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Cray Valley Products For Polyurethanes - Liquid Polybutadienes

Krasol® Resins

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KRASOL® Liquid Polybutadienes

Basic Information

KRASOL® liquid polybutadienes are low-molecular weight polymers of butadiene with varied compositions. Chemically, they are either functionalized, i.e. contain terminal reactive functional groups, or nonfunctionalized, i.e. without terminal reactive groups.

Two basic types are polybutadienes with terminal hydroxyl groups, KRASOL® LBH and non-functional polybutadienes KRASOL® LB. Each of these two basic types is available in three molecular weights: 2000, 3000 and 5000 g/mol. Polymers with higher molecular weights can be supplied upon request. From the two basic types, new series of KRASOL® polymers can be produced by subsequent reactions (reaction with isocyanates or by maleinization).

The basic types of KRASOL® liquid polybutadienes are colorless viscous liquids of oil-like or honey-like consistency at ambient temperatures. Solid elastomeric materials are produced from them by subsequent processes, mainly by reactions with isocyanates, which yield special polyurethanes or by reactive crosslinking (e.g. oxidation, radiation or by chemical reactions of double bonds or terminal groups).

Significant advantages of liquid polybutadienes are their easy processing, reactivity, unique and special properties of crosslinked products and the possibility of a great variety of applications.

Product Lines of KRASOL® Polymer Liquid Polybutadienes

KRASOL® Polymers can be divided into five groups based on chemical compositions and applications:

• Liquid polybutadienes with hydroxyl functional groups	**LBH**
• Liquid polybutadienes without terminal functional groups and products made from them by the addition of fillers or siccatives	**LB,** **PS-01, PP-01**
• Urethane prepolymers and systems based on KRASOL LBH grades; product line including cast elastomers and binders	**NN, LBD, GL**
• Maleinized polybutadienes; available in pilot plant amounts	**LBM**
• Developmental products (with primary hydroxyl groups, hydrogenated etc.); available as samples for evaluation	**LBH-P, HLBH-P**

Specific Properties of Polyurethanes Based on KRASOL® Polybutadienes

Characteristics of KRASOL® Polybutadienes

Anionic polymerization technology used for the production of KRASOL® polybutadienes permits the production of well defined linear polymeric products of a specific microstructure, with exactly set molecular weight in a narrow range and with reactive functional groups built-in on both ends of polymeric chains. These characteristics distinguish KRASOL® products significantly from similar liquid butadiene polymers, produced by other technologies, such as by radical polymerization.

Functionality

KRASOL® LBH contains nearly one hundred percent of molecules of a polymer with two functional groups. This makes its use possible even in such applications where the presence of the number of functional groups higher than two represents a hindrance or a disadvantage. Examples for that are thermoplastic polyurethanes and stable polyurethane prepolymers. Besides the main proportion of bifunctional macromolecules (min. 92%), KRASOL® LBH polybutadienes contain only small amounts of monofunctional polymer and polymer without functional groups.

Microstructure

A significant feature of KRASOL® polybutadienes is their specific microstructure. Roughly two thirds of the butadiene molecules are polymerized in the 1,2-configuration, which means that the polymers contain approximately 65% vinyl groups in their chain. This places KRASOL® in the medium or medium high content of vinyl structures according to established classification. This feature is significant for its chemical reactivity, processing properties and final properties of products made from it. It affects the viscosity of liquid polybutadiene, its glass transition temperature, thermooxidation stability, resistance to UV radiation and other properties.

Molecular Weight Distribution

An additional characteristic feature of KRASOL® liquid polybutadienes is a very uniform composition of the product as to the length of the polymeric chains. The anionic polymerization technology yields products with a very narrow molecular weight distribution (the value of the polydispersity index is near 1). This property can also contribute to the uniformity of structure of crosslinked polymeric products based on KRASOL® polybutadienes .

Overview of Applications of KRASOL® Polybutadienes

Owing to its chemical nature and reactivity, KRASOL® liquid polybutadienes offer extraordinary possibilities in a great variety of application areas. Their conversion to final products is based on various chemical reactions. The following overview shows the possibilities and principles of the applications:

a) Applications based on the reaction of hydroxyl terminated KRASOL® LBH polymers with diisocyanates:

This reaction yields polyurethane products with a multitude of applications. Examples are binders for composite materials, cast elastomers, binders for coatings, thermoplastic polyurethanes, mastics, potting compounds, adhesives, modifiers of polymeric materials and binders for explosives or solid rocket fuels. This manual deals with the use of KRASOL® polybutadienes in polyurethanes in detail.

b) Applications based on the reactions of double bonds of KRASOL® LB or LBH polybutadienes:

The double bonds in polybutadiene macromolecules are capable of reaction with oxygen, peroxides, halogens, anhydrides, dicarboxylic acids, vulcanizing agents and other chemicals to form hardened (crosslinked) products. Crosslinking involving the double bonds in the polybutadiene molecule can also be accomplished by radiation techniques. The use of KRASOL® LB polybutadienes in rubber compounds (e.g. as co-curable process aid in a rubber compound, coagent of peroxidic vulcanization of EPM, EPDM and other elastomers), and applications in anticorrosion coatings or as a binder for the production of artificial sandstone. Non-functional polybutadienes may be used in the liquid form (type LB) or as powder (type PS-01), where the polybutadiene is on a silica carrier.

c) Applications based on other reactions of terminal groups or possibly on simultaneous reactions of terminal groups and double bonds:

The most significant example of products obtained by this manner are maleinized KRASOL® LBM polybutadienes with carboxyl terminal groups. These are useful particularly for the modification of polymers (e.g. epoxy resins), or as emulsion binders for water-based coatings and adhesives.

KRASOL® LBH Polybutadienediol

Properties of Hydroxyl-Terminated Polybutadiene

Standard KRASOL® LBH is a liquid polybutadiene with terminal secondary hydroxyl groups, suitable as a special hydrocarbon diol for the synthesis of polyurethanes. Chemically it is - di(2-hydroxy-propyl)polybutadiene with a minor proportion of monosubstituted and unsubstituted polybutadiene.

$$HO - \underset{\displaystyle CH_3}{CH} - CH_2 -\!\left(CH_2 - CH = CH - CH_2\right)_n\! CH_2 - \underset{\displaystyle CH_3}{CH} - OH$$

The basic polybutadiene chain $-\!\left(CH_2 - CH = CH - CH_2\right)_n\!-$ is actually a statistical copolymer of 1,4-cis, 1,4-trans and 1,2-(vinyl) butadiene isomeric structural units. Typical properties of KRASOL® LBH liquid polybutadienes with molecular weights 2000, 3000, and 5000 g/mol are shown in Table 1. It is possible to prepare products with even higher molecular weights (e.g. 10,000 g/mol). KRASOL® LBH 10,000 is not offered as a standard commercial product and the values shown for this product in the table are for general information only.

Table 1. Properties of hydroxyl-terminated KRASOL® LBH polybutadienes

Property	**Unit**	**LBH 2000**	**LBH 3000**	**LBH 5000**	**LBH 10000**
Molecular weight, M_n	G/mol	1800-2500	2500-3500	4500-5500	9000-11000
Polydispersity Index, M_w/M_n		Typically about 1.1			
Content of OH groups	Mmol/g	0.73-1.11	0.52-0.80	0.33-0.44	0.16-0.22
Hydroxyl number	Mg KOH/g	41.0-62.3	29.2-44.9	18.6-24.9	8.9-12.4
Amount of the bifunctional polymer	% wt.	Min. 92			
Viscosity Brookfield	Pa.s	5-20 (25 °C)	12-30 (25 °C)	20-50 (25 °C)	20-50 (50 °C)
Microstructure 1,4-cis	% wt.	Approx. 18			
1,4-trans		Approx. 17			
1,2- (viyl)		Approx. 65			
Water content	% wt.	Max. 0.04			
Solids	% wt.	Min. 99.5			
Amount of antioxidant	% wt.	Min. 0.12			
Density at 20 °C	G/cm^3	Approx. 0.9			

KRASOL® LBH polybutadienes are clear, colorless viscous liquids with consistencies ranging from oil to honey. Their ability to flow strongly depends on temperature. Their handling is significantly improved by a moderate heating.

KRASOL® LBH polybutadienes are highly miscible with nonpolar organic liquids, oils and bitumens. They do not mix with water and alcohols. They can be easily dissolved in organic solvents, particularly hydrocarbons (e.g. toluene, gasoline), ethers and halogenated hydrocarbons. It is possible to disperse large amounts of fillers, such as mineral fillers or carbon blacks in the polymer. Chemical reactivity of the terminal hydroxyl groups and of the double bonds in the basic polybutadiene chain allows the use of KRASOL® LBH liquid polybutadiene in many applications.

KRASOL® LBH polybutadienes are protected against thermooxidative aging during transport and storage by the addition of a nonstaining phenolic multifunctional antioxidant. Additional stabilizers such as UV stabilizers can be added to the polymer.

For the practical use of KRASOL® LBH polybutadienes, the reactions of the terminal hydroxyl groups are the most significant. The most widely used are the reactions with diisocyanates that produce polybutadiene polyurethanes. However, the hydroxyl groups are capable of other reactions typical for secondary alcohols. They react with halogens (e.g. chlorine) and anhydrides of acids (e.g. maleic anhydride). They can be esterified or silylated. They can also react with other functionalized macromers or polymers, such as polyesters, polyamides, polyurethanes, epoxy resins and with a variety of others.

Besides hydroxyl groups, it is possible to utilize for the chemical conversions the reactivity of unsaturated double bonds in the polymeric chain. The double bonds of the vinyl side-groups are particularly reactive. The double bonds can be hydrogenated, oxidized, and halogenated, which results in products with new properties.

New developmental products are KRASOL® LBH-P polybutadienes with primary hydroxyl groups and molecular weights in the same range as the basic grades of KRASOL® LBH.

New types of hydrogenated polybutadienes with primary hydroxyl groups (KRASOL® HLBH-P) are being developed.

Applications for KRASOL® LBH Polybutadienediols

The most significant use of KRASOL® LBH polybutadienes is the production of polyurethane materials. In that KRASOL® LBH is used as a special kind of polyol, which reacts with diisocyanates to form polybutadiene-polyurethanes. Their specific features, particularly hydrophobic nature of the hydrocarbon chain without heteroatoms and elastic properties of the polybutadiene domains, lend these materials some exceptional properties, which differ from common polyurethanes based on esters or ethers. Polyurethanes based on KRASOL® LBH polymers are discussed in detail starting on page 8.

Typical examples of practical applications of KRASOL® LBH polybutadienes in polyurethane systems are:

- Cast elastomer compounds, potting compounds, sealants and mastics
- Polyurethane coatings
- Polyurethane adhesives
- Component improving hydrolytic stability of polyether/polyester based polyurethanes
- Polyurethane prepolymers used as binders for composite materials, most frequently from ground vulcanized rubber, polyurethane foam, sand, stone aggregate
- Thermoplastic polyurethanes
- Modifiers of plastics (e.g. polyamides) and polymeric blends (toughening, flexibilization, compatibilization, plasticizing)
- Potting and electrical insulation materials
- Special foamed materials

The most widely used applications of KRASOL® LBH liquid polybutadienes are described later in this brochure.

Polyurethanes Based on KRASOL® LBH Polybutadienediol

Specific Properties of Polyurethanes Based on Polybutadienediols

Liquid polybutadienes with terminal OH-groups, KRASOL® LBH (or KRASOL® LBH-P), can be used as special polyols for the synthesis of polyurethanes (PU). The unique structure of PU systems derived from them leads to some properties, which are superior not only to common polyether or polyester PU, but also to common vulcanized rubber. Advantages and disadvantages of polybutadiene-urethanes in comparison with common high quality polyester or polyether polyurethanes are shown in the following overview:

Advantages of polybutadiene-urethanes in comparison to common polyester and polyether urethanes:

- Rubbery character
- Exceptional resistance to hydrolysis
- Exceptional resistance to chemicals (inorganic acids, bases and salts)
- Excellent electrical insulation properties
- Very good elasticity at low temperatures
- Possibility of reinforcement by using common rubber fillers
- Possibility of a high degree of extension by oils without substantial loss of properties

Disadvantages of polybutadiene-urethanes in comparison to common polyester and polyether urethanes:

- Lower mechanical properties
- Lower resistance to organic solvents, oils and others
- Higher viscosity of polybutadiene polyols in comparison to polyether polyols

Specific differences between anionically polymerized (KRASOL® LBH) and radically polymerized (e.g. Poly bd resins,) hydroxyl terminated polybutadienes in PU systems are dealt with further on in this brochure.

Chemical Reactions in the Synthesis of Polyurethanes

The preparation of polybutadiene-urethanes is essentially the same as that of common PU systems. Krasol® LBH is used as the polyol component. Other essential components of the system are bifunctional or multifunctional isocyanates, such as toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI) and isophorone diisocyanate. Low-molecular weight bifunctional alcohols or amines, such as 2-ethyl-1,3-hexanediol (EHD), N,N-diisopropanol aniline (DIPA) and M-CDEA, function as chain extenders; multifunctional alcohols (e.g. glycerol) act as crosslinkers. The formulations often contain catalysts, fillers, colorants, surface-active compounds and others in addition to the basic components.

The desired PU product is defined by the chemical reactions of components carrying reactive groups. The most important chemical reactions occurring during this process are the following reactions of the isocyanate groups:

Reactions with hydroxyl groups lead to urethane; reactions with amine groups lead to urea. Both these reactions lead to the growth of polymeric molecules of polyurethane.

$$\varnothing\ \text{- NCO + HO -}\ \oplus \quad \Rightarrow \quad \varnothing\ \text{-NH-CO-O -}\ \oplus$$

isocyanate and hydroxyl groups ⇨ urethane

$$\varnothing\ \text{- NCO + } H_2N\text{ -}\ \oplus \quad \Rightarrow \quad \varnothing\ \text{-NH-CO-NH -}\ \oplus$$

isocyanate and amine groups ⇨ derivative of urea

Reaction with water produces urea (with amine as intermediate product) with simultaneous liberation of carbon dioxide.

$$\varnothing\ \text{- NCO + } H_2O \quad \Rightarrow \quad \varnothing\ \text{- } NH_2 + CO_2$$

isocyanate group and water ⇨ amine and carbon dioxide

This reaction is utilized in the preparation of polyurethane foams as well as in the curing process of composites with polyurethane binders. However, it can be a source of defects in the production of solid materials. This can be prevented by using sufficiently dried components. Reaction with water can be a cause of damage of the isocyanate component of PU systems during storage. Therefore it is important to prevent penetration of moisture to the stored materials.

Reaction with urethanes produces allophanates with urea biurets. Both reactions occur at elevated temperatures and lead to crosslinking of polyurethanes.

Polyurethane Prepolymers

Reaction of KRASOL® LBH polybutadienediol with an excess of diisocyanate produces polymeric products with terminal isocyanate groups referred to as polyurethane or isocyanate prepolymers. The most widely used prepolymers based on KRASOL® polybutadienes are those prepared with aromatic diisocyanates, such as TDI and MDI.

Process of Synthesis

The synthesis of prepolymers is a batch process in a heated reactor with an agitator, with a nitrogen inlet and openings for the charge of components. KRASOL® LBH is supplied in a satisfactory quality and it is not necessary to purify before the synthesis.

The typical process for the production of a TDI prepolymer is as follows: the reactor is filled with Krasol® LBH, and then heating and stirring starts. At the same time nitrogen is introduced. The polymer is heated to approximately 60 °C (140 °F). Then the necessary amount of TDI is added and the mixture is let to react at 60 - 90 °C (140 - 194 °F) for 1 - 4 hours. Then the product is filled under nitrogen blanket into metal containers. These containers have to be tightly closed. The product is very stable and has a shelf life exceeding 6 months.

If liquid MDI is used as the isocyanate component, the prepolymer is usually prepared with a high excess of monomeric isocyanate. MDI prepolymers prepared with a low excess of diisocyanate are highly viscous. This process is different from the previous one: the reactor is filled with MDI and preheated Krasol® LBH is added to it. The required reaction time is 1 hour at 70 - 80 °C (158 – 176 °F). The stability of the prepolymer in a well sealed container is usually several months and depends, among other things, on the stability of the used MDI. MDI prepolymer not intended for long-term storage, can be prepared also without a protective atmosphere in a drum with an effective stirrer and heated with a portable heater.

Suitable Types of Isocyanates and Examples of Formulations

KRASOL® LBH polybutadienediols are suitable for the preparation of TDI prepolymers. TDI is well miscible with the polybutadiene and the formed prepolymers are clear and stable. Because of the toxicity of TDI, the ratio of isocyanate/polyol is usually low in order to minimize the content of free TDI in the prepolymer. The effects of the TDI/KRASOL® LBH ratio in the reaction mixture on the properties of the prepolymer are shown in Table 1.

Table 1. Prepolymers based on KRASOL® LBH 3000 and TDI

Formulation (parts by weight)	**1**	**2**	**3**	**4**	**5**
KRASOL® LBH 3000	100	100	100	100	100
TDI	10.46	11.77	13.08	14.39	16.34
NCO/OH ratio	1.60	1.80	2.00	2.20	2.50
Properties of the prepolymer					
Appearance	Clear	Clear	Clear	Clear	Clear
NCO content (%)	1.94	2.36	2.94	3.29	4.10
Viscosity at 25 °C (mPa.s)	362000	176000	110000	73000	52000
Viscosity at 40 °C (mPa.s)	74000	40000	25000	18000	13000
Free TDI (%)	0.22	0.59	0.98	1.83	3.34

Table 2. Prepolymers with NCO content of approx. 10 % prepared from different types of MDI with NCO/OH ratio about 6.0

Formulation (parts by weight)	**1**	**2**	**3**	**4**	**5**
KRASOL® LBH 3000	100	100	100	100	100
Suprasec 2385	61.99	-	-	-	-
Suprasec 2004	-	55.00	-	-	-
Baymidur 5003	-	-	59.30	-	-
Ongronat HS-44-40	-	-	-	55.00	-
Ongronat HS-44-50	-	-	-	-	55.00
Properties of the prepolymer					
Appearance	Turbid	Opalescent	Turbid	Clear	Clear
Viscosity at 25 °C (mPa.s)	18000	10400	13000	8300	8200

When evaluating different commercial MDIs, it was found that some of them are poorly miscible with polybutadienediol, leading to a phase separation of the resulting prepolymer. It is therefore important to pay attention to the selection of the suitable MDI product. Suprasec 2385 (Huntsman) is one of the isocyanates suitable to prepare stable, although still turbid prepolymers. MDI products with a higher content of the 2,4´-isomer (e.g. Suprasec 2004 from Huntsman, Baymidur VP KL 3-5002 from Bayer or Ongronat HS-44-40 from Borsodchem) exhibit very good miscibility with liquid polybutadienes. Additional suitable types of isocyanates are listed in Table 2 and also in the section titled Principles for the Development of a Formulation.

The effects of the ratio of isocyanate/KRASOL® LBH on the properties of prepolymers is shown in Table 3, where Baymidur VP KL 3-5002 was used as the isocyanate component of the system.

Table 3. Prepolymers using liquid MDI Baymidur VP KL 3-5002

Formulation (parts by weight)	**1**	**2**	**3**	**4**	**5**
KRASOL® LBH 3000	100	100	100	100	100
Baymidur VP KL 3-5002	23.01	10.68	38.35	57.52	76.69
NCO/OH ratio	2.40	3.20	4.00	6.00	8.00
Properties of the prepolymer					
Appearance	Clear	Clear	Clear	Clear	Clear
Amount of NCO (%)	3.65	5.41	6.96	10.19	12.72
Viscosity at 25 °C (mPa.s)	247000	76000	31000	9900	6100
Viscosity at 40 °C (mPa.s)	57000	20000	7700	3600	2300

Table 4. Prepolymers from KRASOL® LBH 2000 and 4,4´-MDI

Formulation (parts by weight)	**1**	**2**	**3**	**4**
KRASOL® LBH 2000	100	100	100	100
4,4´-MDI	23.70	28.22	33.86	45.15
NCO/OH ratio	2.10	2.50	3.00	4.00
Properties of the prepolymer				
Appearance	Turbid	Turbid	Turbid	Turbid
Amount of NCO (%)	3.5	4.4	5.7	8.0
Viscosity at 25 °C (mPa.s)	356000	110000	64000	22000
Viscosity at 40 °C (mPa.s)	72000	27000	17000	6100
Viscosity at 80 °C (mPa.s)	3700	1900	1200	700

In the production of thermoplastic polyurethanes, the so-called pure MDI (i.e. 4.4´-MDI) is used most frequently. Prepolymers of KRASOL® LBH polybutadiene and pure MDI are also stable; they do not exhibit a phase separation. Characteristics of these prepolymers in dependence on the ratio isocyanate/polyol are shown in Table 4.

Commercially Produced KRASOL® Prepolymers

In the commercial line of KRASOL® liquid polybutadienes, there are several grades of isocyanate prepolymers. TDI-based KRASOL® LBD 2000 and KRASOL® LBD 3000 prepolymers are used for the production of polyurethane elastomers, sealants and mastics. Products of the series KRASOL® NN are prepolymers of polybutadiene and liquid MDI. Some of them contain a viscosity modifier (mineral oil). Detailed specifications of prepolymers are in corresponding Technical Data Sheets.

Polyurethane Elastomers

Polyurethane elastomers based on KRASOL® LBH polyols can be prepared in a wide variety of properties. Their final characteristics depend on the components used, conditions of preparations etc. This chapter deals with the basic factors determining the properties of polybutadiene-urethane systems.

Process of Synthesis

The methods of preparation of polyurethanes can be classified in a variety of manners: by the sequence of addition of the reactants (one-step, two-step process) or by the number of components, which the user has to mix together (one-component, two-component system, etc.)

In the one-step (or one-shot) process, the components are mixed together and the resulting mixture is then reacted. Two-step process runs in two reaction steps, which are carried out at different times. In the first step the polyol and isocyanate react to form a prepolymer with terminal isocyanate groups (Section *Polyurethane Prepolymers*). In the second step, the prepolymer reacts with the chain extender and/or with a crosslinker to form the final product.

For illustration, a typical process of preparation of a one-step elastomer is shown here: individual components of the polyurethane mixture (KRASOL® LBH, chain extender, crosslinker, possibly filler, oil, stabilizer) according to the formulation are charged into the mixing equipment and mixed thoroughly. Often it is advantageous to add isocyanate and catalyst last. During the mixing, it is recommended to use vacuum to remove gases from the mixture. The homogeneous mixture prepared by this process is poured or pumped into a mold or coated on a substrate. The cure can be done at normal or elevated (80 -100 °C or 176 - 212 °F) temperature.

The two-step synthesis of elastomers from the basic polyurethane components is time consuming and requires special equipment. It is therefore often simpler to use for the production of PU elastomers ready-made polybutadiene-isocyanate prepolymers offered by Sartomer.

All the components used in a specific formulation for a polyurethane elastomer can be divided into two parts, i.e. into the hydroxyl part and the isocyanate part, and supplied to the final user as a two-part system. The elastomer is then produced by simply mixing the two parts in the prescribed ratio under given conditions. The user, however, cannot make any major modifications of the formulation. An example of such a system is KRASOL® GL-02.

Principles for the Development of a Formulation

The formulation used has a significant effect on the properties of the elastomer. One-step PUs are softer in comparison with two-step products, have lower tensile strength and higher elongation at break (compare Table 5, Formulations 1 and 2).

Stoichiometric ratio of reacting groups, i.e. NCO from diisocyanate and OH from polyol, chain extender and crosslinker, is a critical factor in the synthesis of polyurethanes. Optimum properties of elastomers can be achieved with the NCO/OH ratio between 1.0 and 1.1 (Table 5, Formulations 2 to 7).

Hard segments in polyurethanes form as adducts of isocyanates and low-molecular weight diols, triols or diamines. Flexible chains of diols form the soft segments. The content of hard segments in the composition is calculated as the sum of weight fractions of the isocyanate, chain extender and, if applicable, of crosslinking agent in the mixture. Increasing the content of hard segments increases the hardness of the elastomer and the tensile strength (up to about 35% of hard segments); the elongation at break decreases (see Table 5, Formulations 8 to 12).

Table 5. Properties of polyurethane elastomers in dependence on procedure, isocyanate index and content of hard segments (curing conditions: 20 hours at 80 °C)

Formulation (parts by weight)	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
KRASOL® LBH 3000	100	100	100	100	100	100	100	100	100	100	100	100
Baymidur 5002	34.7	34.7	30.7	32.0	34.2	35.2	36.0	-	-	-	-	-
Suprasec 2385	-	-	-	-	-	-	-	21.8	27.2	36.3	43.5	54.4
Voranol RA 100	19.6	19.6	24.0	21.6	20.6	18.7	17.0	8.0	12.0	18.7	24.0	32.0
DBTL	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
NCO/OH	1.05	1.05	.80	0.90	1.00	1.10	1.20	1.05	1.05	1.05	1.05	1.05
Hard phase (%)	35	35	35	35	35	35	35	23	28	35	40	46
Procedure[a]	1 st	2 st	2 st	2 st	2 st	2 st	2 st	2 st	2 st	2 st	2 st	2 st
Properties												
Hardness (Shore A)	67	79	50	71	79	76	75	60	69	77	81	86
Tensile strength (Mpa)	10.9	16.2	2.4	5.5	14.0	14.4	11.7	8.0	9.3	13.9	11.6	11.2
Elongation at break (%)	630	520	200	330	540	410	430	450	330	370	170	110
Tear strength (N/mm)	56.6	68.9	-	-	-	-	-	-	-	-	-	-
Abrasion (mm^3)	443	208	-	-	-	-	-	-	-	-	-	-
Brittle point (°C)	-35	-40	-	-	-	-	-	-	-	-	-	-

[a] 1st – one-step (one-shot) procedure; 2 st – two-step (prepolymer) procedure

Suitable grades of aromatic isocyanates include TDI, pure 4,4´-MDI and some grades of liquid MDI, e.g. Suprasec 2385 a 2004 (Huntsman), Baymidur VP KL 3-5002 and VP KU 3- 5003 (Bayer), Isonate M 143 (Dow), Ongronat HS-44-30, HS-44-40 and HS-44-50 (Borsodchem). Suitable aliphatic isocyanates are, for example, hydrogenated MDI - Desmodur W (Bayer) or isophorone diisocyanate. Examples of formulations are in Table 6.

Chain extender branched low-molecular weight diols, such as N, N-diisopropanol aniline (DIPA) or 2-ethyl-1,3-hexandiol (EHD), which are well miscible with KRASOL® polybutadienes, are recommended (see Table 6). A number of commonly used diols, e.g. 1,4-butanediol or diethylene glycol, have a limited miscibility with polybutadienes. Low-molecular weight diamines, for example, Lonzacure M-CDEA, can be used to cure polybutadiene-isocyanate prepolymers (see Table 7).

If exclusively bifunctional isocyanates and chain extenders are used in combination with KRASOL® LBH polyols, the polyurethane product exhibits thermoplastic behavior. The softening temperature of these polyurethanes is given by the structure of the hard segments and can be in some cases rather low (around 100 °C). The stability of polyurethanes at higher temperatures can be improved by the addition of crosslinking agents (see Table 6). Some of the suitable crosslinking agents are e.g. glycerol, triisopropanol amine and ethylene-diamine-N,N,N´,N´-tetra-2-propanol.

Catalysts used commonly for polyurethane systems are also suitable for compositions based on KRASOL® polybutadienes. For example, organometallic catalyst dibutyltin dilaurate and amine catalyst triethylene diamine are widely used for these systems. The level of catalyst has to be selected with regard to the reactivity of the components used and to the conditions of cure (see Table 6, Formulations 1 to 3).

KRASOL® LBH polybutadienediols are stabilized by a multifunctional antioxidant of phenolic type (Irganox 1520, CIBA). To increase stability of PU compositions based on KRASOL® combined stabilizers, such as Tinuvin B75 (from CIBA) or also Uvinul 3434C (from BASF) in amounts of 1-2% on polyurethane, are recommended.

Table 6. The use of isocyanates, chain extenders and crosslinking agents (the ratio NCO/OH = 1.05; content of hard segments = 35 %; cure time 20 hrs. for all formulations)

Formulation (parts by weight)	**1**	**2**	**3**	**4**	**5**	**6**	**7**
KRASOL® LBH 3000	100	100	100	100	100	100	100
TDI	29.2	-	-	-	-	-	-
Suprasec 2385	-	39.9	-	-	-	-	-
Baymidur 5002	-	-	-	34.7	38.7	41.9	41.9
Desmodur W	-	-	39.9	-	-	-	-
DIPA	25.3	-	-	19.6	-	-	-
EHD	-	12.5	13.2	-	15.9	-	-
Diethylene glycol	-	-	-	-	-	12.9	-
1,4-Butanediol	-	-	-	-	-	-	10.9
Glycerol	-	1.2	1.2	-	-	-	-
DBTL	0.01	0.001	0.07	0.001	0.001	0.001	0.001
Procedure[a]	2 st	2 st	1 st	2 st	2 st	2 st	2 st
Curing temperature (°C)	80	80	23	80	80	80	80
Properties							
Hardness (Shore A)	80	80	74	75	73	71	78
Tensile strength (Mpa)	13.2	10.8	14.4	15.6	15.6	9.9	11.5
Elongation at break (%)	490	170	470	530	480	400	370
Softening temperature (°C)	120	155	150	120	-	-	-

[a] 1 st – one-step (one-shot) procedure; 2 st – two-step (prepolymer) procedure

Properties of Elastomers Based on KRASOL® Polybutadienes

An important specific feature of polybutadiene elastomers is, among other things, the ability to incorporate relatively high amounts of hydrocarbon oils without a substantial deterioration in the mechanical properties of the final product. Elastomers, prepared by the reaction of TDI KRASOL® LBD 3000 prepolymer with diamine Lonzacure M-CDEA, were extended by a mineral oil, Enerthene 2368, in amounts from 0 to 17% (see Table 7). The addition of oil reduces the viscosity of the prepolymer,

Table 7. Polyurethane elastomers prepared by the reaction of Krasol® LBD 3000 and Lonzacure M-CDEA (NCO/NH2=1.00) extended by Enerthene 2368 oil

Formulation (parts by weight)	**1**	**2**	**3**	**4**	**5**
Krasol® LBD 3000	100	100	100	100	100
Enerthene 2368	0	6	12	18	24
Lonzacure M-CDEA	13.6	13.6	13.6	13.6	13.6
Amount of oil in the elastomer (%)	0	5	10	14	17
Viscosity of the oil extended prepolymer					
At 25 °C (mPa.s)	75000	46000	40000	30000	21000
At 40 °C (mPa.s)	22000	12000	10500	6200	6000
At 80 °C (mPa.s)	1500	1000	900	750	600
Processing characteristics					
Pot life at 80 °C (min)	5	5	5	5	5
Demolding time at 100 °C (minutes)	45	50	50	60	60
Properties of the elastomer					
Hardness (Shore A)	82	80	80	78	78
Tensile strength (Mpa)	18.1	17-19	18.1	14-16	16.2
Elongation at break (%)	400-	400-450	490	380-420	440
Rebound resilience (%)	51	50	50	52	52
Abrasion resistance (ARI %)	96	86	91	108	94
Thermal characteristics[a]					
Glass transition temperature (°C)	-40	-40	-50	-40	-50
Softening temperature (°C)	270	280	270	240	230

[a] dilatometric measurement by thermomechanical analyzer TMA-CX04R (Intertec Ltd., Czech Republic)

Processing is improved as a result. With increasing amount of oil, the hardness Shore is reduced somewhat, but other mechanical properties are essentially not affected.

For the modification of polyurethanes based on KRASOL® polybutadienes, it is also possible to use various types of bitumens and a large selection of solid fillers (limestone, clay, carbon black, silica etc.). This gives the user a wide range of possible formulations for sealants, potting compounds, coatings, mastics and adhesives.

Hydrolytic and chemical resistance of Polybutadiene-urethanes in aqueous media is much higher than that of conventional polyurethanes based on polyesters and polyethers. For example, an elastomer based on KRASOL® polybutadiene exhibited after 28 days of immersion in 60% sulfuric acid and in 40% nitric acid only a reduction of stress-strain properties (see Table 8), while a similar polyurethane based on polytetramethylene glycol (PTMG) was under these conditions completely destroyed after only 3 days.

Table 8. Resistance of elastomer from KRASOL® LBD 3000 / Lonzacure M-CDEA (see Formulation 1 in Table 7) to aqueous media

Conditions	**Change of properties (%)**			
	Hardness Shore A	Tensile strength	Elongation at break	Volume
Water vapor, 100 °C, 28 days	+1.0	-37.2	-43.1	-0.39
60 % sulfuric acid, 23 °C, 28 days	+1.2	-12.8	-18.6	+1.26
40 % nitric acid, 23 °C, 28 days	+3.8	-54.4	-68.3	+2.40
50 % sodium hydroxide, 23 °C, 28 days	-0.8	-2.8	-9.0	+0.58

Operational Safety

KRASOL® LBH polybutadienediols are polymeric materials without any health hazards. A Material Safety Data Sheet (MSDS) is supplied with each shipment of the material. Results from their toxicological tests can be provided upon request. Processors should request MSDS for all other components used in their polyurethane systems from their manufacturers.

The isocyanate component represents the health risk in polyurethane systems. The main danger is in the inhalation of their vapors or aerosols. The more volatile isocyanates (TDI, aliphatic isocyanates) are therefore more dangerous than less volatile isocyanates (e.g. MDI). Isocyanates are among chemicals produced in large quantities (annual world consumption is several million tons). When using them, it is necessary to take strict safety measures.

The principles of safe work with isocyanates include the use of protective garments, such as gloves, protective suits, shoes and goggles, effective ventilation of the work place and prohibition of smoking and consumption of food. In cases where there is the risk of increased concentration of isocyanates (e.g. when coating with polyurethanes by spraying), it is necessary to use respirators. Detailed information about toxicity, hygienic principles and proper handling of products based on isocyanates are provided by their manufacturers.

KRASOL® LBH vs. Radically Polymerized Polybutadienes in Polyurethane Systems

KRASOL® LBH polybutadienediols, produced by anionic polymerization at Sartomer and hydroxyl terminated polybutadienes produced by Sartomer by radical polymerization (e.g. Poly bd, R45HTLO) are very similar, but not identical polymers.

They have many identical features in polyurethane systems: water repellency, very good barrier properties against penetration of water and water vapor, outstanding hydrolytic and chemical resistance, electrical insulation properties, and ability to be extended by oils and reinforced by fillers.

However, when the physico-chemical properties of KRASOL® LBH and of radically polymerized polybutadienes are compared in detail, differences are found (see Table 9).

Table 9. Differences between anionically polymerized KRASOL® LBH polybutadienediols and radically polymerized hydroxyl terminated polybutadienes

	KRASOL® LBH (anionic)	**Poly Bd® R45HTLO (radical)**
Microstructure, vinyl content (%)	60-70	Approx. 20
Functionality	Lower than 2.0 (approx 1.9)	Higher than 2.0 (2.4-2.6)
Type of OH groups	Secondaryh or primary[a]	Primary
Viscosity at 25 °C (mPa.s)	13000[b]	7000
at 40 °C (mPa.s)	3500[b]	3200
at 80 °C (mPa.s)	400[b]	600

[a] polybutadienediols KRASOL® with primary OH groups (KRASOL® LBH-P) are developmental products

[b] value for KRASOL® LBH 2000

From the above differences it can be concluded that it is not always possible to replace KRASOL® LBH by a radically polymerized polybutadiene in a polyurethane formulation and vice-versa, without a resulting change of properties (e.g. processing properties, hardness, stress-strain properties, dimensional stability). In order to attain the required characteristics, it is necessary to modify the formulation (e.g. amount of catalyst, addition of a crosslinker).

In polyurethane systems KRASOL® LBH polybutadienes exhibit generally the following advantages over radically polymerized hydroxyl terminated polybutadienes:

- Can be used in thermoplastic polyurethanes (their functionality does not exceed 2.0)
- Lower viscosity and good stability of isocyanate prepolymers (due to their functionality not exceeding 2.0)
- Possibility of modification of properties of polyurethane by the choice of molecular weight of the KRASOL® LBH polyol.

The disadvantages of KRASOL® LBH polybutadienes are:

- Higher glass transition temperature (given by the microstructure with a higher content of 1,2-structure). During cooling KRASOL® based polyurethanes lose elasticity at about -40 °C (-40 °F), while polyurethanes prepared from radically polymerized polybutadienes only at –80 °C (-112 °F).
- Worse dimensional stability and lower softening point (caused by a lower functionality and consequently lower crosslink density of the polyurethane). Both these properties can be improved considerably by the addition of a low-molecular weight crosslinker.

Monitoring the Process of Crosslinking of Polyurethane Compositions

Processing properties of a polyurethane system (pot life, gel time, tack-free time, demolding time, curing time) are an important part of its characterization. There are many methods, used for this purpose, from simple to demanding ones, performed by expensive instruments. For polyurethane systems based on KRASOL® polybutadienes the following three methods were found to be successful:

- Measurements by the Scanning Vibrating Needle Curemeter (SVNC, from RAPRA) is based on recording the changes of set vibration of a needle submerged in the polymeric mixture being cured. This method allows a relatively accurate determination of the characteristics in the initial phase of cure (pot life, gel time).
- Viscosity measurements on Brookfield viscometer. The pot life corresponds to the time needed to reach the viscosity about 100,000 mPa.s.
- Estimation of the gel time is done by inserting a test wire into the material being cured in regular intervals. The gel time is the time, at which the trace of the test wire is still visible 30 seconds after it was inserted and pulled out.

Applications for Polyurethanes Based on KRASOL® LBH Polybutadienediol

Polyurethane Binders for the Production of Composite Materials

Isocyanate prepolymers produced from KRASOL® LBH liquid polybutadiene and selected grade of MDI can be used as high quality binders for the production of composite materials from ground rubber scrap, polyurethane foam and cork. These one-component polyurethane binders crosslinked by the atmospheric moisture are produced commercially under the trade name KRASOL® NN. Some of the grades contain a viscosity modifier.

Line of KRASOL® NN Binders

The commercial line contains three grades of KRASOL® NN binders for the production of composite materials. Individual grades differ in content of NCO groups, oil content, viscosity and type of application. Crosslinking may occur at normal or elevated temperature and this affects the final properties of the composite material. The processing characteristics are adjusted by the addition of the catalyst which is a part of the delivery. A list of individual grades and their properties are in Table 1.

The binders cured at ambient temperatures are particularly suitable for the molding of large-size parts in closed molds and for surfaces of athletic fields and playgrounds. Optimum temperature for their processing is in the range 15 - 30 °C (59 - 86°F).

Binders for crosslinking at elevated temperatures are used in a large volume production of molded parts in heated hydraulic presses. The processing temperature is usually 90 - 120 °C (194 – 248 °F).

Table 1. Binders KRASOL® NN for the production of composite materials

Name	Physical and chemical properties			Curing temperature (°C)	Application
	Oil content (%)	NCO content (%)	Viscosity at 25 °C (Pa.s)		
KRASOL® NN-22	0	8.0-9.7	12-22	15-30	Production of composites from ground rubber scrap with a long demolding time. Production of large parts and industrial carpets
KRASOL® NN-23	50	4.0-5.0	0.5-3.0	90-120	Binder with a moderately long demolding time for the production of rubber composite materials, safety tiles, antivibration and antiskid carpets, soundproof panels; suitable as binder for ground polyurethane foam scrap and cork
KRASOL® NN-25	20	10.9-12.1	0.7-1.7	15-30	Production of composites from ground rubber scrap used for outdoors sporting facilities by the “in situ” mthod
				90-120	Special binder for ground polyurethane foam scrap

KRASOL® NN binders find application mainly for ground rubber scrap, polyurethane foam scrap or ground cork or other materials, such as sand or stone aggregate. Depending on nature and grain size of the ground material, it is possible to obtain a large number of products with varied applications.

The binder content is usually 7.5 - 20 wt. % depending on the ground material and the application of the final product.

KRASOL® NN polybutadiene-urethane binders exhibit an outstanding adhesion to the ground cured rubber material and other nonpolar materials. Composite materials prepared on the basis of these binders have excellent physical and mechanical properties, good elasticity at low temperatures and very good hydrolytic and chemical resistance.

Procedure for the Production of Composite Materials

Composite materials are produced by combining the ground material by the polyurethane binder and subsequent molding in a compression mold or by direct application to a substrate by spreading. The final utility of the product is determined by the nature of the ground material, its physical and mechanical properties, by the shape of the mold or of the product as well as by the amount of the binder. Processing characteristics can be set by the type of binder, crosslinking temperature, and by the amount of the catalyst. The rate of crosslinking is determined also by the presence of water. It is present as natural moisture on the surface of the ground material. If the moisture is not sufficient, it is necessary to wet the surface of the ground material by spraying with water. A typical formulation with the use of single component KRASOL® NN polyurethane binders for the production of composite materials is in Table 2.

Table 2. Typical Formulation for the Production of Composite Materials

Composition	Parts by weight	Note
Ground material	80-92.5	The amount of binder depends on the type of ground material and required final properties
Water	0.75-2	
Catalyst	0-1.2	The amount catalyst depends on the cross-linking temperature and required processing properties

The technological process of producing these composite materials is very simple. Many different common types of mixing equipment can be utilized, while the process can be either batch or continuous. It can be fully automatic or highly labor intensive. The technological operations for the production of composite materials are in Table 3.

Table 3. Technological Process for the Production of Composite Materials

Operation	Operation time (minutes)	Note
Weighing and charging raw materials	5-15	Depends on amounts and method
Mixing	1.5-10.0	Depends on binder viscosity and effectiveness of the mixing equipment
Mold filling	2-15	Depends on size and shape of product
Molding (or spreading)	5-1440	Depends on binder, temperature, amount of catalyst and thickness of product
Demolding and storage of product	5-30	

Types of Ground Rubber Material for the Production of Composite Materials

The most widely used application for KRASOL® NN binders is in processing of ground cured rubber scrap from usual rubber compounds, mainly based on SBR and EPDM. It is possible to use ground material prepared by standard as well as by cryogenic grinding. Ground scrap from tire retreading process can also be used. The grain size of the ground material is selected according to the desired properties of the final product.

Powdery rubber particles and granules size up to 1 mm (0.040 in.) are suitable mainly for solid molded parts with physical and mechanical properties close to those of standard vulcanizates. Ground material with grain sizes in the range 1 - 4 mm (0.040 - 0.16 in.) is most widely used. It is suitable for a great variety of applications, particularly for athletic surfaces, safety tiles and damping segments. Material with grain sizes larger than 4 mm (0.16 in.) can be used only for products which are not subject to large mechanical stresses. Depending on the type of the ground material used, the compression molded composite products have volume weights in the range 0.400 -1.1 g/cm^3.

Besides ground rubber, other ground polymeric materials, such as ground polyurethane scrap may be used. In such applications, a larger amount of binder (20 wt.%) is added. Also, the filling space has to be larger. The crosslinking can be done also by steam, because possible foaming is not detrimental. KRASOL® NN binders can also be used for ground cork and even for such materials as gravel, stone aggregate and sand.

Examples of Applications

KRASOL® NN binders are most widely used in tire recycling. Ground rubber particles are converted by the use of KRASOL® NN binders into new products with considerable utility. The value of recycling of worn-down tires is not only in creating new products but also in its contribution to the improvement of environment. Possible applications of composites from ground:

- Athletic surfaces
- Tiles for safe playgrounds
- Interlocking flooring
- Damping segments for rail transportation
- Vibration damping and antiskid mats
- Panels for railroad crossings
- Sound-absorbing panels
- Molded parts

More details about the technology of composite materials are in a separate pamphlet, which can be obtained upon request.

Physical and Mechanical Properties of Composite Materials

The composite material attains its final properties after approximately seven days after it is produced. After that time, it can be subjected to mechanical loads or to additional processing, such as cutting or splitting. Physical and mechanical properties of composite materials from ground rubber (see Table 4) are influenced particularly by the following factors:

- Type, nature and grain size of the ground scrap
- Amount and kind of binder
- Method of preparation
- Volume weight of the composite material

Table 4. Physical and mechanical properties of composite materials from ground rubber with particle size 1 - 4 mm using KRASOL® NN binders

Property	Unit	Value	Standard
Tensile strength	(Mpa)	0.5-3.0	ISO 37
Elongation at break	(%)	25-80	ISO 37
Hardness	(Shore A)	60-70	ISO 868
Rebound elasticity	(%)	45-60	ISO 4662
Permanent deformation under pressure (25 °C, 72 h)	(%)	10-25	ISO 815

Resistance of Composite Materials to Chemicals and Weather

Composite materials based on KRASOL® NN binders and ground rubber resist to diluted acids, alkali, solution of salts and to sea water. They also have an outstanding hydrolytic resistance to hot steam. Because of the nonpolar polybutadiene chain and absence of hydrolyzable groups, this resistance is considerable higher than that of other available polyurethane binders. However, they exhibit a lower resistance to solvents, oils, gasoline and diesel oil, which is determined by the properties of the ground rubber scrap. The binder alone only swells by these liquids and after they are evaporated it gains back its original properties.

KRASOL® NN polybutadiene-urethane binders contain an aromatic diisocyanate. As a result, they turn yellow and degrade when exposed to UV radiation. This degradation of composite materials is only on the surface, however, and therefore does not affect the physical and mechanical properties and utility of the product. If necessary, the products from composite materials can be coated by protective layers or coatings.

Coloring and Surface Treatment of Composite Materials

Composite materials with different shades of color can be obtained by adding color concentrates to the reactive mixture. Suitable color concentrates are produced by several manufacturers, e.g. Ciba-Geigy. A colored protective layer with an increased abrasion resistance can be produced by molding ground colored EPDM or of a colored rubber sheet, cured by a standard method or possibly of synthetic lawn. Another approach is to apply liquid elastomeric systems, such as KRASOL® GL series. Flameproof composite materials can be produced by the addition of powder flame retardants based on aluminum hydroxide.

Operational Safety and Effects of KRASOL® NN Binders on Environment

When handled and used properly, KRASOL® NN binders do not represent any health or environmental hazards. Principles of operational safety and environmental aspects of the handling and use of KRASOL® NN binders are listed in detail in the corresponding technical literature.

Cast Elastomers and Potting Compounds

Two-component casting compounds based on KRASOL® LBH 3000 liquid polybutadiene can be compounded to crosslink at ambient temperature and form an elastic material. These are systems KRASOL® GL-02, KRASOL® GL-03 and a developmental formulation KRASOL® SZ-13.

Part A of casting systems contains hydroxyl terminated polybutadiene and the crosslinking agent. The Part A of KRASOL® SZ-13 casting system contains bitumen. Part B is a prepolymer of the hydroxyl terminated polybutadiene and liquid MDI. The reaction rate of these systems is adjusted by the addition of an organometallic catalyst (DBTL).

KRASOL® GL casting compounds are used for the production of elastic molds, for surfaces of athletic fields, in electronic and electrical industries for potting and fixation of delicate parts.

KRASOL® SZ has been developed for the repairs of roads, filling of horizontal joints and cracks in asphalt or concrete foundations and for filling dilatation joints of bridges and buildings.

Processing of Casting Compounds

Both KRASOL® GL and KRASOL® SZ can be processed manually or by a machine. Prior to use, both components of the system must be mixed thoroughly. Then, both are mixed together in the recommended ratio and the catalyst is added. After the reaction mixture is blended thoroughly it is applied. The optimum ratios of reacting components, recommended amounts of catalyst as well as the processing properties of the reaction mixture are in Table 5.

Table 5. Composition of casting compounds and their processing properties

Grade	Component ratio		Amount of catalyst[a]	Processing properties at 23 °C (73 °F)		
KRASOL®	Part A	Part B	Per 100 g of mix (ml)	Pot life (min)	Gel time (min)	Demolding time (hours)
GL-02	1	1	1.3	30	60	24
GL-03	1	2	1.1	50	120	48
SZ-13	1	1	2.0	45	55	24

[a] 0.1 % DBTL in paraffinic oil

KRASOL® GL can be combined with varied pigments or fillers. These substances may accelerate or retard the curing process; therefore, it is always necessary to evaluate each such new ingredient. Processing properties can be adjusted by the amount of catalyst. The cure rate depends also on temperature. For example, at the lowest recommended temperature 10 °C (50 °F), the gel time is extended considerably.

Mechanical Properties of Casting Compounds

Mechanical properties of KRASOL® casting compounds are shown in Table 6. It is obvious, that KRASOL® GL-03 has lower mechanical properties when compared to the KRASOL® GL-02 casting compound. This is caused by the presence of oil in the Part B, which reduces the viscosity of the reaction mixture of the casting system and at the same functions as a plasticizer. In the system KRASOL® SZ-13 it is evident, that the presence of bitumen does not affect mechanical properties significantly.

Table 6. Mechanical properties of KRASOL® GL-02, GL-03 and SZ-13 casting compounds

Property		Unit	KRASOL® GL-02	KRASOL® GL-03	KRASOL® SZ-13
Hardness Shore		Shore A	47-55	35-40	47-52
Tensile strength		Mpa	6.6-7.6	2.0-3.0	6.3-6.7
Elongation at break		%	300-400	100-200	270-330
Rebound elasticity		%	38-42	44-48	38-42
Permanent deformation at 25 °C		%	50	45	47
Glass transition temperature, T_g		°C	-40	-55	-55
Softening temperature, T_m		°C	170	175	180
Abrasion resistance	ΔV	Mm^3	250-300	200-250	-
	ARI	%	50-55	45-50	-

Binders for the Production of Coatings

One-component polyurethane coatings find their application in a great variety of applications, such as for protection of steel structures and poles against corrosion. Binders for these coatings are isocyanate prepolymers based on the reaction of a polyol with an aromatic or an aliphatic diisocyanate. KRASOL® NN-22 prepolymer, based on KRASOL® LBH and liquid MDI, has exceptional properties as a special polyurethane binder for coatings.

Table 7. Characteristic properties of Krasol® NN-22

Property	Unit	Result
Viscosity Brookfield at 25 °C	(Pa.s)	15-20
NCO content	(%)	8.0-9.7
Density	(g/cm^3)	0.99
Dry matter	(%)	100

Polyurethanes have a very good resistance to water and aqueous solutions of acids, bases and salts. Materials prepared from the prepolymer based on MDI exhibit a low resistance to UV radiation. Therefore KRASOL® NN-22 prepolymer is used predominantly for base anticorrosion coatings. The following coating formulations have been developed:

1. High-solids coating with zinc powder (designation KZ)
2. Coating with bitumen (designation KA)
3. Coatings with barrier pigments and fillers (designation KM and KS)

Coatings Formulations and Characteristics

Formulations for coatings, developed by the manufacturer of KRASOL®, are shown in Table 8.

Table 8. Formulations for the coatings KZ, KA, KM and KS [% wt.]

Raw material	Specification	KZ	KA	KM	KS
Zinc powder	Particle size: 7.5 µm Oil absorption: 5-8 g oil/100 g pigment	76.40			
Bitumen	Softening temperature: 105-115 °C Ash: max. 0.4 wt. %.		20.00		
Aluminum paste	Solvent: Gasoline (36 wt. %) Shape and particle size: laminar, approx. 45 µm			6.00	
Ferrous mica	Particle size: approx. 40 µm Oil absorption: 14-18 g oil/100 g pigment			16.80	20.70
Chromium oxide	Particle size: 0.35 µm Oil absorption: 11g oil/100 g pigment			5.60	5.60
Talc	Density: 2,8 g/cm^3 Oil absorption: 36 g oil/100 g pigment		14.80	11.20	11.60
Mineral spirit	Technical gasoline 140-200 Mixture of paraffinic hydrocarbons with boiling range 140-200 °C	9.55	17.25	37.60	35.30
Xylene	Mixture of three isomers, distilling in the range 135-145 °C		17.25		
Rilanit 45	Dispersion agent Manufacturer: HENKEL, Germany Consistency: paste	0.50			
Suprasec 2385	Liquid MDI Manufacturer: Huntsman Polyurethanes NCO groups: 7.2-7.4 mmol/g	1.45	0.80	3.00	2.90
Krasol® NN-22	Isocyanate prepolymer Manufacturer: Kau• uk a.s. NCO groups: 1.9-2.3 mmol/g Viscosity: 12-22 Pa.s	12.00	29.50	18.6	23.50
Niax A4	Amine catalyst Manufacturer: Witco, Belgium	0.10	0.40	0.20	0.40

KZ - coating providing a long-term electrochemical protection, used as a primer for combination systems. It is applied in thickness range 100 - 150 µm.

KA – coating designated to the protection of highly exposed structures, which are permanently submerged in water or exposed to other chemicals. It can be used as a primer or as a coat over zinc primer in thickness greater than 100 µm.

KM, KS - coatings providing corrosion protection with barrier effect, which prevents penetration of water or other corrosive substances through the coating film. They are applied in the thickness range 100 - 150 µm. They may be used as primers or top coatings for common steel structures with zinc primer.

Table 9. Characteristics of the Coatings

Property		Unit	Standard	KZ	KA	KM	KS
Non-volatile matter		% wt.	ISO 3251	90	67	65	65
Density		g/cm^3	ISO 3838	2.6	1.1	1.3	1.4
Surface drying	1. step	minutes	ISO 1517	30	90	30	25
	2. step	minutes		100	180	45	45
Cross-cut test		-	ISO 2409	0	0	0-1	0-1
Flow time (cup, diameter 4 mm)		sec.	ISO 2431	40-50	Thixotropic behavior		

Coatings Manufacture

One-component polyurethane coatings are cured by atmospheric moisture. In addition to the air moisture, the binder can react also with moisture adsorbed on the surface of pigments and fillers. This may lead to crosslinking and gel formation in the coating. Therefore, it is necessary to add a drying agent to the filler and pigment before the addition of the binder (KRASOL® NN-22). For that purpose it is convenient to utilize the fast reaction of isocyanate with water. In the reference formulations based on KRASOL® NN-22, liquid MDI is used.

In general, the production of polyurethane coatings has three phases:

1. Dispersing pigments and fillers

The required amount of solvent is charged into the well-dried vessel of the dispersing equipment and then the proper amounts of pigments and fillers are added while the liquid is stirred constantly. In case of the coating KZ it is necessary to add dispersant in the form of a paste in the same solvent. In coating KA bitumen is first dissolved in the mixture of solvents and only then the remaining components are added.

2. Dehydration of the dispersed mixture

Isocyanate is added to the mixture in the amount, which is about double of the moisture content.Therefore it is necessary to determine moisture content of the raw materials used.

3. Addition of binder and catalyst

After the dehydration of the dispersed mixture the binder is added. The catalyst is added at the end.

Corrosion Tests of the Coatings

The selection of the coating system for a specific application depends on a multitude of factors, such as surface preparation, the coating method and the drying method. The protective function also depends on chemical and physical characteristics of the system (type of binder, thickness of the dry film). These properties can be evaluated by accelerated aging. Tested are in particular resistance to water or moisture, to salt vapor, wet adherence and barrier properties. Results from corrosion tests of coatings based on KRASOL® NN-22 binder are in Table 10.

Table 10. Coatings tests results

Property	Standard	Unit	KZ	KA	KM	KS
Cupping test	ISO 1520	mm	5.5	9.2	2.5	3.2
Impact resistance	ISO 6272	cm	80/40	100/100	100/100	100/100
Cross-cut test	ISO 2409	Degree	0	0	0-1	0-1
Specular gloss (60° /85°)	ISO 2813	%	1.1/3.3	2.6/5.3	1.4/2.6	0.8/1.2
Type of environment for application/durability	ISO 12944		C 4 high	C 4 high	C 4 high	C4 High
Overall anticorrosive, adhesive and barrier effectiveness			excellent	excellent	excellent	excellent

The results show that coatings based on the KRASOL® NN-22 binder may be applied as outer coating in industrial and coastal environment with a mild salinity. They may also be used as interior coating in chemical plants, swimming pools, shipyards and docks. The coating KZ is applied as a primer, the others either as primers or as top coatings. Results from corrosion tests indicate that coatings KZ, KA, KS a KM are comparable to the best commercially available products.

Sealants

Polyurethane materials described in this chapter are developmental products, which are currently not yet part of the commercial line.

These are two-part systems based on KRASOL® LBH polybutadiene designated as KRASOL® TP-02 and KRASOL® TPA. The difference between these two materials is, that KRASOL® TPA contains 15% of bitumen. Each system has two variants with different volume weight of the product depending on the catalyst used:

1. Niax A 100 - frothing of the reaction mixture by 20 %
2. Niax A 300 – frothing of the reaction mixture by 100 and more %.

KRASOL® TP-02 and KRASOL® TPA systems may be used for the insulation of roofs (applying by surface spraying), for filling cavities (application by casting into cavities), sealing of rock drillings, anchoring of parts, sealing dilatation gaps of bridges and buildings (application by injection under pressure).

Advantages of the system:
Simple application, low viscosity (3 - 5 Pa.s), good bonding to various surfaces (rocks, concrete, bricks), autoinjection (pressure developed during foaming causes additional penetration of the material into cracks and gaps), easily controllable cure rate, resistance to water and aqueous solutions of acids and bases.

Properties of the KRASOL® TP-02 System

KRASOL® TP-02 has been developed specifically for sealing rock drilling in the construction of tunnels. This system is designed for low temperature cure (5 – 7 °C or 41 – 45 °F, i.e. typical temperature inside tunnels) with gel time around 20 minutes Table 11 lists processing and mechanical properties of the system KRASOL® TP-02.

Table 11. Processing and mechanical properties of the KRASOL® TP-02 system

Parameter	**Unit**	**System designation**			
		KRASOL® TP-02 / A 100		KRASOL® TP-02 / A 300	
Amount of catalyst per 100 g mixture of system **KRASOL® TP-02**	%	0.25	0.25	0.35	0.35
Temperature of components before reaction	°C	15-17	15-17	15-17	15-17
Mold temperature	°C	5-7	25	5-7	25
Gel time	minutes	25	20	30	25
Beginning of foaming	minutes	15	10	20	10
End of foaming	minutes	50	40	200	50
Cure time	hours	24	up to 24	24	up to 24
Frothing	%	15-20	15-20	80-100	100-120
Volume weight	g/cm^3	0.7		0.5	
Hardness	Shore A	50-52		<30	
Rebound elasticity	%	35-37		-	
Tensile strength	Mpa	1.5±0.2		1.0±0.2	
Elongation at break	%	70±10		85±10	

The gel time and foaming of KRASOL® TP-02 system can be controlled not only by the amount of catalyst but also by the temperature of reacting components. When KRASOL® TP-02 system is cured at 25 °C (77 °F) the reaction times are reduced. If catalyst Niax A 300 is used, greater degree of foaming occurs. KRASOL® TP-02 system with catalyst Niax A 100 had higher mechanical properties than system with catalyst Niax A 300. This is due to the difference in volume weight of the foam.

Properties of the KRASOL® TPA System

The optimum amount of bitumen in the system is 15% by weight; bitumen is added to the hydroxyl component. When higher amount of bitumen is used with catalyst Niax A 100 the foam volume is smaller. With catalyst Niax A 300 the system collapses. Processing properties of the system KRASOL® TPA are in Table 12.

Table 12. Reaction times and mechanical properties of the KRASOL® TPA system

Property	Unit	System designation	
		KRASOL® TPA / A 100	KRASOL® TPA / A 300
Amount of catalyst per 100 g mixture of system **KRASOL® TPA**	%	0.30	0.30
Temperature of components before reaction	°C	15-17	15-17
Mold temperature	°C	25	25
Gel time	minutes	13	19
Beginning of foaming	minutes	5	5
End of foaming	minutes	20	27
Cure time	hours	24	18
Expansion by foaming	%	30	150
Volume weight	g/cm^3	0.70	0.35
Hardness	Shore A	45-47	?30
Rebound elasticity	%	48-50	-
Tensile strength	Mpa	2.5±0.3	1.4±0.2
Elongation at break	%	70±10	85±10

The gel time and foaming of KRASOL® TPA system can be controlled not only by the amount of catalyst but also by the temperature of reacting components. If catalyst Niax A 300 is used, greater degree of foaming occurs. KRASOL® TPA system with catalyst Niax A 100 exhibited a higher volume weight and higher mechanical properties than system with catalyst Niax A 300.

Thermoplastic Polyurethanes

KRASOL® LBH polybutadienediols because of their unique properties (functionality not exceeding two, linearity of the polymer) are suitable components for the production of thermoplastic polyurethanes (TPU). With them, it is possible to produce soft types of TPU without the necessity to add plasticizers. Thus, also the TPU systems can now take advantage of the following exceptional features of polybutadiene-polyurethanes:

- Outstanding hydrolytic resistance
- Excellent electrical insulation properties
- Low moisture permeability

Commercially produced KRASOL® LBH polybutadienediols with terminal secondary hydroxyl groups are available in various molecular weights. The most suitable grades for TPU are LBH 2000 and LBH 3000. Samples of the developmental product KRASOL® LBH-P with primary hydroxyl groups are available upon request.

Formulations and Physical Properties

Examples of TPU based on KRASOL® polybutadienediols and their basic physical properties are shown in Table 13. The TPU materials were prepared by the one-shot process with the ratio NCO/OH =1.03 and cured at 100 °C (212 °F) for 20 hours.

Table 13. Thermoplastic polyurethanes based on KRASOL® polybutadienes

Formulation (parts by weight)	**1**	**2**	**3**	**Test method**
Krasol® LBH 2000	100	-	-	
Krasol® LBH 3000	-	100	-	
Krasol® LBH-P 3000	-	-	100	
2-Ethyl-1, 3-hexanediol	15.1	16.5	-	
1,4-Butandiol	-	-	6.5	
Tinuvin B 75	1.6	1.6	1.3	
Suprasec MPR	39.1	37.4	26.9	
Hard phase (%)	35	35	25	
Physical properties				
Hardness (Shore A)	76	73	60	ISO 868:1985
Tensile strength (MPa)	15.2	14.4	6.8	ISO 37:1994
Modulus 100 (Mpa)	6.5	7.0	2.6	ISO 37:1994
Elongation at break (%)	460	390	890	ISO 37:1994
Glass transition temperature (°C)	-35	-40	-44	TMA[a]
Softening temperature (°C)	90	110	150	TMA[a]

[a] Thermomechanical analysis, measured by the analyzer TMA-CX04R (Intertec Ltd., Czech Republic)

The advantages of 2-ethyl-1,3-hexanediol (EHD) as chain extender are its good miscibility with the polybutadiene and a lower reactivity with the isocyanate. Thus, with using the combination of KRASOL® LBH polyol with secondary hydroxyls with EHD it is possible to prepare one-shot TPUs with any content of hard phase. These TPUs have Shore A hardness 70 - 80, a higher tensile strength and a relatively low softening temperature.

On the other hand, 1,4-butanediol (BDO) has a lower miscibility with polybutadiene; therefore only limited amounts of BDO can be used in formulations. Consequently, TPU with the maximum hard phase content of 25% can be prepared with it. The higher reactivity of BDO requires either the use of the more reactive KRASOL® LBH-P polybutadienediol (primary OH groups) in one-shot formulations, or a prepolymer (two-step) process has to be applied when Krasol® LBH (secondary OH groups) is used. The product resulting from a one-shot process using KRASOL® LBH-P and BDO (Formulation No. 3 in Table 13) has hardness 60 Shore A, a very good elongation at break and relatively high softening temperature.

Process of Synthesis

The TPU synthesis was carried out at normal pressure, under nitrogen blanket with intensive mixing. The reaction vessel was first filled with KRASOL® LBH or LBH-P, EHD or BDO and also stabilizer Tinuvin B75 was added to the mixture. The mixture was heated to 80 - 90 °C (176-194 °F). Then Suprasec MPR preheated to 45 °C (113 °F) was added. After 3 - 5 minutes of mixing the product was cast into molds, in which it was cured at 100 °C (212 °F) for 20 hours. The cure time can be shortened by the addition of a suitable catalyst.

Hydrolytic Resistance

Hydrolytic and chemical resistance of polyurethanes is significantly affected by the nature of the soft phase. Among conventional TPUs the types based on polyethers are generally considered to be materials with the highest hydrolytic resistance. Therefore, the hydrolytic resistance of TPU based on KRASOL® polybutadienes was compared to a commercial TPU produced with a polyether polyol (polytetramethylene glycol, PTMG).

Tests of hydrolytic and chemical resistance were carried out in aqueous solutions of a strong acid (60 % H2SO4), of an oxidizing acid (40 % HNO3) and of a strong alkali (50 % NaOH) at laboratory temperature. The change in hardness of the TPU materials was measured after 28 days of exposure. (see Table 14).

Table 14. Hydrolytic and chemical resistance of TPU based on polybutadiene and on polyether

Material	**Change of Shore A hardness after 28 days exposure (%)**		
	in 60% H_2SO_4	in 40% HNO_3	In 50% NaOH
TPU based on KRASOL®	+14	-3	+11
TPU based on PTMG	Corroded after 1 day	Dissolved after 1 day	+5

TPU prepared with KRASOL® polybutadiene exhibited a much higher resistance to inorganic acids; its stability in the solution of NaOH was comparable. TPU based on KRASOL® polybutadienes have a higher resistance to aggressive aqueous media than TPUs containing ester or ether linkages.

Electrical Insulation Properties

TPUs prepared from KRASOL® LBH or LBH-P polybutadienes have outstanding electrical insulation properties and can be therefore highly suitable materials for insulation of wires and cables. The values of the volume resistance (10^{14} Ω.m) and of surface resistance (10^{16} Ω) for the polybutadiene based TPUs are several orders of magnitudes higher than those of TPUs based on PTMG.

KRASOL® NN Adhesives

Characteristics of Polyurethane KRASOL® NN Adhesives

KRASOL® NN - 22 and KRASOL® NN -23 adhesives are one-part polyurethane adhesives, crosslinking by atmospheric moisture. They are most frequently used for bonding polystyrene foam, plywood and chipboards. They are used with advantage for bonding bitumen-coated paper, rubber composites, belts and sheets to surfaces of wood and concrete. KRASOL® NN adhesives are prepolymers based on liquid KRASOL® LBH polybutadiene a diphenylmethane diisocyanate (MDI). KRASOL® NN-23 contains oil as viscosity modifier. Crosslinking occurs at ambient temperature and is activated by the addition of the catalyst that is a part of delivery.

Due to their nonpolar polybutadiene chain, the KRASOL® NN adhesives exhibit an outstanding adhesion to large number of nonpolar materials. Adhesive joints have excellent physical and mechanical properties, good elasticity at low temperatures and a very good hydrolytic and chemical resistance.

Table 15. KRASOL® NN Adhesives

Name	**Physical and chemical properties of adhesive**			**Application**
	NCO content (%)	Viscosity at 25 °C (mPa.s)	Density at 20 °C (g/cm^3)	
KRASOL® NN-22	8.0-9.7	12000-22000	0.95-1.00	Universal adhesive for bonding of various materials (bitumen paperboard, rubber composites, belts and sheets) to surfaces of wood and concrete
KRASOL® NN-23	4.0-5.0	500-3000	0.91-0.06	Special adhesive for bonding various materials to foam polystyrene slabs and to bond polystyrene foam slabs to each other

Technological Procedure for Bonding

The bonding procedure is very simple. Using proper mixing equipment, the catalyst is added to the KRASOL® NN adhesive. The activated adhesive is applied in a thin layer to both bonded surfaces, which must be dry, clean and free of grease and moisture. Both coated surfaces are exposed to the effects of atmospheric moisture for 10 -15 minutes.

Then they are pressed together. Temperature during the bonding should not be lower than 10 °C (50 °F). Excessive humidity of the environment, too, can adversely affect the quality of the adhesive joint. The activation rate can be controlled by the amount of catalyst added. The adhesive is cured after 24 hours. The final physical and mechanical properties are attained after 7 days.

Operational Safety and Effects of KRASOL® NN Adhesives on the Environment

KRASOL® NN adhesives are harmless to health and environment, if handled and used properly. The principles of safe handling and use and environmental aspects of the applications of KRASOL® NN adhesives are described in detail in the corresponding technical literature.

Attachments

Calculations of Polyurethane Formulations

Polyurethane formulations require that the reaction components be mixed in the desired ratio, derived from the concentration of reactive groups. The basic principle involved is, that one equivalent of OH (or of other group containing active hydrogen) reacts with one equivalent of NCO.

The manufacturers of polyols, isocyanates, low-molecular weight diols, triols etc. express the amounts of functional groups in several ways. Therefore, the following equations are useful for the calculation of polyurethane formulations.

Hydroxyl content (C_{OH}, mmol/g) gives the content of OH groups (mmol) in 1 gram of polyol.

Hydroxyl number (hydroxyl value), (N_{OH}, mg KOH/g) is given by the consumption of KOH (mg) in the determination of OH groups of a polyol by acetylation method: $N_{OH} = C_{OH}\ 56{,}1$

Hydroxyl content (% of hydroxyl groups) ($C_{\%OH}$, %) indicates the amount of hydroxyl group in 100 weight parts of polyol. $C_{\%OH} = C_{OH}\ 1{,}7$

Equivalent weight of polyol (E_{OH}, g/mol) is the weight of polyol (grams), in which there is one mol of hydroxyl groups. $E_{OH}= 1000/C_{OH}$

Analogous terms are used for the characterization of isocyanates:

Isocyanate content (C_{NCO}, mmol/g)

Isocyanate value ($C_{\%NCO}$, %), $C_{\%NCO} = C_{NCO}\ 4{,}2$

Equivalent weight of isocyanate (E_{NCO}, g/mol), $E_{NCO} = 1000/C_{NCO}$

Raw materials

Trade name	Chemical name	Manufacturer
Suprasec 2385	Liquid MDI	Huntsman
Suprasec 2004	Liquid MDI	Huntsman
Suprasec MPR	4,4’-MDI	Huntsman
Baymidur VP KL 3-5002	Liquid MDI	Bayer
Baymidur VP KU 3-5003	Liquid MDI	Bayer
Desmodur W	Hydrogenated MDI	Bayer
Ongronat HS-44-40	Liquid MDI	Borsodchem
Ongronat HS-44-50	Liquid MDI	Borsodchem
Isonate M 143	Liquid MDI	Dow
Tedimon 80	TDI	Enichem
2-Ethyl-1, 3-hexanediol	2-Ethyl-1, 3-hexanediol (EHD)	Hüls
Voranol RA 100	Diisopropanol aniline (DIPA)	Dow
1,4-Butanediol	1,4-Butanediol (BDO)	ARCO
Diethylene glycol	Diethylene glycol	ARCO
Glycerol	Glycerol	Lachema
Lonzacure M-CDEA	4,4-Methylene-bis(3-chloro-2,6-diethylaniline)	Lonza
Irgastab DBTL	Dibutyltin dilaurate (DBTL)	Ciba-Geigy
Niax	Amine catalysts	Witco
Marcol 82	Paraffinic oil	ESSO
Enerthene 2368	Naphthenic oil	BP

Evaluation of Properties of Polybutadiene Based Polyurethanes

The following methods were used to evaluate properties of polyurethane systems based on KRASOL® LBH described in this manual:

Properties evaluated	**Methods**	
	ISO	**ASTM**
PU elastomers and rubber composites		
Hardness Shore A	ISO 868	ASTM D 2240
Tensile stress-strain properties	ISO 37	ASTM D 412
Tear strength	ISO 34-1	ASTM D 624
Compression set	ISO 815	ASTM D 395
Resilience	ISO 4662	ASTM D 1054
Abrasion resistance	ISO 4649	-
Brittleness temperature	ISO 812	ASTM D 746
Effect of liquids	ISO 1817	ASTM D 471
Coatings		
Density	ISO 3838	ASTM D 1475 ASTM D 1481
Non-volatile matter	ISO 3251	ASTM D 2369 ASTM D 1644
Flow time	ISO 2431	ASTM D 1200
Surface drying	ISO 1517	ASTM D 1640
Film thickness	ISO 2808	-
Specular gloss	ISO 2813	ASTM D 523
Corrosion protection – laboratory performance test methods	ISO 12944	ASTM D 1654
Impact resistance (Falling-weight test)	ISO 6272	ASTM G 14-88
Cross-cut test	ISO 2409	-

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