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Capa® POLYCAPROLACTONE DIOLS IN CAST ELASTOMERS USING 4, 4 DIPHENYLMETHANE DIISOCYANATE (MDI)

The physical properties of cast elastomers produced from MDI, Capa® polycaprolactone diols and butane diol are given in this leaflet.

Capa® based polyurethanes are particularly noted for:

i) Lower cost, due to the fact that Capa® based urethanes have a lower density than those derived from polyadipates.

ii) Outstanding resilience giving rubbers with low hysteresis properties.

iii) Very good low temperature performance.

iv) Good hydrolysis resistance, especially when special grades are used.

GENERAL DISCUSSION OF PROPERTIES

Density

Elastomers based on Capa® polycaprolactone diols have a significantly lower density than those produced from other polyester diols; the difference can be as much as 8% lower. Since elastomers are generally used on a volume basis, the lower densities of those produced from Capa® polyols offer a considerable cost advantage.

Resilience

Table 1 compares the resilience of Capa® based MDI systems with Adiprene L100 and an adipate based MDI system. It can readily be seen that the Capa® based systems give outstanding resilience resulting in low hysteresis properties.

Table 1
Comparative Resilience of 90 Shore A Polyurethane Systems

TEMP (°C)	% RESILIENCE MEASURE BY LUPKE PENDULUM			
	Capa® 2100 / BD / MDI	Capa® 2220 / BD / MDI	POLYADIPATE / BD / MDI	ADIPRENE L100
25	30	62	48	38
70	63	76	65	62

Hydrolysis Resistance

Tables 2 and 3 compare the hydrolysis resistance of 90 Shore A systems based upon various polymers. It can readily be seen that the standard grade Capa® 2220 based urethanes have good hydrolysis resistance compared with urethanes based on, for example, adipate polyesters and that Capa® 2200A is the preferred grade where excellent hydrolysis resistance is needed.

Table 2
Comparative Hydrolysis Resistance at 100°C

Polyurethane System	c/o Tensile Strength Retention after Immersion at 100°C			
	2 days	4 days	6 days	10 days
Adiprene L100	57	30	21	19
PTHF/BD/MDI	64	35	32	30
Capa® 2200/BD/MDI	63	39	7	0
Polyethylene/Butylene adipate	16	10	0	0
Polyethylene adipate	7	0	0	0

Table 3
Comparative Hydrolysis Resistance at 80°C

Polyurethane System	c/o Tensile Strength Retention after Immersion at 80°C						
	5 days	10 days	15 days	20 days	25 days	30 days	35 days
PTHF/BD/MDI	97	93	86	78	69	60	50
Capa® 2200A/BD/MDI	97	93	86	76	62	42	11
Capa® 2200/BD/MDI	97	93	82	57	7	0	0
Polyethylene / butylene adipate / BD/MDI	87	54	10	0	0	0	0

Viscosity

Capa® polycaprolactone diols are also of very low viscosity as shown by comparing them to other polyester diols at 100°C, a temperature commonly used for mixing elastomer components.

Table 4
Polyol Viscosities

POLYESTER DIOL (2000 Mol. Wt.)	VISCOSITY (cps) AT 100°C
Capa® 2200	180
Poly (ethylene/Butylene) adipate	300
Polyethylene adipate	300

The lower viscosity of Capa® polycaprolactone diols ensure better mixing characteristics, long pot lives and greatly improved pourability.

FORMULATION OF ELASTOMERS FROM MDI

Choice of Chain Extender

In general, Butane diol is the preferred chain extender for the highest performance polyurethane elastomers. However, elastomers softer than 80 Shore A based on butane diol will cold harden.

For softer elastomers, ethane diol or diethylene glycol should be used as chain extenders since elastomers made with these do not cold harden.

Choice of Index

It is recommended that an index of 1.07 is used for optimum elastomer performance.

Method of Calculation

A simple general formula is used for calculation of formulations.

$$x = \frac{C}{(M - C)} \times \left[\left(\frac{aM}{DI} \right) - (100 - a) \right]$$

$$y = 100 - a - x$$

where x = % chain extender
y = % polyol
C = M.W. chain extender (90-Butane diol)
M = M.W. polyol
a = % diisocyanate
D = M.W. diisocyanate
I = Isocyanate Index

For Capa® 2200, butane diol and isocyanate index of 1.07, this reduces to:

$$x = 0.40a - 4.71$$

The normal batch to batch variations in the molecular weight of Capa® 2200 can be tolerated without changes in formulation.

Table 5
Formulations using Capa® 2100 (80 - 95 Shore A)

% Capa® 2100	65.83	58.62	54.36
% MDI	30	34.4	37.8
% Butane Diol	4.17	6.98	7.84
Hardness Shore A Shore D	80 30	40 40	95 46
Density g/cm^3	1.17	1.19	1.20
Lupke Resilience % 25°C	30	30	-
70°C	75	63	-
Modulus Kg/cm^2 25%	13	32	45
100%	30	65	110
300%	80	315	450
Tensile Strength Kg/cm^2	430	520	550
Elongation %	420	360	350
Crescent Tear Strength Kg/cm^2	76	80	110
Extension Set (70°C)	2	2	6
Compression Set (70°C)	13	25	25
Cold Flex Temp. °C	-24	-19	-17

Table 6
Formulations Using Capa® 2200 (80 - 96 Shore A)

%Capa® 2200	69.73	62.74	58.54	48.74
% MDI	25	30	33	40
% Butane Diol	5.27	7.26	8.46	11.26
Hardness Shore A Shore D	80 33	90 42	95 46	96 57
Density g/cm^3	-	1.18	1.19	-
Lupke Resilience % 25°C	66	62	55	-
70°C	77	76	71	-
				-
Modulus Kg/cm^2 25%	19	35	80	-
100%	40	65	101	170
300%	113	200	177	355
Tensile Strength Kg/cm^2	458	535	538	500
Elongation %	400	420	430	420
Crescent Tear Strength Kg/cm^2	55	91	110	160
Extension Set (70°C)	2	2	7	-
Compression Set (70°C)	27	21	20	15
Cold Flex Temp. °C	-35	-39	-30	-17

APPENDIX I

METHODS OF CAST MDI ELASTOMER PREPARATION
Summary

a) A total prepolymer is prepared by reacting polyol and MDI at 80℃ for one hour.

b) The prepolymer at 80℃ is mixed with the chain extender at room temperature, degassed and the mixture poured into heated moulds.

c) After curing, the moulded elastomers are removed from the mould and post cured for 24 hours at 110℃.

ELEMENTS OF PROCESS

1. Prepolymer Preparation

The total prepolymer that is required can easily be made in small quantities for laboratory or small scale plant evaluation. Quantities of less than one kilo can be made by mixing the molten MDI and polyol in a glass bottle and placing this, sealed under nitrogen in an oven at 80℃ for one hour with occasional shaking. 5 kg quantities can be made in a glass vessel equipped with a heating mantle, stirrer, thermometer and nitrogen inlet. The isocyanate should be added to the polyol and the mixture maintained at 80℃ for an hour, under nitrogen or vacuum.

There are no definite upper limits on the scale on which this process can be carried out, other than the need for efficient mixing, close control of the addition of the polyol and the temperature of the process. If the temperature exceeds 80℃ significantly then there is a risk of undesirable branching leading to poor performance in the finished elastomer.

The prepolymer once made can be stored for significant periods (up to six months) provided it is kept in sealed containers desirably under dry nitrogen. Water and oxygen must be excluded. Storage should be at ambient temperature and preferably above freezing. Once the prepolymer has been removed, the reaction vessel can be cleaned out by filling with toluene or acetone, boiling up and discarding the washings.

2. Processing

The prepolymer, freshly made or reheated to 80℃ after storage, is weighed out in the appropriate quantity into either a disposable vessel or a steel vessel that can be cleaned by heating to 5 - 600℃ after use. The prepolymer is then degassed until gas evolution stops. Conveniently, a vacuum pump can be used with an outlet tube carrying a flange and a soft rubber seal to seal on to the vessel containing the prepolymer. If an electric vacuum pump is not available, a water pump suitably protected against suck back with traps has been found to be satisfactory since the vacuum requirements are only 20 - 25 mm.

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Some producers of cast elastomers who store prepolymers prefer to degas the material in bulk and then to maintain it at the appropriate temperature under nitrogen and use it in small quantities without further degassing. If machines are used, the tanks of these machines are usually fitted with degassing facilities.

After degassing, the chain extender (normally 1,4 - Butanediol) is added cold to the prepolymer at 80°C and mixed thoroughly but avoiding excessive air entrapment. The mixture is then swiftly degassed and poured into the mould. Many cast elastomer producers prefer to redistill the chain extender or to heat it under vacuum to ensure that it is perfectly dry before use. This avoids the last degassing stop, providing that care is taken to avoid beating any air into the system if mixing by hand.

After casting, the container can either be discarded or re-used after allowing the residual contents to cure, or if make of steel (mild steel or preferably stainless), the vessel can be heated in an adequately ventilated oven to a high temperature to burn off the residual elastomer.

The mixed gas free system is carefully poured into a mould coated with a suitable mould release agent (see appendix) and preheated to 110 - 140°C. The working time available for pouring the system after mixing is typically 3 - 7 minutes, dependent on the hardness of the ultimate elastomer. The mould is then placed in an oven at 110 -140°C and maintained at this temperature for the requisite time on a hot place (see below) and the moulded item is then removed from the mould.

Cure Requirements (Uncatalysed)

	% MDI		
	20	**30**	**40**
Pot Life	6 mins	6 mins	3 mins
Demould	120 mins	45 mins	15 mins

3. Moulds

For production purposes, aluminium or steel moulds (preferably the latter) are required. For prototype work metal filled epoxy resins, or polyurethane elastomers can be used. It is desirable that the material of construction should be thermally conductive where thick sections are to be moulded, thus avoiding excessively high temperatures in the curing process.

Attempts have been made to avoid the use of mould release by coating the surface of the mould with PTFE. However, results are conflicting, probably depending on the porosity of the surface left after coating with PTFE.

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4. **Catalysed Systems**

It is appreciated that the cure times of the softer formulations are unacceptably long, particularly where existing materials are fast cure Adiprene systems. The use of normal polyurethane catalysts speeds up the reaction considerably. However, in many cases it may make the pot life inconveniently short for processing by hand. It is hoped by examining various latent catalysts (i.e. those that are inactive below 90 - 100°C) to overcome this problem, without substantially changing the chemistry of the process and thus affecting the

APPENDIX II

1. **Mould Releases**

Certain mould releases have been found to give outstanding results, It is reasonable to assume that mould releases working well with Adiprene and Vulkollan would also be suitable for Polycaprolactone elastomers.

2. **Adhesives for Metal Bonding**

For protection of castors and rollers that have polyurethane tyres or coverings, the metal surface of the centre must be prepared. This is done by sand blasting the surfaces that are to be bonded and then degassed with trichloroethylene or toluene. The centre can then be dried in an oven.

One or two coats of adhesive can be applied with a brush or spray gun which must be cured at 100 - 110°C for 15 minutes.

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