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Thermal degradation of photoreactive solvent-free acrylic pressure-sensitive adhesives based on 2-ethylhexyl acrylate

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ABSTRACT

The thermal degradation of photoreactive acrylic self-adhesives (PSAs) containing 99,5 wt.% of 2-ethylhexyl acrylate (2-EHA) and 0,5 wt.% unsaturated photoinitiator 4-acryloyloxy benzophenone (ABP) has been performed at 250°C. The type and amount of the pyrolysis products give important information about the mechanism of thermal degradation of this kind of photoreactive PSAs. It was evaluated using GC-analysis that during the thermal degradation of PSAs based on 2-ethylhexyl acrylate such main thermal decomposition products as 2-ethylhexen-1, 2-ethylhexanol-1, and 2-ethylhexyl (meth)acrylate were formed.

Degradacja termiczna fotoreaktywnych klejów poliakrylanowych na bazie akrylanu 2-etyloheksylu

STRESZCZENIE

Przeprowadzono termiczną degradację fotoreaktywnych poliakrylanowych klejów samoprzylepnych zbudowanych z 99,5 % wag. akrylanu 2-etyloheksylu (2-EHA) oraz 0,5 % wag. nienasyconego fotoinicjatora 4-akryloilooksybenzofenonu (ABP) w temperaturze 250°C. Na podstawie otrzymanych produktów termicznej degradacji przedstawiono możliwy model termicznej degradacji badanych fotoreaktywnych klejów samoprzylepnych. Korzystając z pomocy chromatografii gazowej stwierdzono obecność takich pirolitycznych produktów, jak 2-etyloheksen-1, 2-etyloheksanol-1 oraz (met)akrylan 2-etyloheksylu.

1. INTRODUCTION

Conventional solvent-borne acrylic pressure-sensitive adhesives (PSAs) are generally copolymers of C_4-C_8 alkyl acrylates and polar monomers, such as acrylic acid. Optionally, modifying monomers like methyl, ethyl, butyl acrylate or vinyl acetate may also be incorporated in the copolymer structure during polymerization process. Optimum cohesive and adhesive properties of the copolymers are attained by a proper balance of its molecular mass (usually very high), polarity, and the glass transition temperature ranging from -25 to -70°C . The conventional acrylic PSAs are generally applied onto the desired substrates as solvent-borne or water-borne layers and subsequently dried. However, on account of solvent and energy costs, time consumption in the drying process, and constraints imposed by environmental pollution regulations, the relevant role plays the solvent-borne pressure-sensitive adhesives. The new generation acrylic PSAs are solvent-free photoreactive UV-crosslinkable adhesives.

Photoreactive solvent-free acrylic pressure-sensitive adhesives are synthesized in organic solvents as viscoelastic polymers with permanent tack (initial adhesion) and the balance of two properties adhesion (peel adhesion) and cohesion (shear strength) [1]. Solvent have to be evaporated in order to get solvent-free PSAs from synthesised solvent-borne PSAs. Removing of polymerization medium was conducted under a vacuum at high temperature after the polymerization is finished. After evaporation, solvent can be turned back to the process circulation and used again for polymerization. PSA deprived of organic solvent can follow polymerization in a reactor, in a thin layer evaporator, or in extruder. An evaporator or an extruder use does not guarantee manufacturing of photoreactive hot-melt with high enough polymer content. The most efficient method of solvent elimination from solvent-borne PSA is the removing more than 99 wt.% in polymerization reactor directly after synthesis process. Its advantage is the removal of large quantities of polymerization medium from solvent-borne PSAs within very short time.

After polymerization, the organic solvent was first removed from the polymerization reactor under atmospheric pressure with rising temperature from room temperature to 130°C . The second step of distillation was the removing of organic solvent at the temperature of 130°C and under vacuum 1 mmHg with the use of oil vacuum pump [2].

In the long history of technology, photoreactive pressure-sensitive adhesives (PSAs) and UV-crosslinkable self-adhesive articles are a rapidly expanding tech-

nology on PSAs area resulting from new properties and quality of chemical crosslinking bonding. This crosslinking process and a new class of UV-crosslinkable acrylic PSAs founded interesting application for production of self-adhesive tapes, labels, protective films, sign and marking films, masking tapes, dental and medical materials [3].

Typical photoreactive acrylic PSAs often includes alkyl soft acrylates as 2-ethylhexyl acrylate. The copolymers containing 2-ethylhexyl acrylate (2-EHA) and 4-acryloyloxy benzophenone (ABP) are useful used for manufacturing of acrylic PSA with excellent tack, adhesive performance on soft carriers as polyethylene foam [4]. Interesting is an application of these kind of photoreactive copolymers, used as UV-crosslinkable acrylic PSAs for manufacturing of wide range of self-adhesive materials. It is very interesting the thermal resistance of this group of UV-crosslinkable PSA materials. The thermal degradation of PSAs based on acrylic copolymers has been reported, based on pyrolysis-gas chromatography [5].

Gas Chromatography (GC) is a universal separation technique to complex mixtures by thermal degradation of acrylic PSA. GC is commonly used to analyze mixtures for identification and quantification. Various ancillary GC techniques such as headspace/GC, pyrolysis/GC, and other multidisciplinary techniques are available to conduct this concept. GC techniques are cost effective and encompass a wide range of analytical problems. Assay and trace level analyses are achieved with minimal sample preparation. A wide variety of special detectors are available for quantification and specific identification of various classes of compounds. Gas chromatography, coupled with controlled temperature pyrolysis technique, provides a rapid method for the identification of acrylic polymers and allows pyrolysis/GC and pyrolysis/GC/MS identification of thermal decomposition products of polymeric materials [6].

2. MATERIALS AND METHODS

2.1. Raw materials and synthesis of solvent-free acrylic PSAs

All raw materials for synthesis of acrylic PSAs 2-ethylhexyl acrylate (2-EHA), 4-acryloyloxy benzophenone (ABP), ethyl acetate and AIBN available from ChemCycle/Germany were technical grade. The solvent-borne pressure-sensitive adhesive based on 2-ethylhexyl acrylate have been synthesized using 99.5 wt.% 2-ethylhexyl acrylate (2-EHA) and 0.5 wt.% 4-acryloyloxy benzophenone (ABP) in ethyl acetate using between 0.1 and 0.5 wt.% 2,2'-azo-bis-

diisobutyronitrile (AIBN), according to monomers content, as the thermal initiator to start radical polymerization.

The polymerization in ethyl acetate was conducted under the following conditions:

- addition of monomers mixture blended with AIBN into ethyl acetate before the polymerization (reactor charge): 50 wt.%
- dosage time of residual monomers with residual AIBN 1 h
- time of post-reaction 6 h
- polymer content after polymerization 60 wt.%

The synthesized in ethyl acetate solvent-borne photoreactive acrylic pressure-sensitive adhesives (PSAs) were described by following important properties, as viscosity, weight average molecular weight M_w , number average molecular weight M_n and polydispersity P_d (Tab. 1). The molecular weight studies were performed in tetrahydrofuran with a liquid chromatograph LaChrom system: RI Detector L-7490 and LaChrom UV Detector L-7400 from

Gas chromatograph : Intersmat IGC 131
 Detector : FID
 Column : quartz capillary column 25 QC2/BP1
 – length: 25 m
 – diameter: 0.25 mm
 Carrier gas : nitrogen, pressure 0.8 bar
 Oven temperature : temperature program:
 50°C (0 min) to 250°C (32 min)
 heat rate: 10°C/min
 Sample : 0.3 µl

The pyrolysis apparatus was reassembled and connected to the gas sampler valve in place of the constant volume tube. Plugs were placed in the regular sample inlet and in the vent openings of the gas sampler valve. Products resulting from the pyrolysis were swept into the gas chromatographic column with nitrogen. The identification and composition of the polymer were determined by comparison of the chromatogram of the sample with chromatograms of known monomers and pyrolyzates of known polymers.

Table 1. Molecular weights and polydispersity of acrylic PSAs containing 2-EHA and ABP synthesized with different concentration of radical initiator AIBN

| Concentration of | | Viscosity [Pa·s] | \bar{M}_w [g/mol] | \bar{M}_n [g/mol] | $P_d = \frac{\bar{M}_w}{\bar{M}_n}$ |
|---------------------|----------------|---------------------|------------------------|------------------------|-------------------------------------|
| 2-EHA/ABP [wt.%] | AIBN [wt.%] | | | | |
| 99.5/0.5 | 0.1 | 14.2 | 617 000 | 199 000 | 3.10 |
| 99.5/0.5 | 0.2 | 10.8 | 442 000 | 132 000 | 3.35 |
| 99.5/0.5 | 0.3 | 6.3 | 339 000 | 89 000 | 3.81 |
| 99.5/0.5 | 0.4 | 3.9 | 210 000 | 41 000 | 5.12 |
| 99.5/0.5 | 0.5 | 1.9 | 108.000 | 12 000 | 9.00 |

Merck-Hitachi, equipped with a PLgel 10⁶L column from Hewlett-Packard.

After polymerization, from acrylic PSA synthesized by the use of 0.3 wt.% AIBN the organic solvent ethyl acetate was first removed from the polymerization reactor under atmospheric pressure with rising temperature from room temperature to 130°C. The second step of distillation was the removing of ethyl acetate and residue monomers at the temperature of 130°C and under vacuum 1 mmHg with the use of oil vacuum pump DOA-V510-BN from GAST Manufacturing Inc. The second step last until all solvent was evaporated.

2.2. Degradation process of synthesized acrylic PSAs

The thermal degradation experiments were performed by pyrolysis-gas chromatography and pyrolysis-gas chromatography/mass spectrometry techniques at following parameters:

3. RESULTS AND DISCUSSION

As major decomposition products we have identified by gas chromatography 2-ethylhexene-1, olefin corresponding to the 2-ethylhexyl ester side group in the synthesized copolymers, alcohol 2-ethylhexanol-1 corresponding to the 2-ethylhexyl ester side group, the monomers: 2-ethylhexyl acrylate and the corresponding 2-ethylhexyl methacrylate. Time evolution of 2-ethylhexene-1, 2-ethylhexanol-1, 2-ethylhexyl acrylate and 2-ethylhexyl methacrylate in terms of the proportion of monomer units involved is illustrated in Fig. 1.

In the Fig. 2 has been shown the forming of important products by thermal degradation at temperature of 250°C by the pyrolysis of solvent-free photoreactive acrylic PSAs based on 2-ethylhexyl acrylate during the thermal degradation time interior 32 minutes. The greatest forming speed in the case of monomer 2-

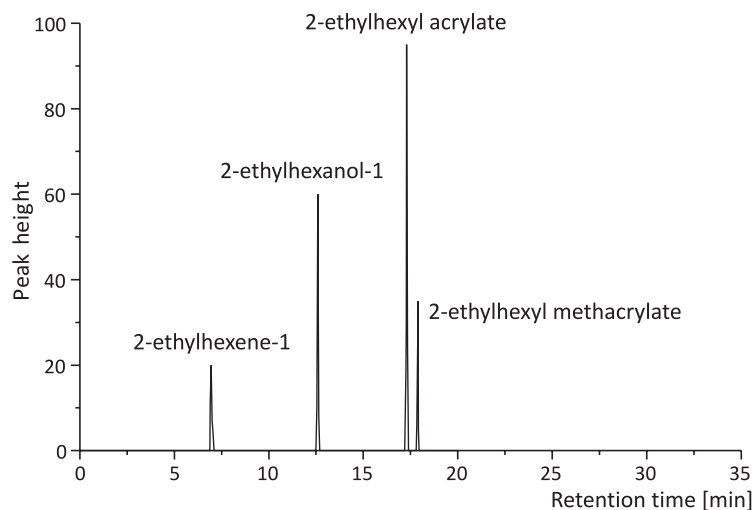


Figure 1. GC of the degradation products of investigated photoreactive acrylic PSA

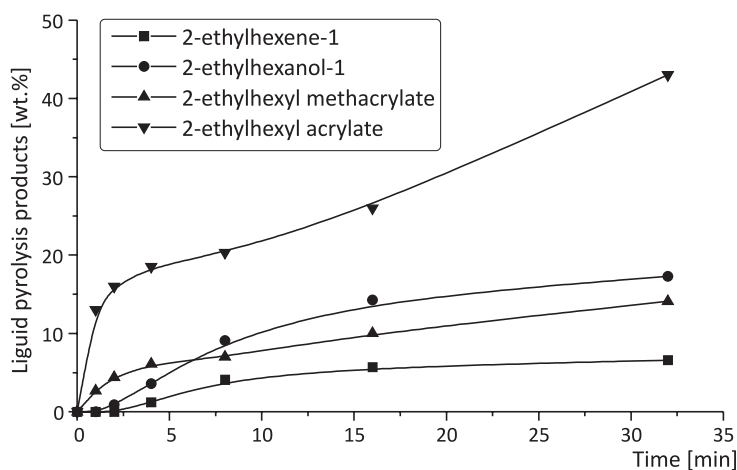


Figure 2. Production of relevant by-products during degradation of acrylic PSA based on copolymer 2-ethylhexyl acrylate (2-EHA) and 4-acryloyloxy benzophenone (ABP)

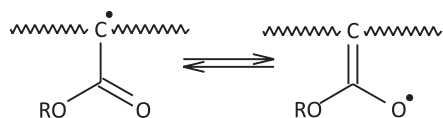


Figure 3. Radical responsible for thermal decomposition of poly(alkyl acrylates)

ethylhexyl acrylate from main acrylic chain was observed. The slowest was the forming of olefin 2-ethylhexene-1 from side acrylic chain.

The initial step in the degradation of the primary acrylics is therefore likely to be scission at some unspecified point in the polymer molecule. Czech and Pelech [7] suggest that these initially formed radicals would remove tertiary hydrogen atoms

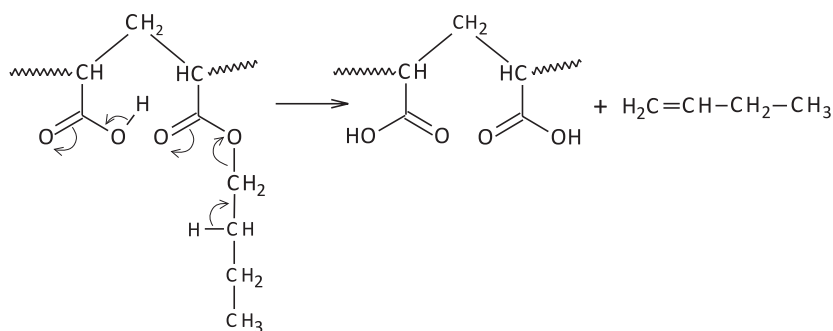


Figure 4. Thermal decomposition reaction of acrylic PSA formed olefin for PSA based on butyl acrylate

from the polymer backbone to give the relatively stable radical (Fig. 3) and that all the major decomposition reactions in poly(alkyl acrylate) are initiated by this radical.

Evidence that this theory may reasonably be extended to other poly(primary alkyl acrylates) is provided by their closely similar responsible thermograms and the general comparability of their patterns of reaction products. It would be difficult to explain how such a variety of products could be formed in a one-stage process, unless all the reactions have a common precursor.

During the thermal degradation of acrylic PSAs based on 2-ethylhexyl acrylate to olefin is evolved from these acrylic polymers in a molar ratio close to unity, at least in the early stages of the reaction. It therefore seems probable that a reaction shown in Fig. 4 is operative. There is no evidence for autocatalytic production of olefin so competition with reaction (Fig. 4), which was proposed to account for the autocatalytic decomposition of poly(2-ethylhexyl acrylate), is assumed to be negligible.

The amounts of olefin 2-ethylhexene-1 produced seem to vary as the number of β -hydrogen atoms in the alkyl group. Although this reaction type is represented as being catalyzed by a radical on a neighboring monomer unit, there is no reason why any available radical should not be the initiator. Further evidence for this kind of reaction is the fact that there appears to be a direct relationship between the production of olefin

and the number of β -hydrogen atoms on the alkyl group. Once the first double bond is formed it will tend to weaken adjacent carbon-hydrogen bonds. Thus hydrogen will be liberated from sequences of adjacent acrylate units resulting in carbon-carbon conjugation in the polymer backbone.

In the case of the acrylic PSA based on 2-ethylhexyl acrylate the 2-ethylhexyl ester it also included the acrylate and methacrylate monomers which are of relatively low volatility. The chain fragment fraction is usually yellow in color, the intensity increasing with time of degradation.

4. CONCLUSIONS

This procedure has been conducted satisfactorily on acrylic PSAs containing copolymers based on 2-ethylhexyl acrylate and 4-acryloyloxy benzophenone. Copolymer from 2-ethylhexyl acrylate and 4-acryloyloxy benzophenone using commercial as photoreactive solvent-free PSAs have been examined to establish whether ester interchange could occur under these conditions of pyrolysis. The results of this study show,

that as the main significant pyrolysis by-products of investigated photoreactive acrylic PSA: 2-ethylhexene-1, 2-ethylhexanol-1, 2-ethylhexyl acrylate and 2-ethylhexyl methacrylate were identified. Mechanism of formation of the all above mentioned compounds can be explained on the basis of the characteristic property of typical acrylic PSA which easily undergo the pyrolytic decomposition to the 2-ethylhexyl derivatives corresponding to the main component acrylic ester of PSA. The residual polymer from copolymer 2-ethylhexyl acrylate/4-acryloyloxy benzophenone becomes progressively more intensely colored as degradation proceeds. The color is probably the result of conjugation involving principally carbon-carbon double bonds, but possibly also carbonyl groups. Carbon-carbon double bonds will be formed in the polymer in reaction (Fig. 4) or as a result of transfer.

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