# Photoreactive UV-Crosslinkable Pressure-Sensitive Adhesives Based on Butyl Acrylate and 4-Acryloyloxy Benzophenone Copolymers

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**Abstract:** It has been previously shown that copolymers synthesized from n-butyl acrylate and unsaturated photoinitiator 4-acryloyloxy benzophenone can be used as pressure-sensitive adhesives (PSA). This paper presents synthesis and application of solvent-borne copolymer system for the preparation of photoreactive UV-crosslinkable acrylic pressure-sensitive adhesives comprising n-butyl acrylate/ benzophenone copolymers, characterized by molecular mass in the range of 180 000 to 480 000 Dalton. These copolymers were tacky but possessed insufficient cohesive strength after UV-crosslinking to be useful as PSA. They resulted in materials having a balance of cohesive and adhesive characteristics required of good PSA. Some of the parameters affecting the pressure-sensitive adhesive properties of the copolymer are: amount of the 4-acryloyloxy benzophenone, molecular mass of the polymeric components, UV-reactivity and properties, such as tack, peel adhesion and shear strength.

**Keywords:** n-butyl acrylate, 4-acryloyloxy benzophenone, acrylic copolymers, pressure-sensitive adhesives (PSA), UV-crosslinking, tack, peel adhesion, shear strength.

## INTRODUCTION

Conventional solvent-borne acrylic pressure-sensitive adhesives (PSA) are generally copolymers of $C_4$–$C_8$ alkyl acrylates and polar monomers, such as acrylic acid or hydroxyacrylates. 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 -70ºC. The acrylic PSA are generally applied onto the desired substrates as solvent-borne or water-borne coatings 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.

Solvent-borne 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]. In the long history of technology, pressure-sensitive adhesives (PSA) and self-adhesive articles as we know them are a fairly recent concept. The history of PSA was described by Villa [2]. The diverse crosslinking methods of acrylic PSA have been discussed in [3]. Ultraviolet-crosslinked solvent-borne acrylic PSA are one component systems. UV-crosslinked acrylic PSA systems were described in [4-9]. Photo-inducted 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 acrylic PSA founded interesting application for production of self-adhesive tapes, labels, protective films, sign and marking films, masking tapes, dental and medical materials.

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** [10].

The behavior of any pressure-sensitive adhesive can be reduced to three fundamental and interconnected physical properties: tack, peel adhesion and cohesion [11].

**Tack** of PSA is not an exactly defined, physical characteristic; it may be defined as separation energy. Nevertheless tack is still considered and rated by many as how well a self-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.

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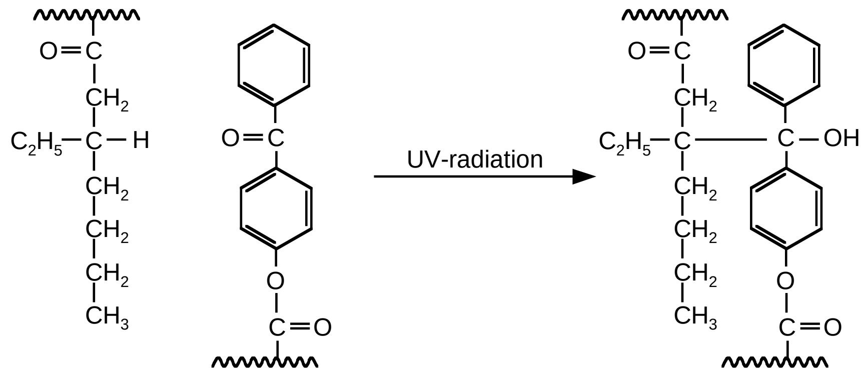


**Figure 1:** UV-crosslinking of acrylic PSAs containing 4-acryloyloxy benzophenone as internal photoinitiator.

**Shear strength** is a real measure of the internal structural resistance of the polymer. Generally, the mechanical and physical (tack, peel adhesion) properties of acrylic PSA 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 acrylic PSA such as viscosity, molecular mass, tack, peel adhesion and shear strength. The investigated PSA were synthesized with 0.1 to 3.0 wt.% of 4-acryloyloxy benzophenone and rest of n-butyl acrylate by polymerization in a typical organic solvents like ethyl acetate and acetone in rate 80 : 20 with 0.1 wt.% of thermal radical initiator AIBN. The polymer content during the polymerization was about 50 wt.%. n-butyl acrylate, ethyl acetate, acetone and AIBN are available from BASF (Germany). The unsaturated photoinitiator 4-acryloyloxy benzophenone is purchased from ChemCycle (Germany).

The photoreactive acrylic PSAs were coated with 60 g/m$^2$ dry polymer directly on a 36 µm polyester foil and crosslinked after drying 10' at 105ºC with UV lamp of type U 350-M-I-DL from IST company by the UV dose of 700 mJ/cm$^2$ at various crosslinking times.

### Measurements

The molecular mass studies were performed in tetrahydrofurane with a gel chromatography LaChrom system: RI Detector L-7490 and LaChrom UV Detector L-7400 from Merck-Hitachi, equipped with a PLgel 10$^6$Å column from Hewlett-Packard.

Viscosities of the solvent-borne copolymers were determined on Brookfield Synchro-Lectric Viscometer Model RVT with Thermosel attachment, using spindle # 27 at 2.5 rpm.

The UV-exposure was measured using an integrating radiometer Dynachem$^{TM}$ Model 500, available from Dynachem Corporation, 2631 Michelle Drive, Tustin, CA 92680.

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

## RESULTS AND DISCUSSION

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

The n-butyl 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 ( $\bar{M}_w$ ) in the range of 180 000 to 480 000 Dalton. These copolymers were clear, tacky, and cohesively weak viscous fluids. The data of Table **1** illustrate the effect of the 4-acryloyloxy benzophenone content on the molecular mass, viscosity, tack, peel adhesion and cohesion of PSA acrylic after UV-crosslinking using 700 mJ/cm$^2$ UV dose and crosslinking time of 60 s.

The results of the Table **1** are presented in Figures **2** to **6**. From the investigated experiments it can be inferred that an increasing of the unsaturated photoinitiator 4-acryloyloxy benzophenone amount corresponds with the increase of the molecular mass

**Table 1: Relevant Properties of UV-Crosslinkable ($\bar{M}_w$,η) and UV-Crosslinked (Tack, Peel Adhesion, Cohesion) Acrylic PSA**

| 4-acryloyloxy benzophenone [wt.-%] | $\bar{M}_w$ [Dalton] | η [mPa·s] | Tack [N] | Peel adhesion [N] | Shear strength (20ºC) [N] |
|---|---|---|---|---|---|
| without | 180 000 | 724 | 40.0 | 28.0 cf | 5 |
| 0.1 | 180 000 | 731 | 38.5 | 27.6 cf | 5 |
| 0.3 | 183 000 | 998 | 37.5 | 27.0 cf | 8 |
| 0.5 | 188 000 | 1100 | 36.0 | 25.6 cf | 12 |
| 0.7 | 205 000 | 1314 | 34.6 | 24.5 cf | 14 |
| 1.0 | 229 000 | 1512 | 30.2 | 19.8 | 26 |
| 1.5 | 287 000 | 1800 | 26.8 | 14.7 | 36 |
| 2.0 | 362 000 | 2380 | 19.5 | 10.1 | 70 |
| 2.5 | 419 000 | 3100 | 12.0 | 8.6 | 95 |
| 3.0 | 480 000 | 4330 | 7.5 | 6.6 | 120 |

cf–cohesion failure.

(Figure **2**) and viscosity increasing (Figure **3**) of the synthesized UV-crosslinkable solvent-borne acrylic pressure-sensitive adhesives (PSA).

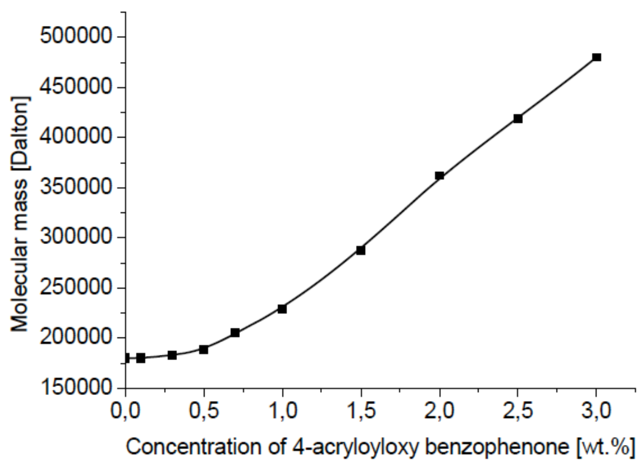


**Figure 2:** Dependence of $\bar{M}_w$ of acrylic PSA on photoinitiator concentration.

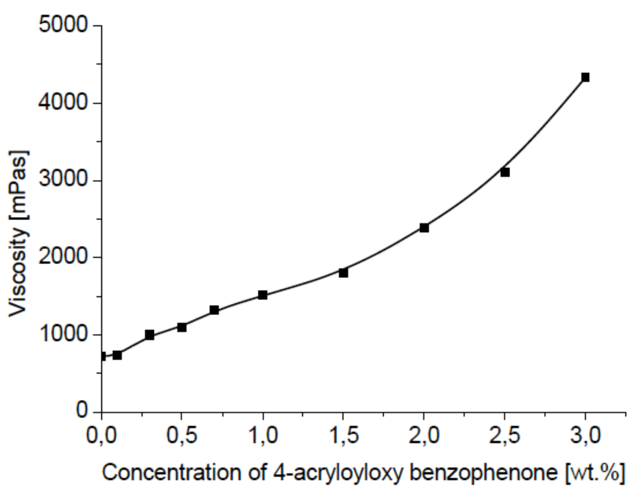


**Figure 3:** Effect of photoinitiator content on acrylic PSA viscosity.

The influence of 4-acryloyloxy benzophenone (internal photoinitiator) concentration on the main PSA properties, such as tack, peel adhesion and shear strength after the crosslinking time of 60 second is shown in Figures **4** to **6**.

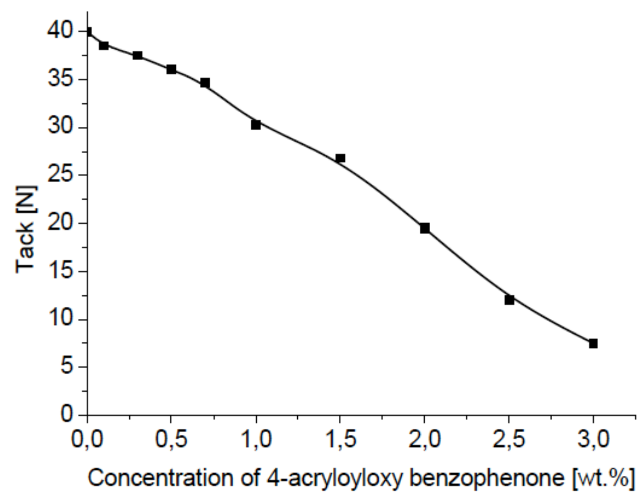


**Figure 4:** Influence of photoinitiator content on acrylic PSA tack.

With the increasing of photoinitiator concentration there has been observed a decreasing of tack of investigated photoreactive solvent-borne acrylic PSAs. In the area of between 1.0 to 3.0 wt.% 4-acryloyloxy benzophenone it was observed that the tack decreases very fast. This phenomenon is typical for crosslinked adhesives.

The highest value of PSAs peel adhesion without cohesive failure (cf) was obtained by using between 0.7 to 1.0 wt.% of 4-acryloyloxy benzophenone. The results of peel adhesion for amount of photoinitiator under 0.8

wt.% brought the highest adhesive performance, however with cohesion failure. These types of results, characterized by insufficient cohesion of acrylic PSA, are unacceptable for their technological use.

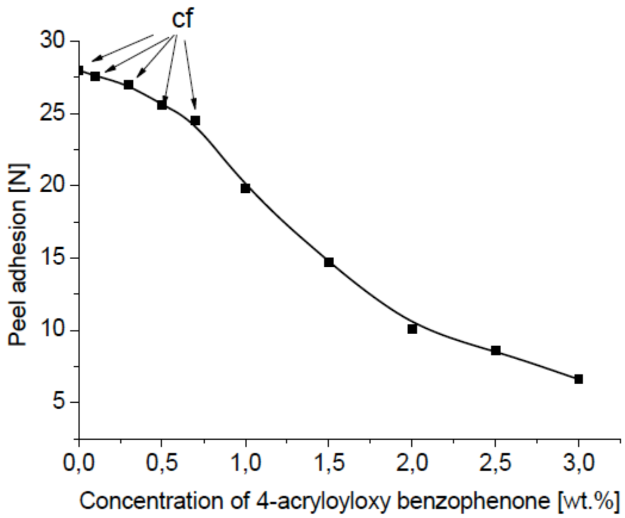


**Figure 5:** Influence of photoinitiator content on PSA peel adhesion.

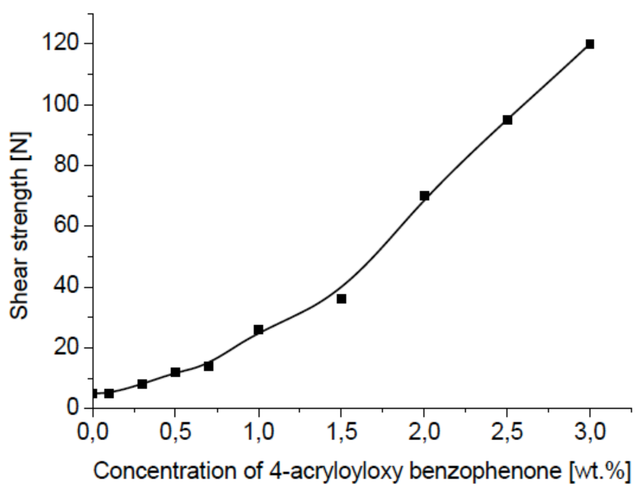


**Figure 6:** Influence of photoinitiator content on PSA shear strength.

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 120 N order of magnitude was possible to be obtained by applying of 3.0 wt.% 4-acryloyloxy benzophenone in the acrylic copolymer chain. With 1.0 and 1.5 wt.% of unsaturated photoinitiator the acceptable cohesion level of 30 and 40 N was achieved.

The phenomenon of performance of UV-crosslinkable acrylic PSAs is a result of the UV-crosslinking, measured as UV-crosslinking time, which takes place when the PSA coated film is exposed to UV radiation. In Figure **7** 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.

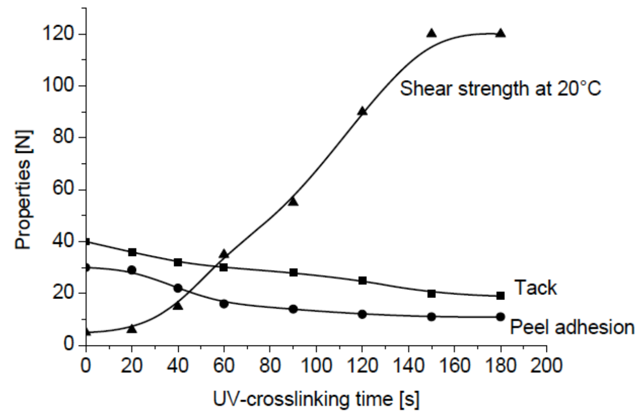


**Figure 7:** Influence of UV-crosslinking time on tack, peel adhesion and shear strength.

In general, it can be said that the use of unsaturated photoinitiator 4-acryloyloxy benzophenone in the amount of 1.5 wt.-% in acrylic PSA copolymers gave the best balance of tack, peel adhesion and shear strength after the UV-crossliniking time between 60 and 180 seconds. For about 90 s of crosslinking time, the optimum of tack, peel adhesion and cohesion of UV-crosslinked acrylic PSAs values by incorporation into polymer chain of the investigated photoinitiator 4-acryloyloxy benzophenone was observed.

## CONCLUSIONS

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

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

- The very interesting performances of UV-crosslinked solvent-borne acrylic pressure-sensitive adhesives based on butyl acrylate were achieved by the incorporation into polymer backbone of 4-acryoyloxy benzophenone during the polymerization.
- Increasing of the amount of copolymerizable 4-acryloyloxy benzophenone increases viscosity and molecular mass of synthesized solvent-borne acrylic PSAs.
- From the investigated copolymerizable photoinitiator concentration the best results of

relevant properties of pressure-sensitive adhesives, such as tack, peel adhesion and shear strength were given by about between 1.0 and 1.5 wt.% of 4-acryloyloxy benzophenone.

- After UV-crosslinking time between 60 and 90 s the investigated performance of acrylic PSAs containing 4-acryloyloxy benzophenone achieves a very high level.
- Generally, the properties of synthesized UV-crosslinkable acrylic PSAs containing in the structure 4-acryloyloxy benzophenone are after UV crossliniking on very high level. Their shear strength shows an excellent level.

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