

Acrylic pressure-sensitive adhesives containing SiO₂ nanoparticles

Zbigniew Czech^{1*}, Agnieszka Kowalczyk¹, Joanna Ortyl², Jolanta Świdarska³

¹ West Pomeranian University of Technology, Szczecin, Faculty of Chemical Engineering, Pułaskiego 10, 70-322 Szczecin,

² Cracow University of Technology, Institute of Organic Chemistry and Technology, Warszawska 24, 31-155 Krakow,

³ Non-Public Health Center, Bolesława Śmiałego 28, 70-348 Szczecin

*Corresponding authors: psa_czech@wp.pl, Agnieszka.Kowalczyk@zut.edu.pl, jortyl@chemia.pk.edu.pl, jolanta-swiderska@tlen.pl

The use of acrylic pressure-sensitive adhesives (PSAs) is increasing in a variety of industrial fields. They have been applied in the manufacture of mounting tapes, self-adhesive labels, protective films, masking tapes, splicing tapes, carrier-free tapes, sign and marking films, and in diverse medical products, such as pads or self-adhesive bioelectrodes. In this study, the application of SiO₂ nanoparticles in acrylic PSA was investigated. The properties of the newly synthesized and modified PSA were evaluated via the tack, peel adhesion, shear-strength and shrinkage. It has been found that the nanotechnologically-reinforced systems consisting of monodisperse non-agglomerated SiO₂ nanoparticles and self-crosslinked acrylic PSAs showed a great enhancement in tack, peel adhesion, shear resistance and shrinkage, without showing the disadvantages known to result from the use of other inorganic additives. In this paper we evaluate the performance of SiO₂ nanoparticles with a size of about 30 nm as inorganic filler into the synthesized solvent-borne acrylic PSA.

Keywords: pressure-sensitive adhesives, acrylics, SiO₂ nanoparticles, tack, peel adhesion, shrinkage.

INTRODUCTION

One of the most important factors in nanoscience and nanotechnology is how one chooses high-impact research, development and application problems. New tools and methods open up new frontiers, as we have seen with the advent of scanning probes in nanoscience, as well as all the advances that have produced, and fuel, the nanotechnology revolution. The first vision of nanotechnology is widely credited to the physicist Richard Feynman, and his 1959 speech titled "There's Plenty of Room at the Bottom" is the beginning of the vision of this science¹. It wasn't until 1974, however, that Norio Taniguchi coined the term "nanotechnology" at the University of Tokyo. According to the Interagency Working Group on Nanoscience Engineering and Technology at the National Science Foundation: "Nanotechnology is the creation and utilization of materials, devices and systems through the control of matter on the nanometer-length scale, that is, at the level of atoms, molecules, and supramolecular structures"².

Modern, high-performance PSA must often meet competing requirements in their molecular structure. For instance, they must produce a hard and firm joint, yet must at the same time cushion dangerous stress peaks; their viscosity must be as low as possible during application, but at the same time, no severe shrinkage should occur during curing. Significant challenges are therefore faced in the development of new PSA.

Crystalline or amorphous nanoparticles, thousands of times smaller than the cross section of a human hair, have unique properties because of their small size³. One of their most important features is that nanoparticles are much smaller than the wavelength of light, and therefore do not scatter it, and are invisible even if billions of them are present in the material. Thus it becomes possible, for example, to produce new optical materials offering additional functions due to the high share of ceramic or metal. Of particular interest for adhesives is that if nanoparticles present in the polymer are well

distributed, they can change the polymer structure and thus change the polymers' properties⁴. This is due to the large surface area of the nanoparticles; more than 100 square meters per cubic centimeter of adhesive⁵. The growing importance of nanotechnology to the adhesives field is reflected in the number of publications and patent registrations in this area⁶ (Fig. 1) and in new adhesive or self-adhesive materials containing nano-fillers⁷⁻⁹.

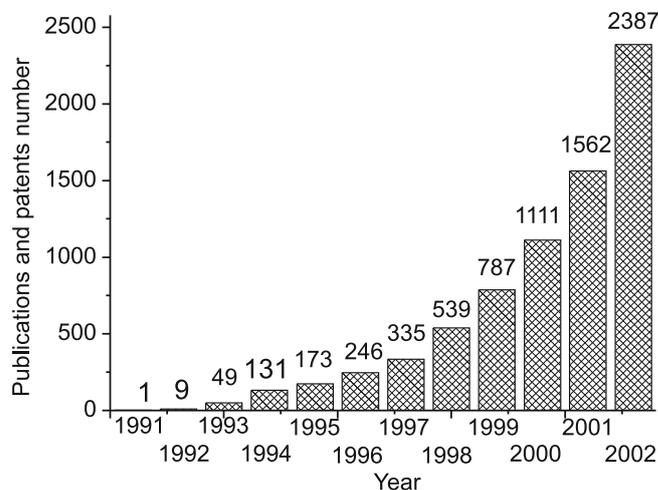


Figure 1. Number of publications and patents in the area of nanotechnology in adhesives between 1991 and 2002

EXPERIMENTAL

Materials and Methods

For the experimental trials the model solvent-borne acrylic PSA was synthesized in ethyl acetate with 50 wt.% polymer content using a mixture of 45 wt.% 2-ethylhexyl acrylate, 45 wt.% n-butyl acrylate, and 10 wt.% of acrylic acid, in the presence of 0.1 wt.% radical initiator AIBN, under the following conditions: polymerization temperature: 78°C, dosage time of monomers with AIBN: 2 h, time of post-reaction: 5 h.

Titanium acetylacetonate (TiACA) from Union Carbide was used as a crosslinker in the concentration of 0.1 wt.%

according to the polymer content as a 10% solvent in propanol-2. SiO₂ nanoparticles from Degussa with the size of about 30 nm were used as inorganic nano-filler. Nanoparticles could be easily dissolved into the synthesized solvent-borne acrylic PSA in concentrations between 0.1 and 3.0 wt.%, depending on the polymer content.

Evaluation of PSA properties

The influence of the SiO₂ nanoparticles on the adhesion and cohesion performance was evaluated by considering the following properties: tack, adhesion, and cohesion. These were determined according to the A.F.E.R.A. (Association des Fabricants Europeens de Rubans Auto-Adhesifs) standard procedures. The exact details can be found in AFERA 4015 (tack), AFERA 4001 (peel adhesion) and AFERA 4012 (shear strength). Administrative address: 60, rue Auber-94408 Vitry Sur Seine Cedex, France.

Shrinkage

Shrinkage was defined as the percentage or millimeter change in the dimensions of a PVC foil covered with PSA. The dimensions were measured before and after PSA crosslinking and attachment to a glass surface, after keeping it for four weeks at a temperature of 60°C. When shrinkage greater than 0.5% or 0.5 mm was observed, other properties were neglected.

Viscosity

The viscosity of the investigated solvent-borne acrylics pressure-sensitive adhesives was determined at 23°C using a Rheomat RM 189 from Rheometric Scientific, using spindle No 3.

Residue monomers

The amount of solid material was determined according to DIN EN 12092, and the residual monomer contents were measured using a gas chromatograph (Unicam 610, J&W DB-1 column, FID detector and integrator Unicam 4815).

Molecular weight

Molecular weight studies were performed in tetrahydrofuran with a liquid chromatography LaChrom system (RI Detector L-7490 and LaChrom UV Detector L-7400 from Merck-Hitachi, equipped with a PLgel 10⁶Å column from Hewlett-Packard).

RESULTS AND DISCUSSION

Influence of SiO₂ nanoparticles on PSA properties

The final synthesized solvent-borne acrylic PSA was characterized by the following important properties after an addition of an isopropyl alcohol stabilizer: amount of solid material 40 wt.%, viscosity 13.8 [Pa·s], concentration of residual monomers < 0.3 wt.%, weight average molecular weight $M_w = 910\,000$ Dalton, number average molecular weight $M_n = 328\,000$ Dalton, polydispersity $P_d = M_w/M_n = 2.77$.

The influence of the tested SiO₂ nanoparticles (at concentrations between 0.1 and 3.0 wt.%) on the tack and peel adhesion of acrylic PSA is illustrated in Fig. 2 (tack) and in Fig. 3 (peel adhesion values measured at

20°C after 20 min and after 24 h). The influence of the tested SiO₂ nanoparticles on the shear strength at 20°C and 70°C is illustrated in Fig. 4.

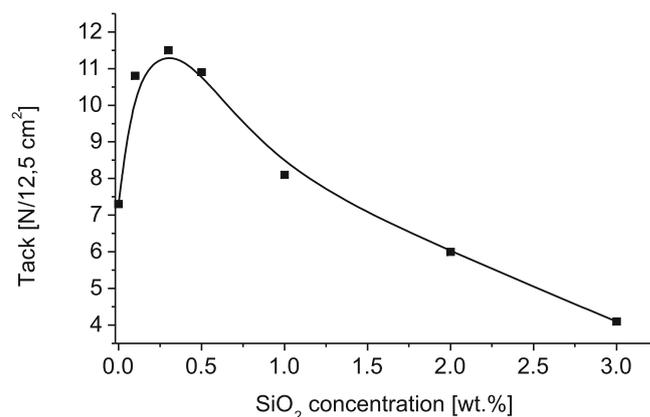


Figure 2. Tack of solvent-borne acrylic PSA versus SiO₂ nanoparticle concentration

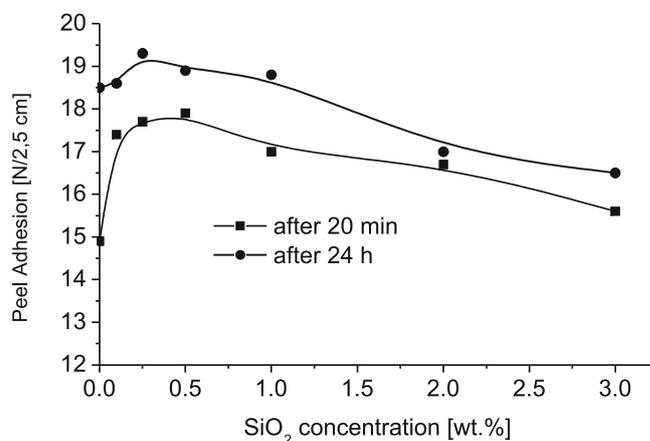


Figure 3. Peel adhesion of solvent-borne acrylic PSA measured after 20 min and 24 h versus SiO₂ nanoparticle concentration

With the addition of small concentrations of SiO₂ nanoparticles, an amelioration of the tack and peel adhesion of the modified PSA was observed. Self-adhesive layers containing about 0.3–0.5 wt.% of SiO₂ nanoparticles showed the best tack and adhesion levels. At higher concentrations of SiO₂ nanoparticles, the tack and peel adhesion values were reduced.

As expected, an increase in the SiO₂ nanoparticle concentration positively affected the cohesion performance

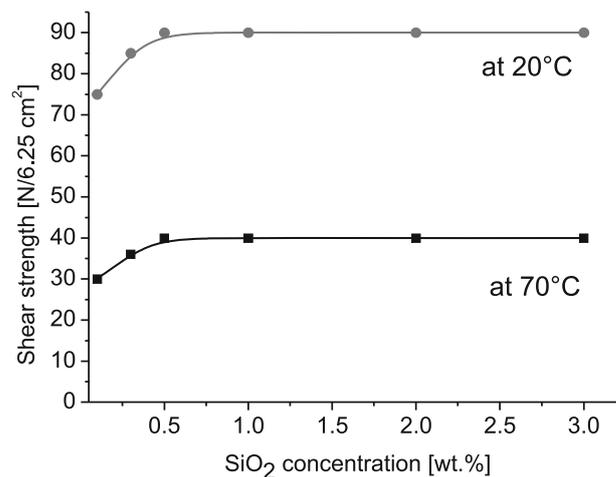


Figure 4. Shear strength of solvent-borne acrylic PSA at 20°C and 70°C versus SiO₂ nanoparticle concentration

of the modified acrylic pressure-sensitive adhesives. The best cohesion level, as tested at 20°C and 70°C, was achieved by using more than 0.5 wt.% of SiO₂ nanoparticles. The influence of SiO₂ nanoparticle concentration on the shrinkage of acrylic PSA is illustrated in Fig. 5.

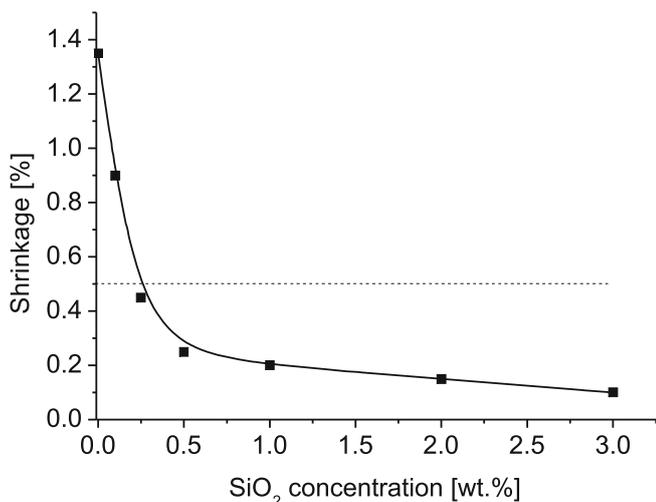


Figure 5. Shrinkage of solvent-borne acrylic PSA versus SiO₂ nanoparticle concentration

Figure 5 shows that the shrinkage resistance of acrylic PSA containing SiO₂ nanoparticles was improved in comparison to acrylic PSAs without nanofiller. For acrylic PSA free of SiO₂ nanoparticles, a high shrinkage value of 1.35 mm was observed. After an addition of SiO₂ nanoparticles, the shrinkage values were reduced. For 0.3 wt.% SiO₂ nanoparticles, an acceptable shrinkage of 0.45 mm was observed, and for 0.5 wt.% SiO₂ nanoparticles, a low shrinkage of 0.25% was achieved.

The observed maxima of tack and peel adhesion of pressure-sensitive layers for ca. 0.3–0.5 wt.% of SiO₂ nanoparticles are through the adhesive layer softness by addition of small concentration of filler to explain. Further increase of nanofillers concentration increases of course the shear strength of investigated acrylic pressure-sensitive adhesives and ameliorates through better cut-ability their shrinkage resistance.

Pot life of acrylic PSA containing SiO₂ nanoparticles

The pot life of acrylic PSA is an important factor in maximizing the possibilities for its application. The crosslinking process in acrylic PSA in which the crosslinkers use carboxyl groups incorporated into a polymer chain is usually conducted in a drying canal at the temperatures between 100–120°C, which achieves the removal of organic solvent from the adhesive layers. A long pot life of a few days or months would allow the storage of crosslinkable solvent-borne PSA, and would allow further coating on a wide range of PSA products.

For the acrylic PSA containing SiO₂ nanoparticles studied here, the longest pot life was achieved with the smallest concentration of SiO₂ nanoparticles; in this case for 0.1 wt.% of nanofiller. The acrylic PSA system containing SiO₂ nanoparticles remained stable for at least one month for 0.1 wt.%, and 20 days for 0.3 wt.% SiO₂ nanoparticles (Fig. 6).

In some cases, where a decrease in the pot life was observed in the presence of more than 1.0 wt.% SiO₂ nanoparticles, an alcohol stabilizer must be added. Without stabilizer, a marginal disadvantage of the acrylic

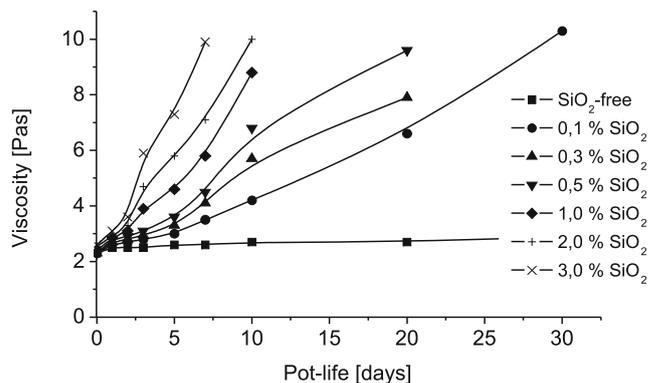


Figure 6. Viscosity run of solvent-borne acrylic PSA containing SiO₂

PSA systems containing SiO₂ nanoparticles is their pot life, which is limited to several days. Probably the acrylic pressure-sensitive adhesive reacts through the carboxylic groups from acrylic acid with SiO₂ nanoparticles which leads to an unacceptable increase of PSA viscosity.

CONCLUSION

The nanotechnologically-reinforced systems consisting of monodisperse non-agglomerated SiO₂ nanoparticles and self-crosslinked acrylic PSAs showed a great enhancement in tack, peel adhesion, shear resistance and shrinkage, without showing the disadvantages known to result from the use of other inorganic additives. Even with concentrations of SiO₂ nanoparticles of up to 0.5 wt.%, transparent, high performance acrylic PSAs with excellent properties were realized, making these acrylic PSAs containing SiO₂ nanoparticles a useful and versatile raw-material source suitable for all kinds of high performance applications. As expected, the effects of the nanofiller were determined by the particle concentration. The performed tests showed that noteworthy effects in the solvent-borne acrylic PSA system were observed at SiO₂ nanoparticle concentrations above 0.5 wt.%, depending on the polymer content.

LITERATURE CITED

- Imerito, T. (2005). Nanotechnology building from the bottom and building the bottom line. *JOM* 57 (12), 18–23. DOI: 10.1007/s11837-005-0177-z.
- Murad, D.S. (2002). It's a small world after all. *Adhesives Age*, October, 40–44.
- Frisch, F. (2003). Nanotechnology gives a boost to adhesive technology. *Adhäsion* 4 (47), 16–19.
- Krüger, G. (2006). Nanoparticles of SiO₂, ZrO₂ and BaSO₄ in Acrylate Dispersions. *Coating* 3, 113–115.
- Sprenger, S., Eger, C., Kinloch, A. & Ambrose, C. (2004) Nanoadhesives: toughness and high strength, *Adhesion Adhesives & Sealants* 3, 20–24.
- Hertel, T. (2004). Kohlenstoff-Nanoröhren: Bausteine der Mikroelektronik von Morgen. *Nachrichten aus der Chemie* 52, 137–140.
- Czech, Z., Kowalski, A. & Ortyl, J. (2011). Tack of pressure-sensitive adhesives (PSAs). *Coating* 1, 22–25.
- Zosel, A. (1985) Adhesion and Tack of Polymers: Influence of Mechanical Properties and Surface Tensions. *Colloid & Polymer Science* 263 (7), 541–553. DOI: 10.1007/BF01421887.
- Czech, Z. & Wesolowska, M. (2007). Development of solvent-free acrylic pressure-sensitive adhesives. *European Polymer Journal* 43, 3604–3612. DOI: 10.1016/j.eurpolymj.2007.05.003.