Polymer Bulletin 52, 283-288 (2004)
DOI 10.1007/s00289-004-0273-1

Polymer Bulletin

2-Ethylhexyl acrylate/4-acryloyloxy benzophenone copolymers as UV-crosslinkable pressure-sensitive adhesives

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Received: 2 April 2003/Revised version: 9 June 2004/ Accepted: 16 June 2004

Summary

It has been previously shown that copolymer of 2-ethylhexyl acrylate with an 4-acryloyloxy benzophenone can be used as PSA. This paper presents synthesis and application of solvent-based polymer system for the preparation of acrylic pressure-sensitive adhesives (PSA). 2-Ethylhexyl acrylate benzophenone copolymers, having molecular mass in the range of 120 000 to 380 000 Dalton were prepared by free-radical solution polymerization. These copolymers were tacky but possessed insuff-cient cohesive strength after UV-crosslinking to be useful as PSAs. These copolymers resulted in materials having a balance of cohesive and adhesive characteristics required of a good PSA. Some of the parameters affecting the pressure-sensitive adhesive properties of the copolymer are: amount of the 4-acryloyloxy, molecular mass of the polymeric components, UV-reactivity and such properties like tack, peel adhesion and cohesion.

Keywords: 2-ethylhexyl acrylate, 4-acryloyloxy benzophenone, UV-crosslinking, tack, peel adhesion, cohesion.

Introduction

Conventional solvent-based acrylic pressure-sensitive adhesives (PSAs) are generally copolymers of $C_4 - C_8$ alkyl acrylates and polar monomers, such as acrylic acid or hydroxyacrylate. Optionally modifying monomers like methyl or ethyl acrylate and vinyl acetate may also be incorporated in the copolymer structure. 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 acrylic PSAs are generally applied onto the desired substrates as solvent or water based coatings and subsequently dried.

Solvent-based acrylics pressure-sensitive adhesives are synthesized in organic solvents viscoelastic polymers with permanent tack and the balance of two properties adhesion and cohesion [1]. In the long history of technology, pressure-sensitive adhesion and selfadhesive articles as we know them are a fairly recent concept. The history of PSAs was described by Villa [2]. The diverse crosslinking methods of PSA acrylics has been discussed in [3]. Ultraviolet-crosslinked solvent-based PSA acrylics are one component systems. UV-crosslinked acrylic PSA systems were described in [4-7]. Photoinduced crosslinking is a rapidly expanding technology on PSA area resulting from new properties and quality of chemical crosslinking bonding. This crosslinking process and a new class of UV-crosslinkable PSA acrylics founded interesting application for production of selfadhesive tapes, foils and dental materials.

The presence of a hydrogen donor molecule (usually an amine) is necessary, when the benzophenone or multifunctional saturated benzophenones for UV-induced crosslinking process are used. In the case of application of unsaturated benzophenones the crosslinking reaction can be conducted in the presence of oxygen [4].

The crosslinking mechanism of UV photoreactive PSA acrylics containing 2-ethylhexyl acrylate and 4-acryloyloxy benzophenone has been thoroughly investigated and it is presented schematically in Figure 1 [8].

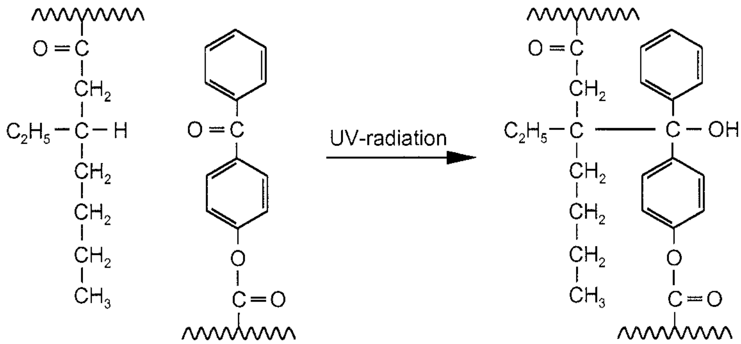

Figure 1. UV-crosslinking of PSA acrylics containing of 4-acryloyloxy benzophenone.

The behavior of any pressure-sensitive adhesive can be reduced to three fundamental and interconnected physical properties: tack, peel adhesion and cohesion [9].

Tack of PSA is not an exactly defined, physical characteristic, it may be defined as a separation energy. Nevertheless tack is still considered and rated by many as how well a pressure-sensitive adhesive sticks to the finger following only slight pressure and short dwell time.

Peel adhesion is the force required to remove a PSA-coated material from a specified test surface under standard conditions (10).

Cohesion is a real measure of the internal structural resistance of the polymer. Generally, the mechanical and physical (tack, peel adhesion) properties of PSA acrylics are dependent on its cohesion.

Experimental

Materials

The following experiments were conducted to study the influence of amount of 4-acryloyloxy benzophenone on the following properties of the synthesized PSA such as viscosity, molecular mass, tack, peel adhesion and cohesion. The investigated PSAs were synthesized with between 0.1 to 3.0 wt.-% of 4-acryloyloxy benzophenone and rest of 2-ethylhexyl acrylate by polymerization in a typical organic solvents like ethyl acetate and acetone in rate 80 : 20 with 0.1 wt.-% of thermical initiator AIBN. The solid content was about 50 wt.-%.

2-ethylhexyl acrylate, ethyl acetate, acetone and AIBN are available from Merck. The unsaturated photoinitiator 4-acryloyloxy benzophenone (4-benzophenone acrylate) are purchased from Dr. Milker Klebstoff GmbH.

The UV-crosslinkable PSA acrylics coated with 60 g/m^2 dry polymer directly a 36 μ polyester foil and were crosslinked after drying 10' at 105°C with U lamp of type U 350-M-I-DL from IST company by different exposure time. The light intensity at the sample position was 100 mW/cm^2.

Measurements

The molecular mass of the synthesized copolymers were determined on Waters Associates 150C Gel Permeation Chromatograph using μStyragel columns and tetrahydrofuran as the eluting solvent. Viscosities of the solvent-based copolymers were determined on Brookfield Synchro-Lectric Viscomter Model RVT with Thermosel attachment, using spindle # 27 at 2.5 rpm.

The performance of the pressure-sensitive adhesive acrylics were measured according to A.F.E.R.A. 4015 (tack), 4001 (peel adhesion) and 4012 (cohesion).

Results and discussion

It has been previously shown that copolymers of a 2-ethylhexyl acrylate with a 4-acryloyloxy benzophenone containing a small amount of photoreactive groups exhibit good adhesively performance.

The 2-ethylhexyl acrylate-4-acryloyloxy benzophenone copolymers, which were prepared by solution polymerization of the monomers in the presence of AIBN had GPC polystyrene equivalent peak molecular weights ($\overline{M}_w$) in the range of 120 000 to 380 000 Dalton. The data of table 1 illustrate the effect of the 4-acryloyloxy benzophenone content of the molecular mass, viscosity, tack, peel adhesion and cohesion of PSA acrylic after UV-crosslinking with 60 s crosslinking time.

The result of the Table 1 are presented in Figures 2 to 3.

Table 1. Relevant properties of UV-crosslinkable and UV-crosslinked PSA acrylics

4-acryloyloxy benzophenone [wt.-%]	$\overline{M}_w$ [Dalton]	η [mPas]	Tack [N]	Peel adhesion [N]	Cohesion (20°C) [N]
0,0	118 000	518	40.0 CF	33 CF	2
0.1	120 000	531	41.5	31 CF	5
0.3	123 000	700	40.5	31 CF	7
0.5	128 000	793	39.0	28.5 CF	10
0.7	145 000	911	37.5	27 CF	12
1.0	188 000	1002	33.0	21	25
1.5	235 000	1215	29.5	16.5	35
2.0	290 000	1633	21.5	13	50
2.5	331 000	2110	15.0	10.5	60
3.0	380 000	2790	8.4	9.5	90

CF – cohesion failure

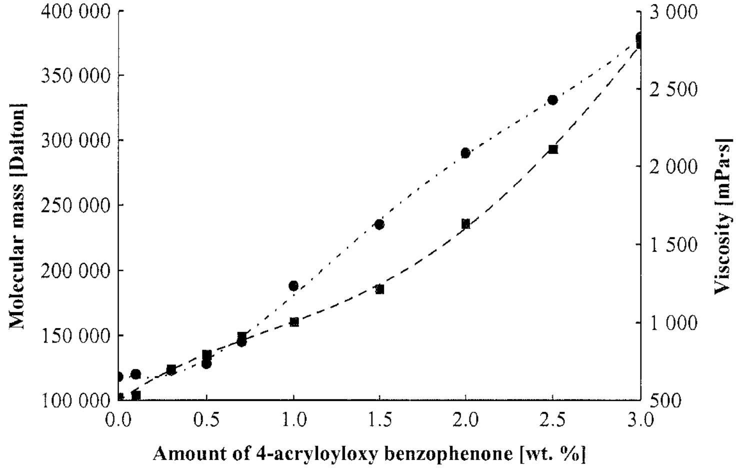

Figure 2. Effect of photoinitiator on $\overline{M}_w$ of PSA (●) and on PSA viscosity (■).

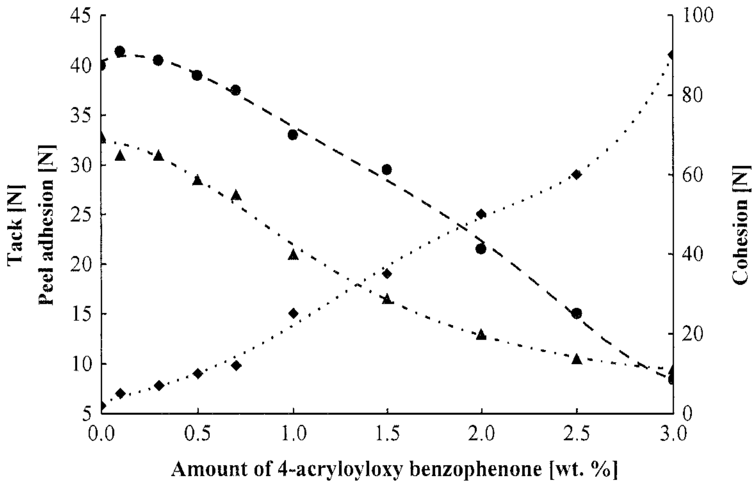

Figure 3. Influence of photoinitiator on PSA tack (●), peel adhesion (▲) and cohesion (♦).

From the investigated experiments it can be inferred that the increase of the unsaturated photoinitiator 4-acryloyloxy benzophenone amount corresponds with the increase of viscosity and the molecular mass of synthesized UV-crosslinkable solvent-based pressure-sensitive adhesives.

The influence of 4-acryloyloxy benzophenone concentration on tack, peel adhesion and cohesion after the crosslinking time of 60 second are shown in Figure 3.

With the increasing of photoinitiator concentration there has been a decreasing of tack of investigated solvent-based acrylates. In the area of between 2.0 to 0.3 wt.-% 4-acryloyloxy benzophenone it was observed that the tack very fast decrease.

The highest value of peel adhesion was obtained by using between 0 to 1.0 wt.-% of 4-acryloyloxy benzophenone. The results of peel adhesion for amount of photoinitiator under 0.8 wt.-% brought adhesive performance with cohesion failure. This types of results are unacceptable for the technological use.

The increase of the concentration of the 4-acryloyloxy benzophenone used for the synthesis of UV-crosslinkable PSA acrylics causes an increase of their cohesion. A very high cohesion value of 90 N order of magnitude was possible to be obtained by applying 3.0 wt.-% 4-acryloyloxy benzophenone in the acrylic copolymers. With 1.0 and 1.5 wt.-% of unsaturated photoinitiator the acceptable cohesion level of 25 and 35 N was achieved.

The phenomenon of performance of UV-crosslinkable PSA acrylics is a result of the UV-crosslinking time that takes place when the PSA coated film is exposed to UV radiation. In Figure 4 the influence of crosslinking time on tack, adhesion and cohesion of PSA by the same concentrations of 4-acryloyloxy benzophenone about 1.5 wt.-% is illustrated.

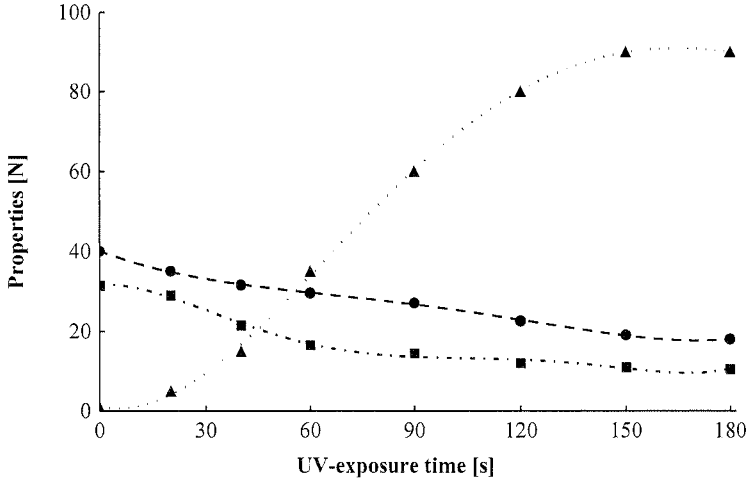

Figure 4. Influence of UV-crosslinking time on tack (•), peel adhesion (♦) and cohesion at 20°C (▲).

In general, it can be said that the use of unsaturated photoinitiators 4-acryloyloxy benzophenone in the amount of 1.5 wt.-% in PSA copolymers gave the best balance of tack, peel adhesion and cohesion after the UV-crosslinking time between 60 and 180 seconds. For about 90 s of crosslinking time the optimum of tack, peel adhesion and cohesion values with the use of the investigated photoinitiator was observed.

Conclusions

UV-crosslinkable acrylic PSAs designed to react with UV light offer a good alternative to other crosslinked solvent-based adhesives.

From the evaluation of the experiments discussed in this publication, it can be concluded that:

- The very interesting performance of UV-crosslinked solvent-based pressure-sensitive adhesive acrylics based on 2-ethylhexyl acrylate were achieved by the use of 4-acryoyloxy benzophenone during the polymerization.
- Increasing of the amount of copolymerizable 40acryloyloxy benzophenone increases viscosity and molecular mass of solvent-based synthesized PSA acrylics.
- From the investigated copolymerizable photoinitiator the best results for relevant properties of pressure-sensitive adhesives such as tack, peel adhesion and cohesion were given by about 1.5 wt.-% of 4-acryloyloxy benzophenone.
- After UV-crosslinking time about between 60 and 90 s the investigated performance of PSA obtained 4-acryloyloxy benzophenone achieves a very high level.
- Generally the properties of synthesized UV-crosslinkable PSA containing 4-acryloyloxy benzophenone are after UV crosslinking very high. The cohesion shows an excellent niveau.
- Prospects for solvent-based UV-crosslinkable PSA acrylics
  UV-crosslinkable solvent-based pressure-sensitive adhesive acrylics containing 2-ethylhexyl acrylate/4-acryloyloxy-benzophenone copolymers with excellent cohesion and high tack and high adhesion will play a major role in the production of self-adhesive products such as decorative PCV foils, synthetic material labels and similar products still in the developmental stage.

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