

Recent Advances and Trends in Reactive Polyurethane Adhesives

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Abstract: The paper highlights technical advances and introduces recent innovations such as smart curing laminating adhesives for flexible packaging with low migration rates of aromatic isocyanates and amines. Latent reactive one-part systems on the basis of surface deactivated solid isocyanates open up new dimensions for heat setting adhesives and waterborne PU dispersions. The new generation of Purnelt Micro Emission adhesives contains less than 0.1% of MDI monomer, thereby drastically reducing the emission of hazardous isocyanate vapors during processing and setting a significantly improved technical standard in occupational safety. Once again, polyurethane adhesives have demonstrated their unique ability to adapt to new process, product, safety and environmental requirements.

Keywords: Polyurethane adhesives, lamination, flexible packaging, latent reactive, surface deactivated, MDI emission, monomer reduction, product stewardship

1. Introduction

In the past decades reactive polyurethane adhesives have found their way into nearly every application area due to their outstanding properties, unique versatility and cost efficiency. They can be readily tailored to display unique combinations of properties. Although the first commercial products were already introduced sixty years ago, polyurethane adhesives are still a lively and exciting technological field with a high innovation potential.

2. Two-Part Polyurethane Adhesives for Flexible Packaging

The lamination of packaging films is one of the most important applications for polyurethane adhesives. The volume of the European market, for instance, is estimated to exceed 50,000 metric tons per year. Solvent-free PU systems in particular are enjoying steady and dynamic growth rates because of their economic benefits and environmental compatibility.

Light and flexible packaging would not be possible without laminates. They result from the bonding of various materials, such as paper, plastic films or aluminum foil. In a coffee vacuum pack, for example, the aluminum foil is the primary barrier against moisture,

oxygen and light. Mechanical strength, like tear and abrasion resistance, and printability are contributed by a polyester layer, and a polyethylene film on the surface of the laminate allows bonding by hot sealing. These characteristics are not attainable if the materials are used alone. The different layers are laminated with the help of special PU adhesives to form a new film composite material. The line speed can exceed 600 meters per minute.

In this application two-part polyurethanes have a clear advantage over moisture-curing one-part adhesives. While the moisture content of paper and cardboard is high enough to accomplish safe cross-linking, this is not the case for plastic films. The inner adhesive layers of a rewound reel would not cure properly due to the shortage of moisture. Beyond that, carbon dioxide bubbles could be formed which would impair the aesthetics of the food package.

The applied two-part polyurethane adhesive has to meet first of all the standard requirements such as excellent adhesion, machine processability and a favorable cost/benefit ratio. Moreover, high performance adhesives have to resist aggressive contents such as fruit juice or dishwashing liquids. When used for the lamination of instant meal packs, the heat resistance has to be high enough to allow the sterilization of retortable pouches to ensure effective killing of any microbes.

Since the film composites come into direct contact

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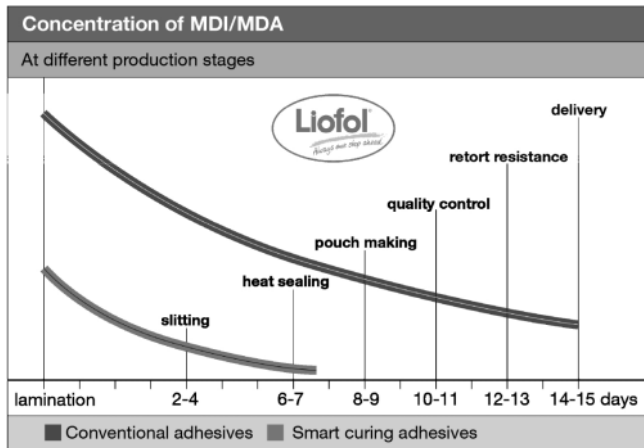


Figure 1. Lamination of flexible packaging, production stages and curing characteristics.

with foodstuffs, new requirements arise which can be summarized under the term ‘migration’. Low molecular weight monomeric diisocyanates and their metabolites are migratable and can therefore overcome the barriers of the plastic films. Through contact with moisture the isocyanate groups of the migrates are continuously converted to amino groups which are specifically deemed to be of critical importance due to their carcinogenic potential.

So diisocyanates and their metabolites, particularly primary aromatic amines (PAA), constitute a health hazard if they are capable of migration into the foodstuff. Stringent regulations have been prescribed by legislature. It goes without saying that residual amines must drop below the threshold limits specified for use in food packaging.

Migration through packaging material can also cause the so-called anti-sealing effect. When monomer isocyanates migrate through plastic films they can form a polyurea layer when they react with atmospheric moisture and slip-agents of the polymer film. This very stable and high melting polyurea layer makes the laminate unsealable. So it is essential to lower the migration tendency as far as possible.

Two-part PU adhesives have relatively slow cure rates. We can distinguish between macroscopic cure, which is essential for processing steps like slitting, heat sealing and pouch making, and the microscopic cure, that is, the compliance with specific migration limits. Ideally both mechanical resistance and filling safety should be reached simultaneously within a very short time.

While conventional PU adhesives for flexible packaging suffer from long migration times up to 14 days or even longer-smart curing systems allow a strong de-

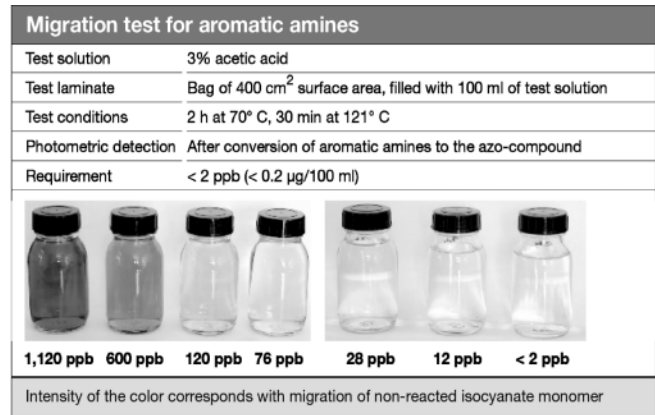


Figure 2. Migration test for aromatic amines.

crease of the time span between lamination and compliance with food packaging regulations (Figure 1).

This is achieved by a drastic reduction of the monomer content as well as by an intelligent chemical curing mechanism that takes place in steps. The polyol hardener of the two-part system reacts much faster with the isocyanate monomer than with the terminal NCO groups of the polymer. Therefore the critical monomers become immobilized at first.

This can be visualized in a simple migration test for the aromatic amines (Figure 2). The testing method is standardized and close to practice. A laminated bag is filled with diluted acetic acid and heated up to 70°C. Migrated aromatic amines can be easily photometrically detected after derivatization to the azo compounds. The intensity of the color corresponds to the extent of migration. Extremely high values can be found if curing is incomplete. Values less than 2 ppb or respectively less than 0.2 µg/100 mL are strongly recommended.

Further progress has recently been achieved with novel dual cure systems [1]. The outstanding performance of polyurethane adhesives has been combined with the high polymerization speed of the acrylic double bond. The one-part formulation allows easy processing without pot-life constraints. The system enables high green strength upon UV irradiation, that is to say, bond-on-command characteristics. On the other hand, cross-linking is not complete directly after irradiation, which makes it possible to irradiate the adhesive before the nip station. Because these adhesives are based on the free radical mechanism, the irradiation step has to take place under an inert gas blanket. The MDI monomer content is less than 0.1%, so the migration test is passed less than one day after lamination. The dramatically reduced cure time enables converters to downsize their warehouses and to cut costs, and is at the same time an essential contribu-

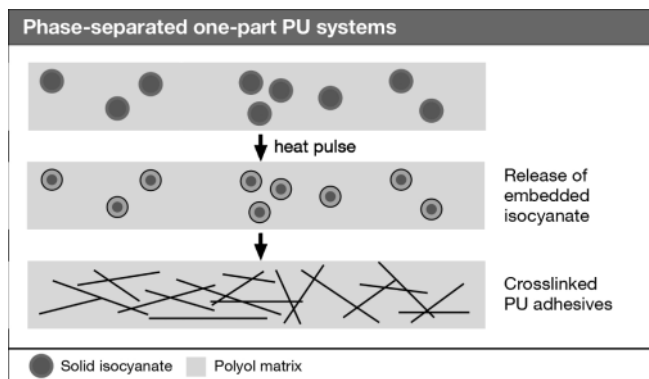


Figure 3. Phase-separated one-part PU systems.

tion to food safety.

3. Phase-Separated One-Part Systems on the Basis of Deactivated Isocyanates

In a conventional two-part PU system the polyisocyanate and the polyol are stored separately and mixed immediately before processing. Special equipment is required for metering and mixing, and much attention has to be paid to the limited pot life. If the residence time is too long, strong build-up of viscosity or even gelation may occur in the mixing head.

Phase-separated one-part systems have been designed in order to overcome this obstacle (Figure 3). Here, both reactants are stored together while being physically separated in two different phases. The isocyanate hardener is finely dispersed in a polyol. During storage at ambient temperatures curing does not take place. The isocyanate is solid and insoluble in the polyol matrix and additionally protected by microencapsulation. A shelf-life of up to one year can be realized on this basis.

A short heat pulse is enough to remove the protective barrier and to release the embedded isocyanate which migrates into the matrix and accomplishes crosslinking. Microencapsulation is the key of such a system (Figure 4). The surface of the isocyanate particles is deactivated by reaction with amines. During this process only a small portion of the isocyanate groups available at the surface react, resulting in a protective shell. The deactivation can be accomplished in situ, for instance by dispersing finely milled, micronized polyisocyanate into a polyol/polyamine mixture. The wall material can be tailored over a broad range by choice of the amine and its concentration. The isocyanate particles can be enclosed, for instance by a rigid urea wall which makes high thermal activation temperatures necessary, or they can be wrapped by a loose, polymeric protective surface

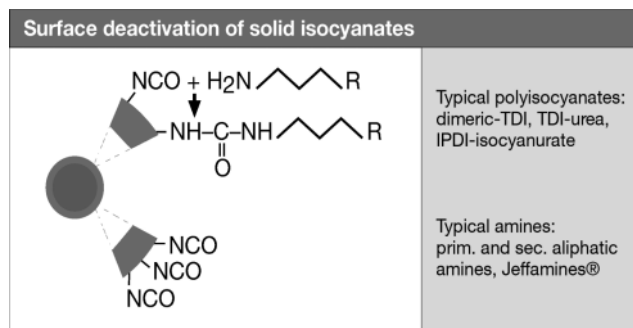


Figure 4. Surface deactivation of solid isocyanates.

layer. The solid, surface deactivated isocyanate particles might be prone to mechanical stress arising from high shear in metering and supply pumps or under the action of doctor blades. The protective shell would be destroyed, resulting in a premature reaction. By use of a proper deactivating amine a largely 'self-healing' system can be accomplished, however. The amine reacts rapidly with the exposed isocyanate surface so that a new inert polyurea layer is spontaneously formed. The curing temperature depends on the nature of the wall material and on the solubility of the isocyanate in the matrix. A range of 70 to 150°C can be realized.

Especially interesting are systems in which curing takes place under mild conditions and leads to homogeneously crosslinked systems at oven temperatures not more than 70 to 80°C. Curing of such a one-part two-phase system occurs without the splitting off and release of low molecular weight compounds. This is a crucial benefit compared to conventional thermosetting polyurethanes, e.g. for paints, where a volatile blocking agent is liberated during the curing reaction. In addition to pasty adhesives, solid, thermoplastic two-phase materials can also be prepared. Such latent-reactive PU hotmelts retain thermoreactivity for months. When extruded on a conveyor belt and cooled down they can be converted to granules or powder by means of cryogenic milling and can be used, for instance, for microdot powder scatter coating of textiles.

The basic principle of phase-separated one-part systems has been successfully transferred to aqueous PU dispersions. The inconvenience and the limitations of two-part dispersions in regard to dosing and mixing requirements, pot-life constraints and process safety are here again the driving force for the development of latent-reactive, self-crosslinking dispersions. The structural polymer is the same as for the conventional 2-part PU dispersions. Ionic groups or hydrophilic chain segments are integrated into the polymer chain of isocyanate-reactive polyurethane polymers as internal, non-migratable

emulsifiers, which imparts excellent properties in respect to self-dispersibility, dispersion stability and film forming properties. The curing agent, that is to say the surface-deactivated solid isocyanate, is basically the same as in the non-aqueous two-phase systems.

The isocyanate groups on the surface are transformed to urea groups, which prevents the undesired reaction with water. The hydrophobic nature especially of the crystalline TDI dimer provides an additional protection against the permeation of water into the isocyanate particles. Special attention has to be paid to the deactivating amine, since it defines the nature of the interface and may have a strong impact on the sedimentation and shear stability. During the lamination process moderate heating up to 60 to 90°C is sufficient to trigger the curing reaction. The protective shell becomes permeable, the polyisocyanate migrates and dissolves in the polymer film, and the crosslinking reaction starts. Full cure will be accomplished in a few days without additional supply of heat.

Typical applications are the lamination of automotive interior trim parts or of kitchen furniture fronts in the woodworking industry.

3.1. Outlook and Development Prospects

Latent-reactive dispersions on the basis of the IPDI trimer are now available which allow the preparation of light stable adhesives. In contrast to the crystalline dimeric TDI, the IPDI-trimer is amorphous. The high glass transition temperature of about 100°C makes a major contribution to the shelf life during storage at ambient temperatures. For systems which comprise dimeric TDI as the hardener, substantial progress on monomer emission could be achieved [2]. Another promising option is isocyanate-free, carbodiimide based dispersions [3].

Precoated layers with a shelf life of months under ambient temperature and moisture conditions can be designed. By use of a crystalline backbone polymer the film surface is non-tacky and blockfree. So roll goods like textiles or technical laminates can be wound, and formed parts can be stacked on top of each other. Even free-standing films can be manufactured if the PU dispersion is applied on release paper and the water evaporated under mild conditions. A carrier free polymer film has the advantage over the precoating of substrates that no migratable low molecular weight compounds like plasticizer from the substrate can penetrate into the film and cause premature crosslinking.

Here again, a brief activation, e.g. by heat pulse or microwave irradiation, is sufficient to trigger the curing reaction which will be completed in a few days without

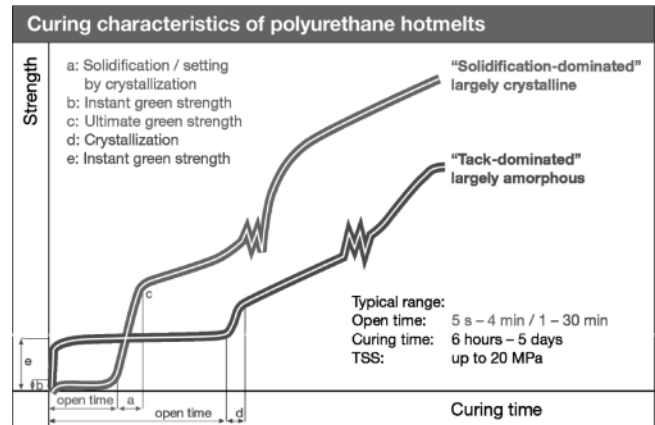


Figure 5. Curing characteristics of polyurethane hotmelts.

additional supply of heat. Such a system is very close to the idea of a ‘bond on command’ adhesive. On top of that, it enables the separation of adhesive application from the bonding process and allows new kinds of production processes.

4. Moisture-Curing PU Hotmelts

Thanks to their outstanding performance profile and their user-friendly nature, moisture-curing polyurethane hotmelts are one of the fastest growing segments in today’s adhesive industry. They are omnipresent in modern assembly and lamination operations, for instance in the wood-working, automotive or bookbinding industries.

Polyurethane hotmelts are a kind of cross between thermoplastic hotmelts and reactive one-part polyurethane adhesives. Thus they embody many advantages such as solvent-freedom, immediate grip, high structural strength and excellent aging resistance.

The so-called ‘solidification-dominated’ PU hotmelts develop strengths on cooling by setting of crystalline polyesterpolyols resulting in the green strength which allows the joined parts to be handled immediately after joining (Figure 5). In a second step the final strength is achieved by reaction with moisture coming from the atmosphere or from the substrates to form virtually linear, high molecular weight polyurethane polyureas.

Such a crystalline system is ideal for applications like profile wrapping or spine gluing, but shows obstacles in manufacturing processes where instant spotting tack or grip are required. A molten low molecular weight crystalline polyester has a waxy consistency, and due to this nature tack and instant green strength in this stage are poor.

Therefore a second PU hotmelt class based on acrylic copolymers has been developed to fill this gap. The

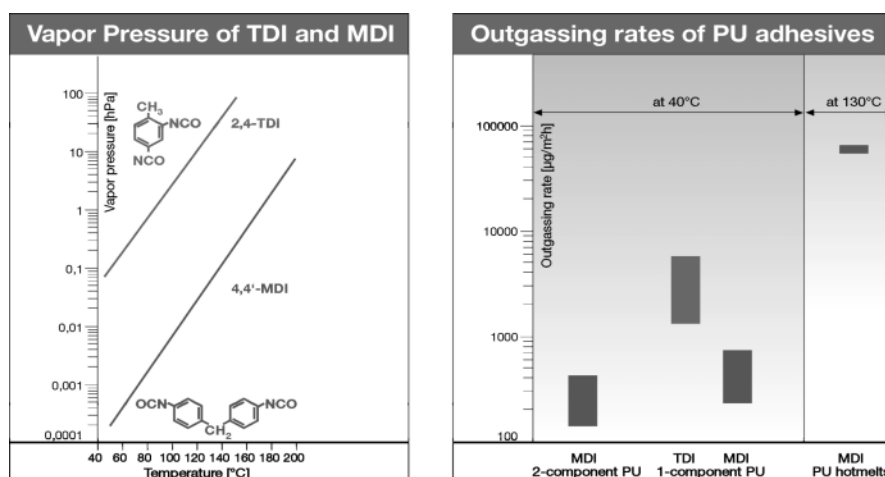


Figure 6. Vapor pressure of TDI and MDI, outgassing rates of polyurethane adhesives [4].

products are largely amorphous and exhibit aggressive tack and to a certain extent pressure sensitive characteristics directly after application. The products have an open time of some minutes and deliver immediate handling strength. These characteristics make them ideal adhesives for a continuous lamination process.

Panels laminated with water-borne adhesives need drying ovens that consume energy and floor space. Two-part and liquid moisture cure adhesives require platen presses and long compression belt sections. Contrary to that, compression of a few seconds in a nip roller or belt press is fully sufficient for a polyurethane hotmelt, which makes high-efficient flow-through processing possible. This reduces investment costs and saves labor, space and time. Major application areas are side panels of recreational vehicles, garage doors, office partitions, and flooring.

4.1. What are Upcoming Developments in this Field?

4.1.1. Dual Cure Technology for Spine Gluing

Akin to the aforementioned PU adhesive for flexible packaging a dual cure hotmelt was developed for the graphics arts industries which uses UV radiation to cure the books to about 80% of their ultimate strength in just a few minutes. Here again, the first stage is a photopolymerization, followed by moisture-curing of the isocyanate groups.

Hardback books are now roundable in-line. This is entirely different from conventional moisture-curing hotmelts which need a curing time of several hours to develop such a strength that the high mechanical stress during the rounding operation can be tolerated. On top of that, quality control can now be performed even within the

binding machine. Bookbinding is an ideal application for a dual cure process because the spine surface is fully accessible to UV. In deeper regions, where exposure to the light source is reduced, crosslinking occurs primarily by moisture curing. Beyond that, the polyurethane part of the dual cure system ensures gluing of difficult-to-bind papers, excellent cold and heat resistance, and durability. So both 'chemistries' play perfectly together.

4.1.2. Granulated PU Hotmelts

In spite of the fact that MDI based polyurethanes are very reactive and that even traces of moisture in the ppm range might lead to skin formation, PU hotmelts are now also available in granules.

The granules can be applied with conventional hotmelt equipment if a few technical prerequisites are fulfilled. Users can now easily change over from a reactive to a conventional hotmelt and vice versa, which allows a favorable and cost-saving entry to PU processing. Beyond that, the melt rate is higher thanks to the large surface area of the granules. With extruder technology these rates are unequaled, facilitating very high machine speeds.

4.1.3. Purnelt MicroEmission™

Compared to the many advantages of PU hotmelts there are just a handful of system-related disadvantages. Although they are solvent-free, they still pose a potential hazard to users, as PU hotmelts emit relatively high levels of monomeric diisocyanates. Reaction statistics show that it is unavoidable that monomer isocyanates are not completely bound during the reaction. A fraction will always remain in the final product.

Monomer isocyanates are harmful and unfortunately

have a high toxic potential. Even in low concentrations they are capable of damaging the respiratory organs, eyes and skin and may provoke allergic sensitization. If not applied properly, they can cause serious health problems. Although the monomer content of commercially available polyurethane hotmelts only amounts to a few percent, these monomers constitute a potential hazard since adhesive application takes place at temperatures of up to 170°C.

MDI is relatively volatile at higher temperatures (Figure 6). At 140°C, the vapor pressure already reaches 0.1 Torr (0.13 hPa). Due to the dilution effect, the value is markedly lower in polyurethane hotmelts and can be estimated according to Raoult's law on the basis of the mole fraction. Due to the high application temperature, the findings of a study carried out a few years ago by the Fraunhofer Institute therefore come as no surprise [4]. The investigation showed that the isocyanate emission rates measured during the processing of PU hotmelts were over two powers of ten higher than those from 1- and 2-part polyurethane adhesives which were applied as usual in industrial practice at relatively moderate temperatures of up to 40°C.

As a first approximation, the outgassing rate depends linearly on the monomer concentration. So the development target was to reduce the monomer MDI content drastically. The current industrial standard is a concentration of a few percent, but one can find products in the marketplace with values even up to 10%. Our company has developed a new product generation Purmelt Micro Emission™-with a monomer content below 0.1% [5]. These new products do not have to be labeled as hazardous materials. So it was possible to remove the Xn (harmful) danger symbol. The emission of hazardous isocyanate fumes during processing has been reduced by 90%-to one tenth of the previous level.

It goes without saying that conventional PU hotmelts do not pose any health hazards when handled properly. But what happens if ventilation fails or safety precautions are disregarded? So it is very beneficial to increase the intrinsic safety of the adhesive.

The basics of this development were revealed in recent patents. One crucial point is that the target 'low MDI monomer content' may lead to a dead end. It is absolutely not sufficient to reduce merely the monomer content, which is difficult enough to do. The performance of the adhesive depends to a large extent on the presence of monomer isocyanates. If the monomer MDI is simply removed, the excellent properties of the adhesive will collapse. So the 'missing' MDI has to be

Purmelt MicroEmission™: Basic principles

- It is by no means enough just to remove monomer MDI
- Otherwise properties strongly deteriorate
- 'Missing' MDI has to be replaced by 'substitute' Demonomerized MDI-chain extender-MDI
- Novel 'Super-MDI' (demonomerized MDI-tandem) gives very good properties (patents pending)
- Significantly improved technical standard in occupational safety
- Fully confirmed by institutes and accident prevention & insurance associations

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Figure 7. Purmelt MicroEmission™: basic principles.

replaced by a substitute, which, however, did not yet exist and which had to be developed.

We called this novel intermediate 'Super-MDI'. Two MDI units are joined with the aid of a chain extender to form a 'tandem'. This adduct, which is less viscous than the hotmelts, can be freed of excess MDI by extraction or thin-film evaporation under high vacuum to the ppm concentration range. The novel intermediate is not volatile and therefore no hazard. This concept is not, of course, limited to PU hotmelts, but is basically suitable for any applications in which MDI has to be replaced for occupational health reasons.

Purmelt MicroEmission™ sets a significantly improved technical standard in workplace safety, which has been fully confirmed by independent institutes and accident prevention and insurance associations [6].

Beside safety issues, other benefits are noteworthy. Having labeling-free products at work means less regulations and less administration, e.g. in regard to storage obligations, monitoring of the airborne isocyanate concentration at regular intervals, and the obligation to appoint a safety officer. Moreover, running a 'green production line' is becoming more and more of a competitive advantage for companies in their relationships with customers.

5. Outlook

In the light of present and future needs like less labor intensive line processes, higher production speed, triggered functions, lightweight structures, new material combinations, and environmental friendliness polyurethane adhesives will certainly continue their success story-thanks to their outstanding performance and unique adaptation capability.

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