Solvent-borne but water-soluble

Based on butyl acrylate plus acrylic acid monomer, new pressure sensitive adhesives have been developed, which are solventborne in the formulation and water soluble after application, and which can be cured either by external crosslinkers or via UV radiation. These PSAs may find useful application in, e.g. medical electrodes or water dispersible labels.

A new generation of acrylic-based PSAs for labels or medical devices

The research on water-soluble polymers with self-adhesive properties is an interesting scientific terrain where many further developments are expected. Solvent-borne, water-soluble, pressure-sensitive adhesives (PSA) based on acrylics are still something of a speciality. They are applied as one-sided and double-sided tapes or as transfer films for web splicing in the paper industry. A challenging area of water-soluble PSAs application is their use for water-dispersible labels, medical devices such as surgical tapes and bio-electrodes [1]. A new generation of water-soluble acrylic based PSAs has been developed. They are crosslinked using external crosslinkers or by the use of UV-Light.

The monomers used to synthesise the samples of solvent-based, water-soluble PSAs for the study were an insoluble "soft" monomer butyl acrylate (BA) and a soluble "hard" monomer acrylic acid (AA) or β-acryloyloxy propionic acid (APA) [3]. The water solubility of the synthesised acrylic copolymers at different pH-values (4, 7 and 11) is illustrated in Figure 1: From that figure it is clear that the increase of pH-value improves the water solubility of acrylic PSAs containing hydrophilic acids in their polymer structure. The dissolving time for polymers containing acrylic acid is shorter.

Experimental

The synthesis of water-borne acrylic PSA was carried out using two solvents: hydrophilic acetone (B.P. 56 °C) and a hydrophobic n-hexane (B.P. 69 °C). Sufficient solvent to reduce the viscosity of synthesised adhesives to less than about 100 Pa s was used. For most solvent-borne water-soluble acrylic PSAs, the quantity of solvent that gives a solids content of from about 40 wt.% to about 50 wt.% is sufficient for this purpose. PSA solutions with less than about 40 wt.% solids are undesirable [4]. The measured temperature in the reactor during the polymerisation process is shown in Figure 2. During the two hours of polymerisation, the temperature rose to about 60°C to 65°C.

Molecular weight is crucial

The molecular weight of acrylic, pressure-sensitive adhesives is of great importance for its mechanical, physical and thermal properties and has been shown to be key to the final self-adhesive performance [5]. The peel performance increases with molecular weight to a maximum value with a subsequent decrease and levelling off as the failure mode changes from cohesive to adhesive. The cohesive or shear properties climb to a maximum as the molecular weight increases. Cohesion tearing occurs even at low shearing loads. This would disqualify the polymer as pressure-sensitive adhesive. The molecular weight and branching are controlled in the polymerisation process by the choice of initiator and the amount used, by the process temperature and the chain-transfer agents [6]. The molecular weight of the solvent-borne, water-based acrylic PSAs ranges with between 450,000 to 1.2 million dalton. The selected PSA, synthesised from 50 wt.% butyl acrylate (BA), 30 wt.% β-acyloyloxy propionic acid (APA) and 20 wt.% acrylic acid (AA), was crosslinked with metal-chelate zirconium acetylacetonate (ZrACA). It is typical for crosslinking systems containing metal chelates that alcohol is added as a stabiliser. After this has vapourised with other solvents during drying, the crosslinking starts spontaneously. Figures 3 and 4 show the influence of the ZrACA content on shear strength at 70°C and on peel adhesion on paper for water-soluble acrylic PSAs, respectively, with different molecular weight Mw.

As seen in the water-soluble acrylic self-adhesives tested, the increase of the PSA molecular weight and crosslinking-agent concentration improve the PSA cohesion. Acrylic PSAs with higher molecular weights have higher shear strength. The shear-strength measurement shows that the higher the molecular weight, the lower the necessary concentration of ZrACA to achieve the same PSA cohesion. After the addition of about 0.4 wt.% of the crosslinker zirconium acetylacetonate (ZrACA), an improvement of the acrylic water-soluble PSA peel adhesion on paper took place. The water-soluble PSA films crosslinked using ZrACA are unusually tacky and aggressive. Above a threshold of 0.4 wt.% ZrACA, the peel-adhesion level decrease. As can be inferred from the Figure 4, peel adhesion on paper correlates closely with the molecular weight of synthesised, solvent-borne, water-soluble acrylic PSAs.

UV-curing allows to vary peel adhesion vs cohesion

UV-crosslinkable, water-soluble, acrylic PSA systems require initiators to start the radical-crosslinking reaction. The new-generation PSAs contain unsaturated photoinitiators which are incorporated into the polymer backbone during the polymerisation. Work is, however, mainly directed to the development of functionalised acrylated, vinylated, allylated, acrylamidated or vinylxylated chromophores of type I and type II photoinitiators [7]. The most efficient copolymerisable photoinitiator is 4-acyloxybenzophenone (ABP). The crosslinking mechanism of photoreactive, acrylic PSAs, containing ABP or benzophenone derivatives incorporated into polymer backbone, has been thoroughly investigated [8] and is shown schematically in Figure 5. During UV exposure, the intermolecular benzophenone derivative H-abstractor structures are excited and react by hydrogen abstraction with the neighbouring tertiary-carbon-atom positions of the polymer side chains. As in commercial acrylic, self-adhesive, hotmelts such as the "acResin" from BASF, the UV crosslinking process...
runs only, or predominantly, via benzophenone groups and tertiary carbon atoms from the polymer chain. With UV-crosslinkable, acrylic PSA, the ratio of peel adhesion to shear strength (cohesion) can be widely varied by controlling the doses of radiant energy applied to the adhesive film after it has been coated. Water-soluble acrylic films formed by UV-crosslinkable adhesive become more cohesive as more radiant energy is applied. At the same time, their peel adhesion decreases. This effect is the result of the crosslinking that takes place when the film is exposed to UV light. Figure 6 shows schematically the effect of the ABP concentration at a constant dose of UV radiation and UV-crosslinking time on the adhesive properties measured on paper and cohesion for water-soluble PSA based on butyl acrylate, acrylic acid and β-acryloyloxy propionic acid with molecular weight of about 650 000 dalton. The highest efficiency of unsaturated photoinitiator ABP with respect to peel adhesion and shear strength was obtained with a level of about 0.1 wt.% ABP. Even small contents of ABP yielded UV-crosslinked acrylic PSAs with outstanding shear strength values.

Biomedical applications
The novel solvent-borne, water-soluble, conventional crosslinkable or photoreactive acrylic PSAs can be applied as biomedical electrodes. As large-area self-adhesive medical electrodes are well-known TENS (transcutaneous electrical nerve stimulation) electrodes, ESU (electro-surgical unit) electrodes, EKG, defibrillation and bio-feedback electrodes.

References

Results at a glance
- A new generation of water-soluble acrylic based PSAs has been developed, which are crosslinked using external crosslinkers or by the use of UV-Light.
- In the case of the photoreactive PSAs, the unsaturated photoinitiators are incorporated into the polymer chain during the polymerisation process.
- The best photoinitiator found was 4-acryloyloxy benzophenone [2]. After crosslinking an excellent water-solubility of PSA layer was observed.

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Figure 6: Peel adhesion on paper and shear strength as a function of ABP amount

- Mw=650000 dalton
- UV-crosslinking time=3 min
- UV dose=150mJ/m²

peel adhesion --- shear strength at 70°C
Figure 1: Water solubility of PSAs at different pH-values dependence of various amounts of acid monomers
Figure 2: Temperature run in the polymerisation reactor during the synthesis of acetone/ n-hexane-borne acrylic PSA
Figure 3: Effect of crosslinker ZrACA content and PSA molecular weight on thermal shear strength.
Figure 4: Effect of crosslinker ZrACA content and PSA molecular weight on peel adhesion on paper
Figure 5: UV initiated crosslinking reaction of water-soluble acrylic PSAs based on BA and ABP