 g/m^2 paper substrate
 90 g/m^2 silicon paper liner

The UV-crosslinked hot-melt acrylics have very good tack, adhesion and cohesion at room and at higher temperatures. The increase of temperature decrease a little bit their adhesiveness and cohesive performance. In the case of PSA acrylic dispersions their performance at higher temperatures are on the very small unacceptable level.

2. 3. Polymerization of the carrier

In the case of polymerization is shifted from the extruder to the substrate web, in that acrylate monomers recipe made as a coating compound are polymerized by UV radiation with the exclusion of oxygen.

The UV-polymerization and UV-crosslinking behavior will be treated from the change of the conversion ratio when photoinitiator is added to the syrup-PSA and actual UV radiation is performed and the molecular mass of the formed polymer.

Fig. 8 shows the relation between the UV energy with various irradiation strengths and the conversion ratio for a fixed addition amount of photoinitiator 4-acryloyloxy benzophenone (ABP). Here, the UV irradiation was performed with covering of the irradiation surface by a polyester foil separator to shut out oxygen.

Fig. 8. Relation between the estimated UV light amount and the conversion ratio.

The polymerization ratio in the UV-polymerization and UV-crosslinking processes is based on the general radical polymerization reaction theory, and it is influenced widely by the amount of radicals generated per unit of time. As a result, a high UV intensity is effective from the point of view of productivity, as it reduces the time required for polymerization and photocrosslinking, but it means a lowering of the adhesive performance, as the molecular mass of the formed polymers decrease.

Next, the crosslinking behavior will be compared for the case when the UV irradiation surface is covered with polyester foil separator and when the UV irradiation atmosphere is changed to an oxygen concentration of 5 wt. % and 1 wt. % respectively by nitrogen substitution. Fig. 9 shows the relation between the number of UV irradiation passes and the conversion ratio under the various conditions.

With an oxygen concentration of 5wt.%, the polymerization and photocrosslinking speed and the molecular mass of the formed polymer both drop widely in comparison to the method with covering with a polyester foil, but with an oxygen concentration of 1 wt. %, the drop is small and it is in the range which can be realized. From this it can be said that at the time of adhesive tape manufacture it is required to either to cover the UV irradiation surface with a polyester foil separator or similar or to perform UV irradiation in an atmosphere with an oxygen concentration of 1 % or less by substitution of nitrogen or similar.

Within approximately one to two minutes (approximately 1000 g/m² coat weight) under these conditions, polymerization is complete, the end stage of which being characterized by a molecular mass such as we are familiar with from solvent polymerization. This is the decisive physical and chemical advantage of this method that does not depend on the molecular mass of the pressure-sensitive adhesive with respect to the process technology.

Fig. 9. Influence of the oxygen amount on the crosslinking behaviour.

Complete freedom from solvents, a further plus point, is, however, counteracted by a relatively high residual monomer content and block coarsening that can only be achieved to a limited extent, indispensable for some applications. By contrast with UV crosslinking which takes only seconds, UV polymerization takes up to two minutes, but at least ten times as long? On the other hand, UV polymerization is more or less independent of the coating thickness of the PSA which means that it is best suited above all for thick coats.

Fig. 10. Web speed vs. coat weight.

The coating costs are derived from the costs per operating hour. A coating rate of 10 m/min can still be assumed up to 1 200 g/m²; fewer than 150 g/m², the coating rate for UV curing is restricted to 80 m/min. In the case of UV polymerization, the dependence of the coating rate on the coat weight is, as anticipated, considerably less marked, as is shown by the bar chart below (Fig. 10).

The coating costs can be derived from this (Fig. 11).

Fig. 11. Coating costs as a function of coating weight.

3. CONCLUSION

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. 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 acrylic adhesives are certainly an alternative worth considering for companies having no machinery of their own for coating adhesives containing 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 acrylic hot-melt pressure-sensitive adhesive coatings created 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.

One unrestrictedly positive aspect is that solvent-free acrylic adhesives are not only in harmony with the increasing concerns for the environments, but they even make a decisive contribution to reducing the strain on the environment because of their omission or almost one hundred percent re-use of solvents.

References

- [1] I. Benedeck, L. J. Heymans., *Pressure-sensitive adhesives technology*, New York: Marcel Dekker Inc., 1997.
- [2] Z. Czech, *Crosslinking of acrylic pressure-sensitive adhesives*, Szczecin Politechnika, Szczecinska, 1999.
- [3] R. Milker Z. Czech, A. Butwin, U. Gluch, E. Madejska, *Coating* 3 (2010) 26-28.
- [4] M. Dupont, C. Mayenez, *Adhäsion* 3 (1989) 22-27.
- [5] K. H. Schumacher, U. Düsterwald, B. Mayer-Roscher, 2. *Münchener Klebstoff- und Veredelungsseminar*, München, Oktober (1998) 112-117.
- [6] Z. Czech, A. Kowalczyk, J. Kabatc, J. Świdarska, *European Polymer Journal* 48 (2012) 1446-1454.
- [7] Z. Czech, A. Kowalczyk, K. Górka, U. Gluch, L. Shao, *Polish Journal of Chemical Technology* 14(3) (2012) 83-87.
- [8] Z. Czech, F. Herrmann, *Patent DE 42 15 148* (1992) Lohmann GmbH & Co. KG.
- [9] Z. Czech, *Patent DE 195 01 025* (1995) Lohmann GmbH & Co. KG.
- [10] Z. Czech, W. Blum, *Patent DE 44 06 977* (1994) Lohmann GmbH & Co. KG.
- [11] N. Matsuoka, H. Matsumoto, *Patent DE 33 05 727* (1983) Nitto Electric Industrial.
- [12] S. Plamthottam, E. W. McFeeters, *US Patent 5,100,728* (1990) Avery Dennison Corporation.
- [13] Z. Czech, *Kautschuk und Kunststoffe* 10 (2002) 492-501.
- [14] Zbigniew Czech, Agnieszka Kowalczyk, Dominika Sowa, *International Letters of Chemistry, Physics and Astronomy* 1 (2013) 63-69.
- [15] Zbigniew Czech, Dominika Sowa, Jagoda Kowalska, *International Letters of Chemistry, Physics and Astronomy* 3 (2013) 21-28.
- [16] Zbigniew Czech, Agnieszka Kowalczyk, Dominika Sowa, Jagoda Kowalska, Paulina Ragańska, *International Letters of Chemistry, Physics and Astronomy* 8(1) (2013) 49-56.
- [17] Zbigniew Czech, Dominika Sowa, Jagoda Kowalska, Paulina Ragańska, *International Letters of Chemistry, Physics and Astronomy* 8(1) (2013) 57-65.