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Development of photoreactive UV-crosslinkable solvent-free acrylic pressure--sensitive adhesives coated at room temperature and used for removable and repositionable self-adhesive materials

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The goal of this article is to review the development of photoreactive UV-crosslinkable acrylic pressure--sensitive adhesives (PSAs) characterized by low viscosity, which can be coated at room temperature in the form of adhesive layers and are characterized by removable properties after UV-crosslinking. Surfactants and stearic acid have been used to improve the performance of the acrylic PSA, too. They are used for the manufacturing of removable and repositionable self-adhesive products, such as easy peel-able decorative films and wide range version of post-it articles.

Keywords: photoreactive, UV-crosslinkable, pressure-sensitive adhesives, acrylic, solvent-free.

INTRODUCTION

In the last fifty years or so, acrylic pressure-sensitive adhesives (PSA) have made tremendous strides from what was virtually a black art to what is now a sophisticated science. The term PSA has a very precise technical definition and was dealt with extensively in the chemical literature[1]. The function of PSAs is to ensure instantaneous adhesion upon application of a light pressure. So much so that both the few larger manufacturers of self- adhesive articles and their even larger suppliers now use very expensive equipment to study pressure-sensitive adhesive behavior: tack, adhesion and cohesion. Three properties which are useful in characterizing the nature of permanent adhere pressure-sensitive adhesives are tack, peel (adhesion) and shear (cohesion). The first measures the adhesive's ability to adhere quickly, the second its ability to resist removal by peeling, and the third its ability to hold in position when shearing forces are exerted. Generally speaking, the first two properties are directly related to each other but are inversely related to the third[2].

In the modern giant field of the pressure-sensitive adhesives the acrylic PSAs are more popular within this group. Other types of PSA in use nowadays include rubbers, silicones, polyesters, polyurethanes, polyether and ethylene-vinyl acetate (EVA) copolymers[3]. The main emphasis is given to the influence of PSAs synthesis using diverse functional monomers and PSAs modification after crosslinking on their special performances. They can be used in the production of self-adhesive single- and double-sided tapes, foil labels, carrier-free tapes, self-adhesive bioelectrodes and decorative PVC sign and marking films[4].

At the end of the 1980s and during the early 1990s 3M, Beiersdorf, BASF and Lohmann presented the first solvent-free pressure-sensitive adhesive acrylics crosslinked with UV-radiation. The synthesized photoreactive solvent-free acrylic PSAs are the only one of the alternatives to the normally conventional crosslinked other acrylic PSAs. The use of ultraviolet (UV) radiation to crosslink acrylic PSA systems in the place, which is to be photocrosslinked. It also requires a photoinitiator which absorbs the impinging light and induces photocrosslinking. Common to UV-crosslinking technology is the application of a suitable conventional photoinitiator. In the case of saturated acrylic pressure-sensitive adhesives, the photogeneration of initiator radicals by the α-cleavage photoinitiators (type I) or H-abstraction photoinitiators (type II) is followed by the reaction with the acrylic chain to produce a new radical that reacts with a neighboring acrylic chain[5].

A very interesting alternative to conventional photoinitiators are the unsaturated photoinitiators. The most typical directions, however, are in the development of functionalized type I and type II initiators e.g. acrylated, vinylated, allylated, acrylamidated or vinyloxylated (Fig. 1)[6].

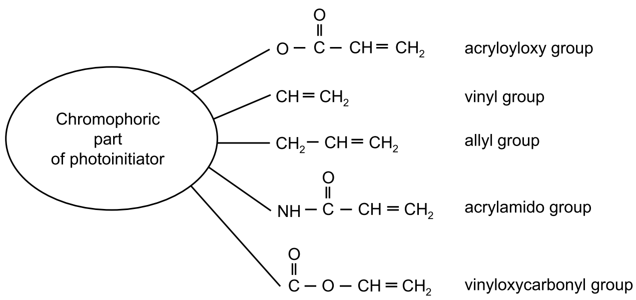

Figure 1. General examples for unsaturated photoinitiators

Copolymerizing the unsaturated photoinitiator into the backbone of the acrylic pressure-sensitive adhesive copolymer allows crosslinking of the acrylic PSAs with ultraviolet radiation, after the formation of the copolymer. Further, incorporation of the unsaturated copolymerizable photoinitiators into the acrylic polymer backbone, before the crosslinking thereof, greatly increases the efficiency of the crosslinking obtainable by inclusion of the photoinitiator monomer in the adhesive, as compared with addition of an aromatic ketone compound which is not initially copolymerized into the copolymer. Because of increased efficiency, only small amounts of unsaturated copolymerizable photoinitiator monomer are needed to achieve useful degrees of crosslinking.

The typical dependence of the tested novel unsaturated photoinitiators showed the best PSA properties which were achieved for type II acryloyloxy-photoinitiator, such as: 4-acryloyloxy benzophenone (ABP) (Fig. 2). ABP was the most efficient H-abstractor for the commonly solvent-based acrylic self-adhesives[7].

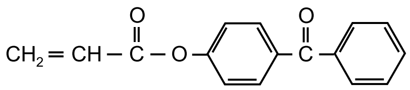

Figure 2. 4-acryloyloxy benzophenone (ABP)

Photoreactive acrylic hotmelt pressure sensitive adhesives are the most recent member within the PSA segment. Their production process involves the classical radical polymerization in a solvent followed by the stripping of the organic solvent which might be reused for the polymerization step. Besides the typical acrylic monomers, an acrylic monomer containing chromophoric groups is built in the polymeric chain during the polymerization process. It functions as an internal photoinitiator allowing the crosslinking needed later. Dependant on the molecular mass of such generated acrylic solvent-free PSAs coating is performed after an addition of photoreactive diluents at room temperature[8].

The term "removable and repositionable" is intended to refer not only to the products which can be temporarily adhered to, removed from, and repositioned on diverse substrates sheets but also to the products to which substrate sheets can be temporarily adhered, removed, and repositioned[9]. The classification of pressure-sensitive adhesive according the adhesion properties is shown in Fig. 3.

Kind of PSA	Adhesion of PSA [N/2,5 cm] (180° peel adhesion)
Excellent permanent	> 14
Permanent	10…14
Semi-removable	6…8
Removable and repositionable	2…4
Excellent removable	<1

Figure 3. Classification of pressure-sensitive adhesive vs. peel adhesion

GOAL OF DEVELOPMENT WORK

The target of this work is the development of the cotable at room temperature low viscosity photoreactive solvent-free UV-crosslinkable acrylic pressure-sensitive adhesives, which are characterized by excellent removability[9]. These acrylic systems are used for the manufacturing of the removable and repositionable self-adhesive products, such as easy peel-able decorative films and the wide range version of post-it articles.

EXPERIMENTAL

Removability

Pressure-sensitive adhesives are considered removable if they are removed cleanly from a test substrate without causing any damage to the test substrate over a range of peel rates and varied periods of dwell at room temperature. A strip 2.5 cm in width of the sheet coated with the PSA to be tested is applied to the horizontal surface of a polyester, treated polyester or other test substrate with at least linear 25 cm in firm contact. Three passes in each direction with a 2 kg hard rubber roller are used to apply the strip. After one day or one week dwell, the free end of the coated strip is double back nearly touching itself so the angle of the removal will be about 135 grade. The free end is then pulled by hand at a variety of peel rates. The removability and peel force are judged according to the following ratings and recorded:

– good-samples that are removed from the test substrate without damaging or leaving residue on the test substrate and which also exhibit high peel force and yet do not damage the paper backing over a range or peel rates,

– aggressive-samples that are removed from the test substrate without damaging or leaving the residue on the test substrate, but which can only be removed from the test substrate at a slow peel rate without damaging the substrate backing,

– raspy-samples that are removed from the substrate without damaging or leaving residue on the test substrate, but which are too stiff to be removed smoothly,

– tear-samples that display too high a peel adhesion to the test substrate, causing test substrate and other substrate backing to tear or delaminate at any peel rate,

– ghost-samples that leave a very thin, adhesive residue on the test substrate when removed from the polyester and treated polyester samples,

– weak-samples that have low tack and low peel adhesion,

– cohesive failure-samples that leave adhesive residue on both substrate backing and the test substrate.

Polymerization and removing of polymerization medium

Solvent-borne investigated photoreactive acrylic PSA was synthesized in ethyl acetate at 80°C at presence of 0.3 wt.% radical initiator AIBN with 60 wt.% polymer content using monomers mixture containing of 63.0 wt.% 2-ethylhexyl acrylate, 30.0 wt.% methyl acrylate, 5.0 wt.% acrylic acid and 2.0 wt.% 4-acryloyloxy benzophenone. All monomers and AIBN were available from BASF (Germany). The monomers mixture was dosage for 2 h into ethyl acetate and after that the 4 h post-reaction was conducted. After the polymerization process organic solvent ethyl acetate was evaporated in the first stage at 130°C. In the second stage of distillation 1 mmHg vacuum was used. The solvent-free acrylic PSA with high viscosity of 60 Pa·s at 100°C was obtained. After the addition of 100 wt.% photoreactive diluents Genomer 1122 from Rahn (Switzerland) according to the polymer content, the viscosity of the solvent-free acrylic PSA was reduced to 8.2 Pa·s. This viscosity makes it possible to perfect the cotability of these PSAs at room temperature.

Using of external surfactants

The manufacture of the removable solvent-free PSAs is being shifted from organic solvent systems to the solvent-free systems in order to reduce air pollution and to eliminate the rising expense of organic solvents. Surfactants are commonly used among other things to reduce the surface energy. They are combined from the same hydrophilic and hydrophobic derivates. The interesting chemical substances are:

– Polyalkylene glycols (f.e. Elfacos GT 282 L),

– Polyoxyethylated octylphenols (f.e. Remcopal N 17 80),

– Polyoxylene phosphates (f.e. EAK 8190).

The practicable concentration of the external surfactants for the removable solvent-free acrylic PSAs was between 0,1 and 5% wt.% according to the solid content. The synthesized photoreactive solvent-free acrylic PSAs containing photoreactive diluents and surfactants were coated at room temperature with 30 g/m^2 coat weight on 36 μm thick polyester film and after that were UV-crosslinked under UV lamp Aktoprint-mini-18-2 from Technigraf (Germany) using the UV dose of 1500 mJ/cm^2.

The following diagram (Fig. 4.) illustrates how the peel adhesion on steel (measured according to AFERA 4001) depends on the type of external surfactants: Elfacos GT 282 L, Remcopal N 17 80 and EAK 8190, and their concentrations.

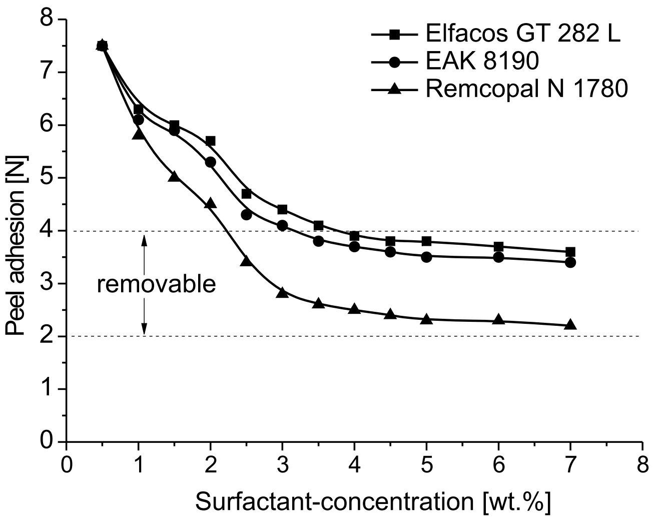

Figure 4. Influence of external surfactants on peel adhesion on steel

As shown in Figure 4, all the tested external surfactants have a positive impact on the peel adhesion of the solvent-free acrylic PSAs according to the typical values for the removable and repositionable self-adhesive products. The increase of the amount of all the investigated surfactants from 0.1 to 7.0 wt.% causes a decrease of adhesion on steel. The increase of the concentration of Remcopal N 17 80 above 2.5 wt.%, in the case of EAK 8190 above 3.5 wt.% and in the case of Elfacos GT 282L above 4.0 wt.% influences positively the removability of the photoreactive solvent-free acrylic PSAs.

Control of the peel adhesive of solvent-free removable PSAs can be achieved using external surfactants. The removable solvent-free PSAs were formulated and tested after UV-crosslinking on the substrates having different surface energies, for example PP and PVC. The peel-adhesion level during the storage time at 60°C for the investigated solvent-free acrylic PSAs contained 4.0 %wt. of the evaluated surfactants and crosslinked using 1500 mJ/cm^2 UV-dose has been shown in Fig. 5.

A key property of this type of the removable solvent-free acrylic PSAs is that the adhesion peel level does not build with time. Using the external surfactants by the modification of the solvent-free acrylic PSAs guarantees that the peel adhesion of the coated samples as reference of removability does not build significantly during the aging time. The best properties of removability were

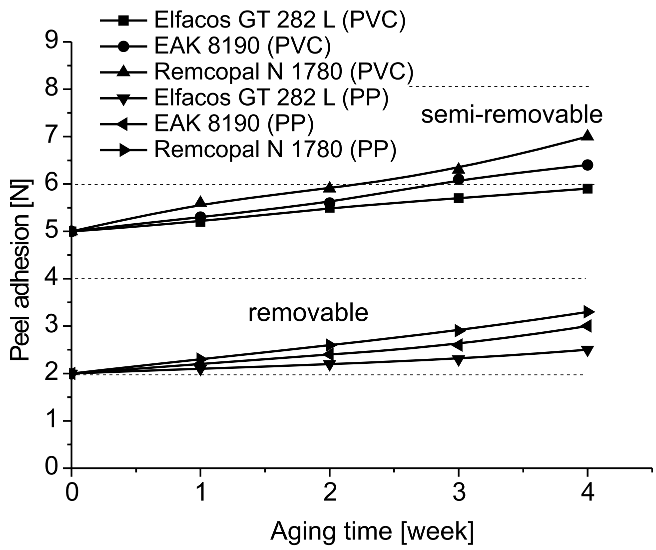

Figure 5. Adhesion performance of the solvent-free removable PSAs on PP and PVC substrates

noticed by using the surfactant Remcopal N 1780. In the case of PVC the semi-removable performance was observed.

Removable solvent-free acrylic PSAs modified with stearinic acid

The removable and repositionable solvent-free acrylic pressure-sensitive adhesive compositions containing stearinic acid are suitable for thin adhesive film applications to paper, or other laminar backing materials, for easy application to and removal from a variety of substrate surfaces. The amount of stearinic acid was added to acrylic PSA in content of 10 wt.% according to solid content. The investigated acrylic PSA containing stearinic acid was UV-crosslinked using the UV dose of 1500 mJ/cm^2.

The solvent-free acrylic PSA containing 10 wt.% of stearinic acid according to the solid content is recommended for use as removable self-adhesive and was tested on peel adhesion on steel, including the aging test for 4 weeks at room temperature and for 4 weeks at 40°C (Fig. 6.).

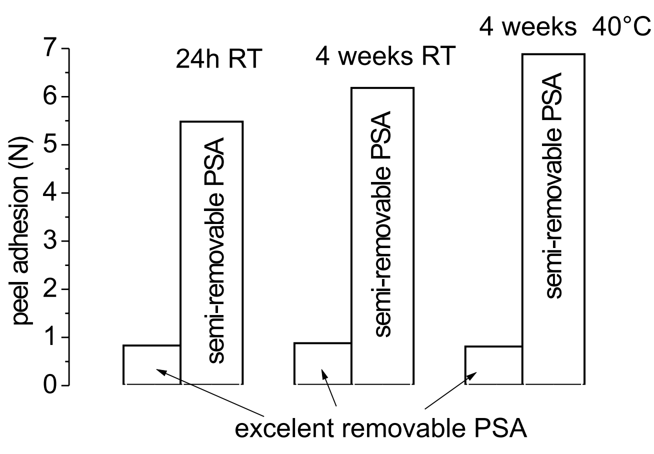

Figure 6. Aging of removable solvent-free acrylic PSA containing stearinic acid

The aging performance after 24 hours at room temperature and after 4 weeks of storage at room temperature and 40°C was investigated as well. In terms of the observed peel adhesion values after aging, the excelent removable

PSA with stearinic acid can be considered to be better than the other semi-removable product without stearinic acid.

INFLUENCE OF THE LAYERS COAT WEIGHT ON TACK AND PEEL ADHESION

The following experiments were conducted in order to study the influence of the adhesive layers coat weight of removable pressure-sensitive adhesives on their very important main performances such as tack and peel adhesion. The removable acrylic solvent-free PSAs modified with 10 wt.% stearinic have been coated on the polyester foil and UV-crosslinked using UV-lamp emitted 1500 mJ/cm^2 UV dose.

The effect of the adhesive layers coat weight on the investigated properties such as tack and peel adhesion understood as removability is presented in Fig. 7.

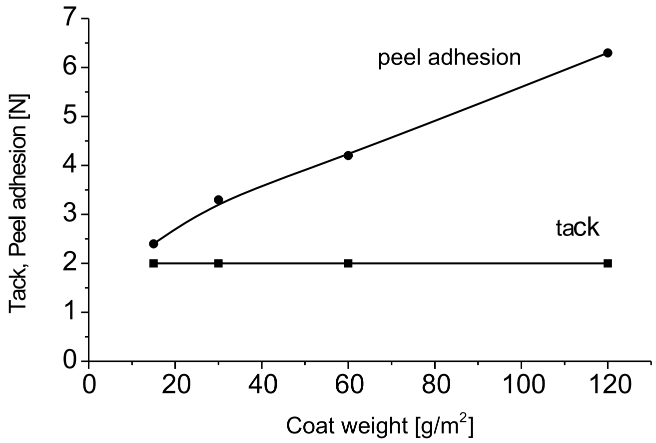

Figure 7. Tack and peel adhesion of removable acrylic PSAs vs. their layers coat weight

Concerning the adhesive layer coat weight of removable solvent-free acrylic pressure-sensitive adhesives the same level of tack was observed. The increase of coat weight from15 to 120 g/m^2 increases the peel adhesion from 2.3 to 6.2 N.

PROSPECTS FOR REMOVABLE AND REPOSITIONABLE SOLVENT-FREE ACRYLIC PSA

Removable and repositionable ecological solvent-free acrylic pressure-sensitive adhesives will play a major role in the development and production of new generation of self-adhesive removable and repositionable memo notes, paper and foil labels, double-sided tapes, carrier-free tapes, protective foils, hydrogels and medical tapes. All these mentioned self-adhesive products must quickly adhere to metal, paper, plastics, glass, wood, skin and other surfaces. The removable and repositionable acrylics solvent-free PSAs are characterized by excellent low tack and low constant level of peel adhesion and the excellent aging performance at room and higher temperature.

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