

New caprolactam-blocked prepolymers for 1K and 2K polyurethane reaction systems

Superior industrial hygiene, controlled curing and excellent component performance

Using Low Free (LF) isocyanate technology, urethane prepolymers that are blocked with ϵ -caprolactam (CAP) were developed. When mixed with diamine chain extenders, they produce ready-to-use one-component reaction systems that can be stored at room temperature for up to 180 days and only react at high temperatures. Alternatively, the processor can formulate application-specific two-component systems with freely selected diamine curing agents. The 1K and 2K systems produce PU elastomers, coatings, adhesives and sealants with a material performance not previously achieved with diol hardeners.

Introduction

In blocked isocyanate prepolymers, all active isocyanate groups are temporarily converted into an unreactive state by reaction with a blocking agent. This blocking agent reacts with the active NCO group making the prepolymer unreactive until it is thermally unblocked, activating the reactions. Typical blocking agents include phenols, nonylphenol (NP), methylethylketoxime (MEKO), alcohols, ϵ -caprolactam, amides, imidazoles, and pyrazoles. Once heat is added to the blocked prepolymer, this reaction reverses and the active

groups can then start reacting with the chain extender. Fast acting amine curatives that would normally react too fast with the prepolymer can now be used, thereby opening the door to many new types of curatives. The blocked prepolymers can also be prepackaged into a one-component (1K) system with the addition of a fast reacting curative, thereby simplifying the processing of final elastomers. These benefits are advantageous in a number of different industries including adhesives, coatings, bindings and elastomers.

Blocked isocyanate prepolymers offer several advantages in the manufacture of PU systems. Since their isocyanate functions are blocked, they provide improved industrial hygiene and can be handled with less effort in terms of occupational safety. This advantage pays off especially in the production and processing of coatings, adhesives and sealants. In the production of PU elastomers, blocked prepolymers are primarily used to simplify and control the production process. This allows the curing reaction to proceed only within a defined temperature window, resulting in fewer side reactions and more uniform elastomer products. These

processing benefits are especially relevant for high quality parts that require long pot lives. In addition, blocked prepolymers enable the use of highly reactive curing agents not otherwise possible, which benefits the mechanical performance of the cast elastomer components.

Isocyanate-free by blocking

The Lanxess Urethane Systems business unit is extending its Adiprene K product range with new urethane prepolymers that are blocked with ϵ -caprolactam (CAP) (**fig. 1**). These CAP blocked prepolymers are based on low free (LF) prepolymer technology, where the content of free isocyanate in the prepolymer can be reduced to below 0.1 %. This technology is applied to prepolymers based on a wide variety of isocyanates, including MDI (methylenediphenyl diisocyanate), TDI (toluene diisocyanate), HDI (hexamethylene diisocyanate) and pPDI (p-phenylene diisocyanate). The CAP blocking reaction completely blocks any active isocyanate groups in the product, including all unreacted monomer. The blocked prepoly-

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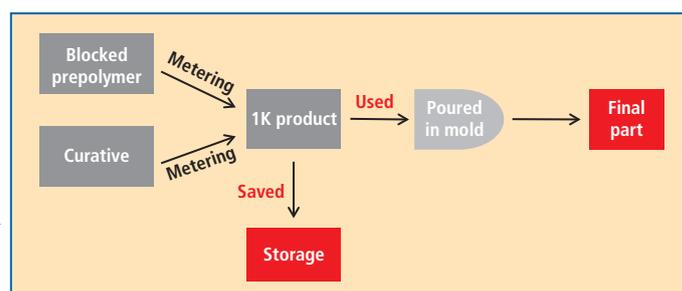


Fig. 1: Schematic illustration of the synthesis of a 1K system and its processing

mers are formulated with curatives to design customer-specific, tailor-made, ready-to-use 1K systems that are not subject to any restrictions with regard to isocyanate occupational safety and hygiene.

A fundamental strength of the new prepolymers is that they are significantly less viscous than CAP-blocked standard prepolymers thanks to LF technology, making them easier to use during processing. As a result of the lower viscosities, CAP-blocked LF prepolymers can be synthesized with non-traditional raw materials, such as more viscous polycarbonate polyols or new amine types, enabling properties not possible with conventional blocked prepolymers.

Simple processing with 1K systems

The new 1K systems are waxy solids at room temperature and have a long shelf life. They can be mixed with pigments and additives at temperatures of 60–80 °C and further processed. Depending on the reactivity of the curative, they can have a very long pot life and are stable for up to 18 h at 60–80 °C (**fig. 2**). As ready-to-use formulations, they simplify the manufacturing process by eliminating the need for mixing and metering equipment, thus reducing investment costs. Diols are not suitable as curatives because they are not reactive enough. Instead, diamines, that are normally too reactive for non-blocked isocyanate prepolymers, can be used, and can produce PU elastomers with improved performance than that of diol-cured reaction systems.

The new blocked LF prepolymers are also available for use in formulating 2K systems. This provides more flexibility because of the ability to freely select the curative as well as the mixing ratio of curative and blocked prepolymer to adapt them individually to the process and component requirements.

Adiprene K LFM E820 is the first commercial representative of the new range of CAP blocked LF prepolymers. It is synthesized on the basis of a polyether polyol and a tradi-

tional Adiprene LF MDI prepolymer. Cured with MDEA (4,4'-methylenebis(2,6-diethyl-aniline)) at 150 °C a PU elastomer with a hardness of 82 Shore A is obtained. Further post curing after demolding can then increase the hardness up to 88 Shore A. Due to its polyether-based backbone, the prepolymer is very well suited for applications in which the PU elastomer's high hydrolysis resistance is essential.

Powerful alternative to other CAP systems

These new LF, blocked 1K systems are also designed as an alternative to other commercial 1K systems based on CAP-blocked prepolymers; they have a lower viscosity and are therefore easier to process. A further benefit is good mechanical properties – especially high tensile strength and tear strength. For example, the tensile strength of the PU elastomer based on Adiprene K LFM E820 is 44.2 MPa (150 °C curing temperature, 1 h post-curing at 150 °C).

Process recommendations

Depending on the size and thickness of the components, the 1K and 2K systems are cured at temperatures of 150–180 °C with cure times of 10–60 min. The deblocking process produces CAP, which remains mostly in the PU polymer. The CAP content influences important material properties such as hardness, tensile strength and toughness. In many applications, the quality of properties of the PU polymer after curing is sufficient to meet requirements, so that CAP residues can be accepted. If it is necessary to significantly reduce the CAP content to increase

the mechanical performance of the polymer, demolding and post-curing at 100–150 °C for 14–24 h is recommended.

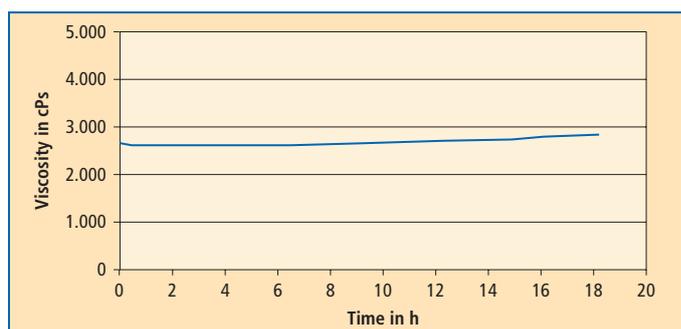
A wide range of products under development

Lanxess Urethane Systems can vary the chemical composition of the new blocked LF prepolymers widely in order to design tailor made products to meet customer needs. Not only are formulations with TDI and MDI being used, but also with aliphatic isocyanates such as HDI (hexamethylene diisocyanate) and IPDI (isophorone diisocyanate) for light-stable and weather-resistant PU polymers. In addition to polyether polyols, polyester, polycarbonate, and polycaprolactone polyols are also incorporated into the prepolymers. Lanxess also offers a wide range of diamine curatives – such as MDEA, DETDA (diethylmethylbenzenediamine) or MCDEA (methylene bis(chloro-diethyl-aniline)). The goal is to provide the user with a wide range of mechanical, thermal and chemical properties and processing conditions.

A multiplicity of application opportunities

The application spectrum of the new blocked LF prepolymers spreads across a wide variety of industries – from food and pharmaceutical to mechanical engineering and automotive engineering, printing and logistics. Thus, high performance and improved safety of the corresponding PU polymers will result in numerous new applications. Abrasive pad binders, for example, are a promising field of application. The PU systems produced with

Fig. 2:
After 18 h storage at 80 °C, the viscosity of a 1K system Adiprene K LFM E820 increases only slightly.



the CAP-blocked LF prepolymers serve as carriers for the abrasive particles and bind them to the substrate. The carriers must exhibit high cut and tear strength and good thermal resistance. In this application, these new prepolymer systems are good alternatives to existing systems blocked with MEKO.

There is further enormous application potential in the coating of industrial rollers and rolls (**fig. 3**). TDI-based ester prepolymers crosslinked with polyols such as TMP (trimethylolpropane) are currently used. The new CAP-blocked LF prepolymers are well-suited for such coatings because they can be processed with long pot lives. Furthermore, the hardness of the PU layers can be broadly controlled, and curing with diamines leads to better mechanical and dynamic properties.

The new blocked prepolymers can also be used in systems for the impregnation of conveyor belts (**fig. 4**). The key demands on PU systems for these applications are long pot life and high resistance to hydrolysis, abrasion, wear and a wide range of chemicals while maintaining high mechanical perfor-

mance. A low surface tension of the reaction system is also important for, among other things, achieving good wetting of the belt fabrics.

Molded parts weighing up to four tons

The option of setting the pot life and casting times very long, predestines the new 1K reaction systems for casting very large casting components. The advantage for the processor is eliminating the need for a mixing and metering system, which pays off in terms of component costs, since these large parts are often manufactured in very small quantities. Lanxess provides systems that allow for the production of components weighing up to four tons. The very controlled thermal curing process prevents local overheating in thick-walled areas and potential degradation that can reduce the mechanical performance of the parts. Potential applications include dynamic bend stiffeners for thick cables such as submarine cables, large off-road tires for ore mine trucks, components for wind turbine rotor blades or large composite structures.

Rotational molding and liquid injection molding

Using these new blocked prepolymers in rotational molding is also being investigated. The predominant material in this process is polyethylene. The new PU systems would allow the production of hollow parts with a higher level of properties, thus extending the range of applications for the technology. The use of blocked LF prepolymers in liquid injection molding would be another logical extension.

Outlook

The Urethane Systems business unit of Lanxess is currently focusing on further extending the range of CAP-blocked LF prepolymers. One focus is systems based on pPDI for components that have to withstand extreme application conditions, including very high temperatures, high dynamic loads and permanent contact with salt water, oil or other aggressive media – such as offshore applications.

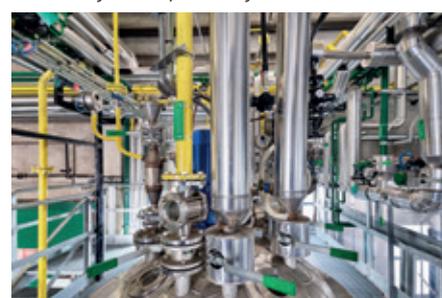
Fig. 3: The coating of industrial rollers and rolls is a large potential field of application for the new CAP-blocked LF prepolymers Adiprene K.



Fig. 4: Casting systems based on Adiprene K show a constant viscosity during the coating of belts and thus spread evenly over the belt surface.



Fig. 5: The pilot plant in Latina, Italy, complements the full-scale global production of LF MDI PU systems operated by Lanxess.



System provider for the global PU industry

Lanxess's Urethane Systems business unit acts as a systems supplier for the global PU industry and operates production sites and application development centers in all major economic regions, including the USA, China, Italy, Brazil and the UK (**fig. 5**). Its product portfolio includes complete PU systems for casting, coating, adhesive and sealant applications. The business unit is considered one of the leading suppliers of conventional and LF prepolymers as well as specialty aqueous PU dispersions (PUD) – with a strong focus on solvent-free and low free (LF) monomer systems. For example, the business unit recently presented new MDI-based LF PU prepolymers to the market for use in the construction industry. They were developed at the research, development and innovation center in Naugatuck, CT, USA. With a free isocyanate content of less than 0.1 %, they meet strict standards in terms of occupational safety and industrial hygiene.