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RESEARCH ARTICLE

New Water-Based Adhesives For Flexible Food Packaging Chemical Design, Performance and Toxicological Safety

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INTRODUCTION

Today the laminating adhesives market for flexible food packaging is dominated by solvent-borne and by reactive solventless polyurethane systems. Reactive solventless adhesives have become very popular to substitute solvent-borne adhesives, because of cost advantages and because of the fact that emissions of organic solvents are avoided. However, there are two limitations of the solventless adhesive technology: Especially laminates having been produced with solventless adhesives for high-end packaging applications have to be stored for several days before being applied for food packaging. These storage times are necessary in order to build up bonding strength for subsequent cut and sealing processes and in order to eliminate low molecular weight ingredients with a toxicological risk potential for the food that is packed. Another disadvantage of solventless adhesives can be that the visual appearance of prints and the transparency of non-printed clear laminates may be significantly worse than that of laminates being produced with solvent-borne adhesives.

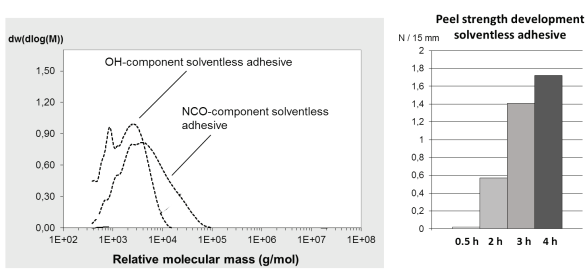
Considering the limitations of current solvent-borne and solventless laminating adhesives the question comes up: Can water-based adhesives be an attractive alternative?

1 LIMITATIONS OF CURRENT SOLVENT-BORNE AND SOLVENTLESS ADHESIVES

1.1 Build-up of bonding strength

The peel strength of a laminate bonding depends to a large extent on the molecular weight of the adhesive. To create a significant bond strength polymeric adhesives should have at least a medium molecular weight of several 10 000 Dalton. A challenge for two component polyurethane adhesives being used today is that the build-up of molecular weight in the adhesive between the films requires a certain period of time.

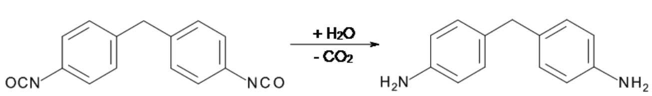
Fig. 1. *Molecular masses of solventless adhesives (GPC) and build-up of laminate bonding strength*



Before the reactive adhesive has reached a sufficient molecular weight, the laminate shows only a very limited resistance to mechanical stress. When using solventless adhesives, which typically start from very low molecular weight components (figure 1), there is a risk that immediately after the second web is laminated, the films move against each other due to a not yet assembled bonding strength. In this case a rapid processing of freshly prepared laminate rolls is difficult. Rewinding and slitting is only possible after several hours of storing the laminate rolls, and the risk of telescoping of the rolls is omnipresent. Heat seal operations can be performed usually only after several days, because the high mechanical stress to the laminate during the sealing process requires a sufficient strong bonding strength of the laminating adhesive.

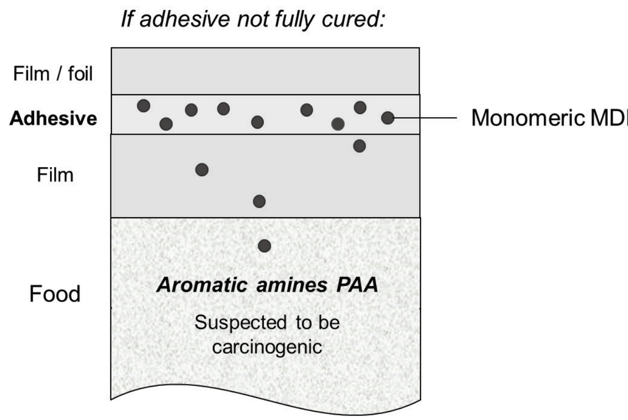
1.2 Toxicological risks of aromatic amines in packed food

In addition to the limited green strength users of reactive polyurethane adhesives are confronted with another problem, and that is the risk of contaminating the food being packed with toxic components. Usually solvent-borne and especially solventless adhesives contain some per cent of monomeric aromatic isocyanates, for example diphenylmethane diisocyanate (MDI). This chemical is used as a component of the adhesives due to its high chemical reactivity to enables a rapid build-up of molecular weight and thereof the bonding strength. If there is some unreacted aromatic isocyanate being left in the adhesive, there is a danger that this isocyanate migrates through the inner laminate film into the packaged food and hydrolyses there to form an aromatic amine.



Such aromatic amines are suspected of causing cancer and must not be detected in the food. As a consequence of this danger there have to be several days between laminate production and filling of the flexible packaging with food. This storage time ensures that the aromatic isocyanate in the adhesive layer has completely been converted to a non-toxic product, by being incorporated into the polymer network of the adhesive. In recent years for solventless adhesives this waiting time could be significantly reduced by chemical innovations, however, even today it is generally at least some days of storage time. For high performance-applications, e.g. retortable packaging, necessary storage times can reach up to 2 weeks in heated chambers.

Fig. 2. Risk hydrolysis of MDI in solventless adhesives to aromatic amines



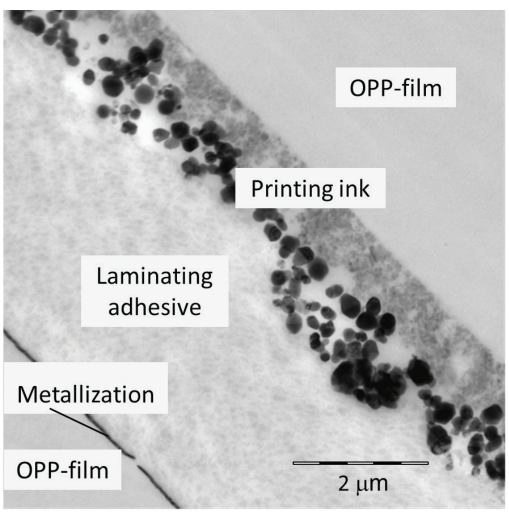
2 WATER-BASED LAMINATING ADHESIVES

Since many years aqueous dispersions have been known as laminating adhesives for flexible packaging, however, in Europe they have only be used in some niche applications. In contrast, they are much more common in North America and have reached a market share of about 20% of all the laminating adhesive systems for flexible packaging.

Aqueous laminating adhesives are used in the form of aqueous polyurethane or acrylic dispersions. For the manufacture of flexible packaging for general purpose applications, the aqueous adhesives are typically applied as one-component systems without adding a reactive additive. For higher quality medium and high performance applications, aliphatic water-emulsifiable polymeric isocyanates as chemical crosslinker can be mixed into the aqueous dispersions to improve both the thermal and chemical resistance of the adhesive.

It is decisive for a good adhesive performance that during the laminating step the dry adhesive on the primary film wets the secondary film in an excellent way in order to achieve a sufficient adhesion. A good wetting, which means forming a close contact in molecular dimensions, may be challenging, as such a secondary film may have a rough surface, e.g. if it is printed with an ink:

Fig. 3. Laminate construction with water-based adhesive for snack food packaging



In figure 3 a reverse printed OPP film has been dry laminated to a metallized OPP film, which had been coated with a new developed aqueous acrylic dispersion as a laminating adhesive. A good wetting onto the rough colour pigment surface is visible here resulting in high bond strengths of the laminate. Another consequence of the good wetting is an excellent brilliance of the print.

With regard to an immediate processing of the laminates an essential difference between aqueous adhesives and solvent-borne as well as solventless adhesives is that the aqueous adhesives are characterized by a significant higher molecular weight. This includes a much lower content of low molecular weight ingredients that may migrate into the food.

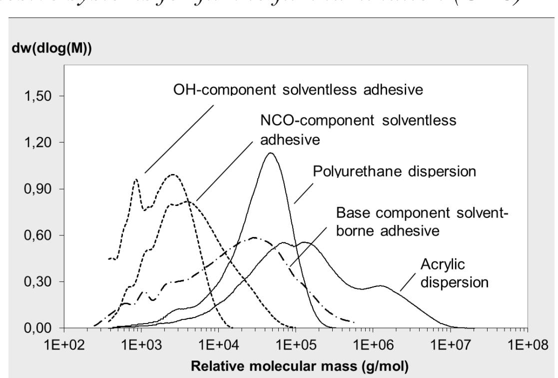
This basic difference in the molecular weight distribution can be illustrated by means of gel permeation chromatography (GPC).

As demonstrated in Figure 4, the average molecular weight of the basic component of the solventless adhesive is located at only 7 000 Dalton and its hardener component even at 2 500. The PU dispersion has a medium molecular weight of 50 000 and the acrylic dispersion has a medium molecular weight of 500 000.

As described in the previous section, for both reactive solvent-borne adhesives and solventless systems, the polymer molecular weight is started to build after the two components being

mixed and the chemical reaction is continuing after the adhesives being coated on the packaging substrates. On the contrary, the water based lamination adhesives completed its polymerization reaction during the adhesive manufacturing process. The high molecular weight was already built in the reactor, not at the lamination process.

Fig. 4. Molecular weight distribution of exemplary adhesive systems for film to film lamination (GPC)



Laminating adhesive components with a molecular weight <1000 are most critical with regard to their potential to contaminate food being packed, because they have the potential to migrate through the inner film into the food. As illustrated in Figure 4, the water-based laminating adhesives contain much less of these critical ingredients than solvent-borne and especially solventless adhesives. Being fully polymerized systems the new aqueous adhesives allow for a filling of the laminate packaging with food immediately after the laminate has been produced. They comply with all relevant food contact regulations.

Hence the benefits of the aqueous dispersions being completely polymerized adhesives are obvious:

- A very high green strength of the laminate for an immediate further processing
- The minimization of the toxicological risks at the food packer

"Laminate and Deliver within a Day" becomes reality with aqueous adhesives and can bring a significant competitive advantage to the producer of flexible packaging.

In addition, the adhesive films formed by water-based adhesives show a comparable clarity with solvent-borne adhesives and do not impair the brilliance of prints, provided that the adhesive is coated with an appropriate coating device. And this is as another advantage that water-based adhesives show on solventless systems, especially if high adhesive coating weighths are applied.

2.1 Adhesive performance of water-based laminating adhesives

By intensive efforts in R & D novel aqueous dispersions have been developed now, which allow for a significantly enhanced performance range of the resulting adhesives at a competitive cost.

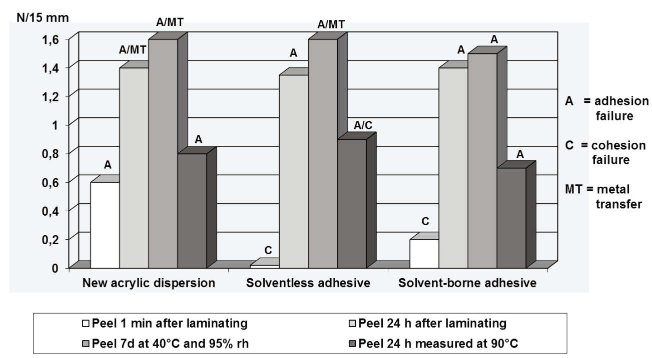
2.1.1 General purpose applications

The key benefit of the new water-based adhesives is reflected in the comparison of their green strengths, which are measured as peel strength 1 min after lamination. While the solventless adhesive in figure 5 has not yet produced any significant bonding strength even after an hour, the lami-

nates with the water-based adhesives show a significant peel strength immediately after lamination. The further peel strength increase with time of the aqueous adhesives is not a consequence of a chemical reaction in the adhesives, but due to the completion of the physical flowing (wetting) onto

the secondary film, which has been dry laminated.

Fig. 5. Peel strength comparison in OPP-ink / adhesive / metallized PE-laminate

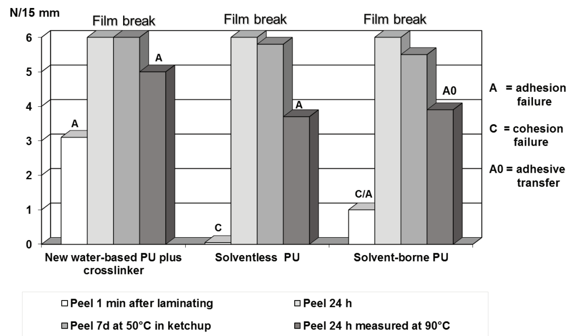


In figure 5 it is also demonstrated that with regard to green strength the aqueous adhesive is also superior to the solvent-borne adhesive, though not to such a high degree as to the solventless system. This is due to the higher molecular weight of the solvent-borne system (figure 4). Because of their high green strength, inline converting processes such as an inline slitting of the laminate roll becomes possible for converters who use water-based adhesives.

2.1.2 Medium performance applications

By adding some per cent of a water emulsifiable polymeric isocyanate crosslinker to the water-based adhesives, a considerable improvement of heat and chemical resistance can be obtained, allowing applications up to the high-performance range.

Fig. 6. Heat and chemical resistance in PET-ink / adhesive / PE –laminate



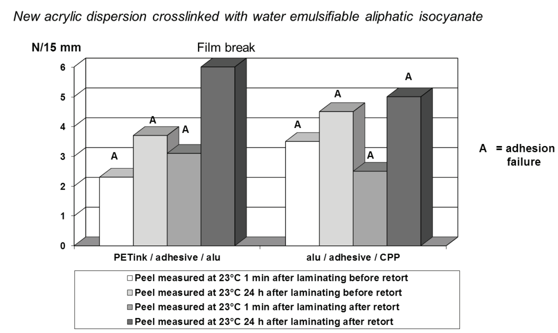
The crosslinker does not contain any aromatic isocyanate and therefore there is now toxicity risk of aromatic amines. Thus, the high toxicological safety of the aqueous systems is not affected by this kind of chemical crosslinking.

As a test for chemical resistance laminate stripes are stored for 7 days at 50°C in ketchup, which contains aggressive acids and oils, prior to measuring their peel strength. For describing their heat resistance the peel test was performed in a heated chamber at 90°C.

2.1.3 High performance (retortable) applications

Retortable flexible packaging has gained a considerable market share in recent years. Typical applications include not only pet food packaging but also packaging of convenience food. By the retort process, e.g. by treating the packed food in an autoclave for 30 min at 130°C, long-life food is produced. Due to the retort process the adhesive has to show an extraordinary resistance to heat, water and chemicals. Today only some solvent-borne polyurethane adhesives meet the technical requirements for retortable flexible packaging. A novel water-based acrylic dispersion has been developed, which matches the technical demands for several retort applications, e.g. pet food packaging in PETink/alu/cPP laminates.

Fig. 7. Water-based retortable adhesives



3 SUMMARY

A series of water-based lamination adhesives have been developed successfully for flexible packaging applications. As demonstrated in this paper, the water-based adhesives offer excellent food safety and adhesive green strength, which in turn make the in-line processing possible to shorten the overall converting process time. In addition an excellent film clarity and print brilliance can be achieved. With these advantages, water-based adhesive is a very attractive choice of lamination adhesives for the growing flexible packaging industry.