CHEMISTRY THAT MATTERS™

NORYL™ AP2001G POLYOL IN POLYURETHANE CAST FORMULATIONS

PROCESSING GUIDELINES

SABIC's Specialties Business
July 2022

CONTENTS

Note: The experimental data contained in this document reflect the processing conditions used by SABIC.

NORYL™ AP2001G POLYOLS IN CAST FORMULATIONS

NORYL AP2001G polyol is a low molecular weight di-functional hydroxyl-terminated polyol based on polyphenylene ether (PPE). Incorporating NORYL AP2001G polyol into a solid elastomer matrix may demonstrate the following structure-property benefits* in traditional cast polyurethane formulations:

- Improved toughness and reduced abrasion
- Increased tensile strength
- Improved strain modulus and elongation
- Retained physical properties at elevated temperatures
- Retained physical properties after aging in hot, wet environments
- Improved resistance to alkaline, acid, water and oil
- Improved adhesion to steel

Potential applications include: coatings, adhesives, sealants, elastomers, foams and composites.

NORYL AP2001G polyol has the following characteristics:

PROPERTIES	TYPICAL VALUES	UNITS	TEST METHODS
THERMAL			
Tg (half width)	140	°C	SABIC method
PHYSICAL			
Physical Form	PELLET	-	SABIC method
Hydroxy Equivalent Weight (HEW)	880	g/eq	SABIC method
Moisture Content	<0.5	%	SABIC method

* Enhancing TDI Cast Elastomers
* Enhancing MDI-BDO Cast Elastomers

USING NORYL™ AP2001G POLYOL IN CAST POLYURETHANE FORMULATIONS

NORYL AP2001G polyol is compatible with a range of polyether polyols and can be blended with other diols or triols to achieve desired product properties. Since the terminal phenolic hydroxyl end-groups have a slower reactivity than the aliphatic hydroxyl in the polyether polyol, a prepolymer should be considered. This document will outline process conditions in the following stages:

Preparing NORYL AP2001G / polyol blends → Preparing prepolymers or quasi-prepolymers → Processing cast formulations

Process Step Considerations

Preparing NORYL AP2001G polyol / polyol blends

NORYL AP2001G polyol + Polyether polyols used: PPG, PTMG → NORYL AP2001G polyol / polyol blend

Preparing prepolymer or quasi-prepolymer

NORYL AP2001G polyol / polyol blend + Diisocyanate → Prepolymer (TDI) Quasi-prepolymer (MDI)

Processing cast formulations using prepolymer (or quasi-prepolymer)

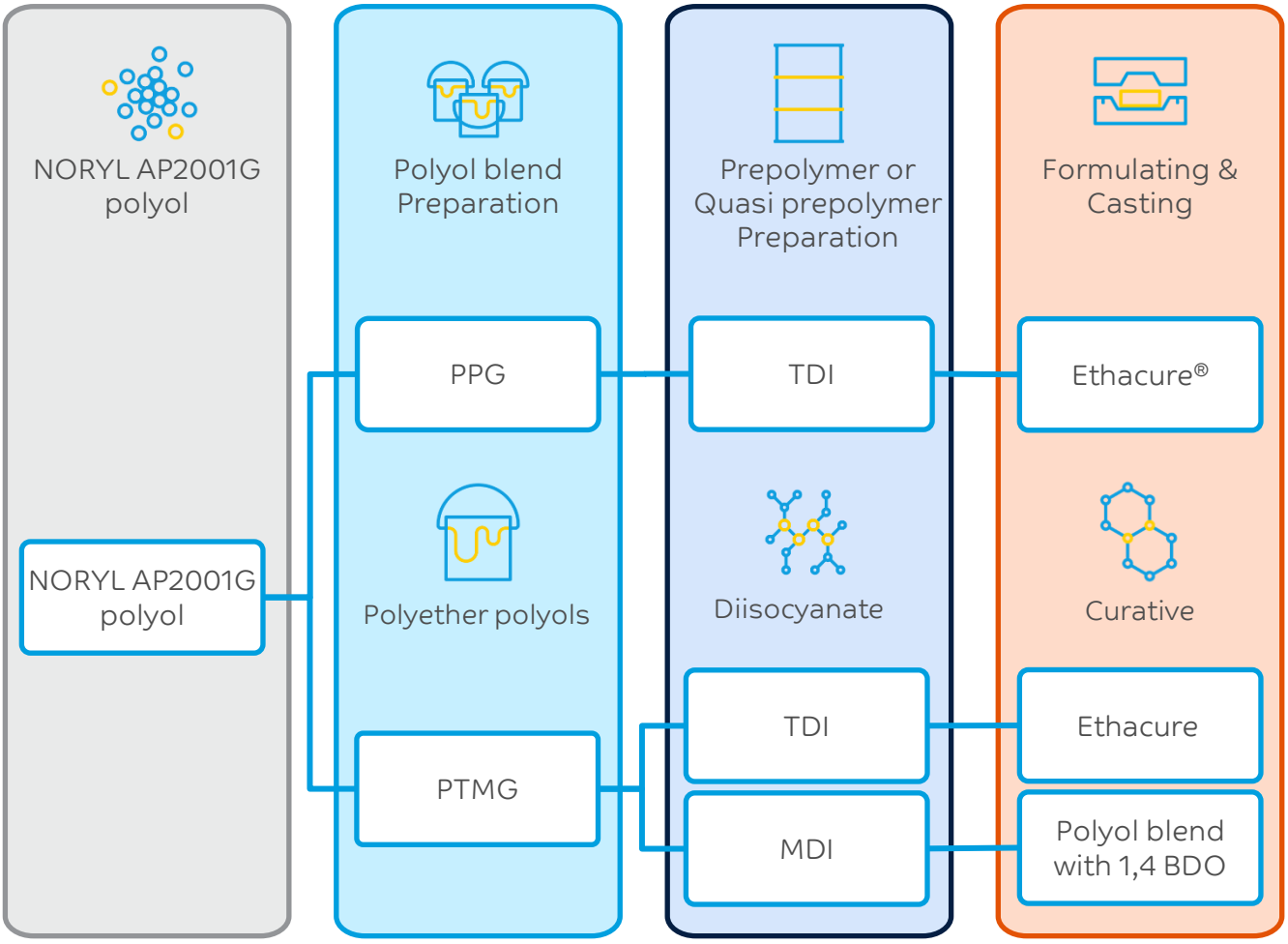
Prepolymer (TDI) Quasi-prepolymer (MDI) + Curative Ethacure 300 1,4-BDO + NORYL AP2001G polyol / polyol blend → Cast polyurethane

FORMULATION SPACE CONSIDERATIONS

NORYL™ AP2001G polyol is compatible with a range of polyether polyols and can be blended with other diols or triols to achieve desired product properties. Since the terminal phenolic hydroxyl end-groups have a slower reactivity than the aliphatic hydroxyl in the polyether polyol, a prepolymer should be considered. This document will outline process conditions in the following stages:

Preparing NORYL AP2001G / polyol blends → Preparing prepolymers or quasi-prepolymers → Processing cast formulations

Formulation Considerations



REACTIVITY CONSIDERATIONS

NORYL™ AP2001G polyol has phenol end groups. Phenols react more slowly than alcohols with isocyanates. Therefore, it is important to carefully design the reaction stoichiometry and sequence of additions to ensure full bonding of the AP2001G polyol into the urethane backbone. The relative rates of reaction at 20 ^{o}C are approximately 300:1, which leads to full reaction of the polyol first and NORYL AP2001G polyol second. This is demonstrated by the modelling of the reaction shown in Figure 1.

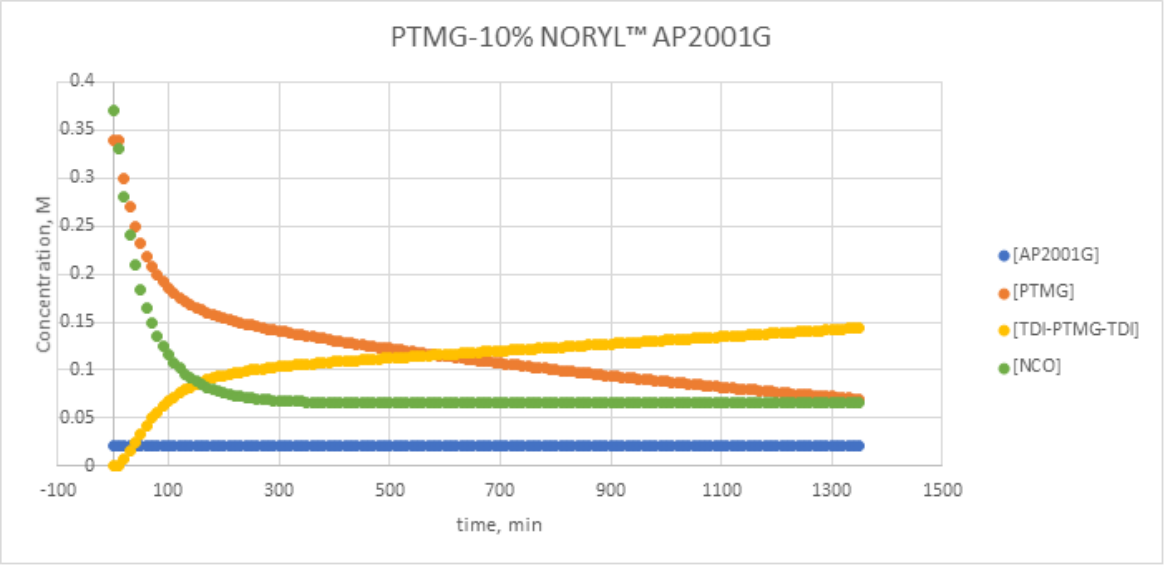


Figure 1. Relative concentrations for a 2.05:1 TDI:-OH reaction

There needs to be enough NCO in the original formulation to react with all of the AP2001G end groups. SABIC employed a 2.05:1 stoichiometry in our tests to allow for the presence of extraneous moisture in the reagents and ensure full capping of the AP2001G. We monitored the FTIR signal for NCO until it remained constant. Titration of the NCO content of the final prepolymer was also performed.

An approach to a low free NCO prepolymer is to ensure a full reaction of AP2001G with isocyanate by employing a higher initial concentration of AP2001G (eg. 40%), followed by dilution with additional polyol (PPG or PTMG) to achieve the desired final concentration.

In MDI formulations, when making a quasi-prepolymer, the large excess of NCO to –OH should overcome the kinetic limitation. SABIC did not experience issues in the AP2001G incorporation with MDI quasi-prepolymers. When making true MDI prepolymers, the same kinetic limitations as TDI would apply.

PREPARING NORYL™ AP2001G POLYOL / POLYOL BLENDS

PREPARING NORYL™ AP2001G POLYOL / POLYOL BLENDS

Preparing NORYL AP2001G polyol / polyol blends | Preparing prepolymers or quasi-prepolymers | Processing cast formulations

Preparing NORYL AP2001G polyol/ polyol blends

Key Considerations:

- NORYL AP2001G polyol is soluble in polyether polyols, thus both PPG and PTMG were considered. NORYL AP2001G polyol is less soluble in polyester polyols, so these were not considered.
- Polyether polyols (PPG or PTMG) should be de-moisturized for 24 hours at 75-80 °C under vacuum of 1-3 mmHg with continuous mixing prior to use.
- Consider viscosity data when determining NORYL AP2001G polyol loading level (see Figures 1 and 2 for PPG1000 and PTMG1000 solutions). When using higher molecular weight polyols, consider lower loading levels of NORYL AP2001G polyol to achieve desired viscosity.

Blending Procedure:

The blends of NORYL AP2001G polyol (in solid particle form) with PTMG or PPG were prepared using the following procedure:

1. Preheat polyol (PTMG or PPG) at 100 °C under nitrogen sweep and agitation.
2. Add NORYL AP2001G polyol in small portions to avoid agglomeration.
3. Continue agitation and maintain nitrogen sweep for 2 hours at 100 °C.
4. Transfer to storage container if necessary.

VISCOSITY DATA: NORYL™ AP2001G POLYOL / POLYOL BLENDS

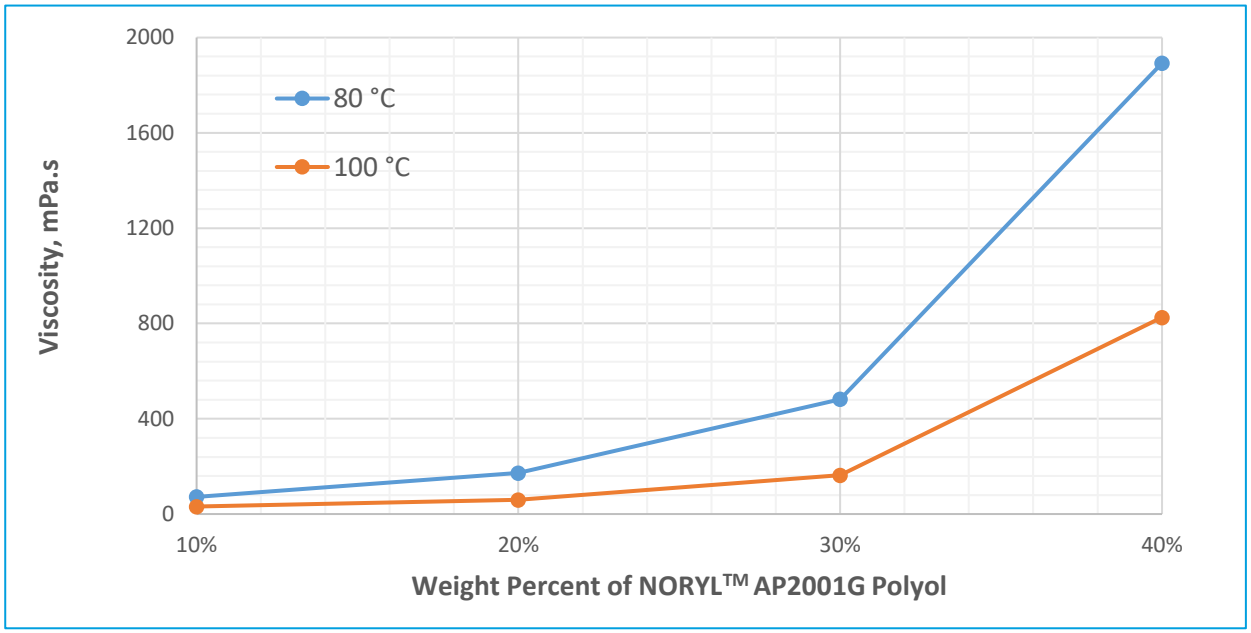


Figure 1: Trend in viscosity vs concentration of NORYL AP2001G polyol in PPG1000 at 80 °C and 100 °C.

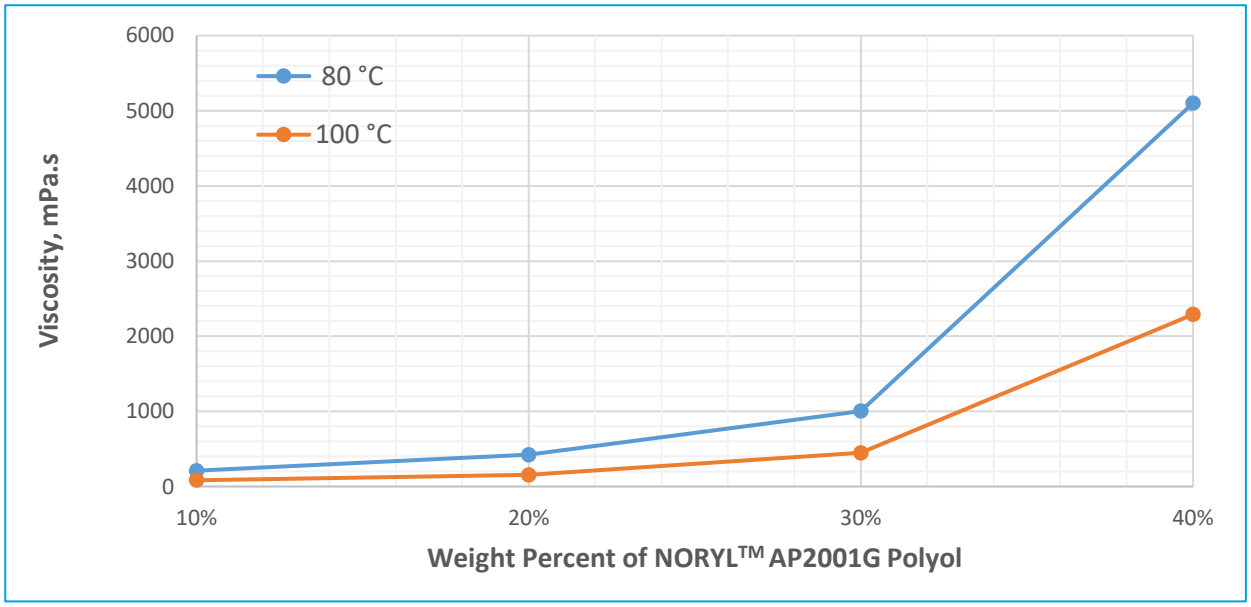


Figure 2: Trend in viscosity vs concentration of NORYL AP2001G polyol in PTMG1000 at 80 °C and 100 °C.

TYPICAL PROPERTIES: NORYL™ AP2001G POLYOL / POLYOL BLENDS

Preparing NORYL AP2001G polyol / polyol blends | Preparing prepolymer or quasi-prepolymer | Processing cast formulations

Preparing NORYL AP2001G / polyol blends

NORYL AP2001G polyol

+

Polyether polyols used:
PPG
PTMG

→

NORYL AP2001G polyol / polyol blend

Typical Properties of NORYL AP2001G polyol in PPG1000:

Test	Limits	Results	Test Method
NORYL AP2001G polyol loading (wt. %)		40	
Hydroxyl Value, mg KOH/g	-	87.4	Internal Method
Water (wt%)	<0.06	0.03	Karl Fischer Titration
Viscosity at 80 °C, cP	-	5260	Brookfield Viscometer
Viscosity at 100 °C, cP	-	1210	Brookfield Viscometer
Appearance at 50 °C	-	Reddish colored viscous liquid	

Typical Properties of NORYL AP2001G polyol in PTMG1000:

Test	Limits	Results	Test Method
NORYL AP2001G polyol loading (wt. %)		40	
Hydroxyl Value, mg KOH/g	-	86.9	Internal Method
Water (wt%)	<0.06	0.05	Karl Fischer Titration
Viscosity at 80 °C, cP	-	6410	Brookfield Viscometer
Viscosity at 100 °C, cP	-	1578	Brookfield Viscometer
Appearance at 50 °C	-	Reddish colored viscous liquid	

PREPARING PREPOLYMER AND CASTINGS USING TDI

PREPARING PREPOLYMERS WITH TDI

Preparing NORYL™ AP2001G polyol / polyol blends | **Preparing prepolymer with TDI** | Processing cast formulations

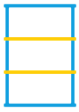
Preparing prepolymer

NORYL AP2001G polyol / polyol blend

+

Diisocyanates used: TDI

→



Prepolymer (TDI)

Key Considerations:

Matching solution viscosities of all components by preheating may improve mixing characteristics. Gentle heating (40-100 °C) of the resins may be required to obtain a uniformly mixed system.

- To identify highest workable concentrations in an overall formulation, consider the viscosity trend.
- Achieving a homogeneous solution will depend on solution temperature, time and overall formulation.
- To avoid potential phase separation with the polyol components, add polyol blend with NORYL AP2001G polyol in stages.

Ensure polyol water content is less than or equal to 0.06%. At lab scale, consider the following procedure:

- Homogenous polyol blends can be dehydrated under vacuum of ~3 mmHg at 70 °C for at least 24 hours with continuous mixing in a round bottomed flask.
- Confirm water content after drying using ASTM D4672 (SABIC used Karl Fisher Titration).

PREPARING PREPOLYMERS WITH TDI

Preparing NORYL™ AP2001G polyol / polyol blends | **Preparing prepolymer with TDI** | Processing cast formulations

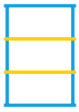
Preparing prepolymer based on TDI

NORYL AP2001G polyol / polyol blend

+

Diisocyanate used: TDI

→



Prepolymer (TDI)

Prepolymer should be prepared using an NCO:OH molar ratio of 2.05:1

Prepolymer procedure:

1. Charge TDI in a 1 L glass reactor equipped under N_2 sweep and agitation.
2. Heat reactor to an internal temperature of 70 °C with a mantle and proportional heat control.
3. Slowly add the polyol blend to maintain the reactor temperature at 70-75 °C.
4. Monitor reaction by following the NCO% using the di-n-butylamine method (ASTM D-5155).
5. Once the reaction reaches the theoretical NCO%, cool the mixture to room temperature.
6. Store the prepolymer in a glass jar under N_2 at room temperature.

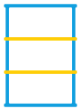
Table 1: Prepolymer preparation considerations

Prepolymer Preparation	**PPG2000**			**PTMG2000**		
NORYL™ AP2001G polyol (wt. %)	0	8.30%	16%	0	8.30%	16%
Temperature of reaction, °C	70	75	75	75	75	75
Duration of reaction, hr	6	4.5	3.5	3.5	3.2	3.2
Theoretical NCO%	3.5	3.54	3.57	3.58	3.52	3.59
Final NCO%	3.54	3.5	3.6	3.54	3.51	3.52
Viscosity at 70°C, mPa·s	580	2400	15400	3340	5400	32400
Viscosity at 80°C, mPa·s	320	1200	5050	1700	3900	15100
Transitions via DSC (Cooling), °C	-59.4	-56.1	-49.3	-1.7	-72	-67.5
Transitions via DSC (Heating), °C	-55.7	-50.1	-46.9	21.6, 24.8	-67.5, -21.1, 23.3	-60.8, -0.1, 22.3

PREPARING CAST FORMULATIONS: PPG BASED PREPOLYMER WITH TDI

Preparing NORYL™ AP2001G polyol / polyol blends → Preparing prepolymer with TDI → **Processing cast formulations**

Processing cast formulations using prepolymer



Prepolymer
PPG / AP2001G / TDI

+

Curatives used:
Ethacure®

→

Cast polyurethane

Key Considerations:

- Cast elastomers were prepared by reaction of NCO-prepolymers with Ethacure 300 at an isocyanate index of 1.05 (see Table 2).
- The cast elastomers, sheets and buttons, were cured for one hour at 80 °C in a Carver hydraulic press.
- After demolding, the samples were conditioned for seven days at room temperature prior to testing.

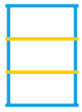
Table 2: Formulation and casting considerations: PPG based prepolymers with TDI

Ingredient (g)	Casting A (Control)	Casting B (90/10 blend)	Casting C (80/20 blend)
PPG-TDI prepolymer	55.25		
PPG-AP2001G-90/10 prepolymer		55.30	
PPG-AP2001G-80/20 prepolymer			55.18
Ethacure 300	4.75	4.70	4.82
Temperature of component, °C	80	80	80
Gel time, s	>375	622	514

PREPARING CAST FORMULATIONS: PTMG BASED PREPOLYMER WITH TDI

Preparing NORYL™ AP2001G polyol / polyol blends → Preparing prepolymer with TDI → **Processing cast formulations**

Processing cast formulations using prepolymer



Prepolymer
PTMG / AP2001G / TDI

+

Curatives used:
Ethacure®

→

Cast polyurethane

Key Considerations:

- Cast elastomers were prepared by reaction of NCO-prepolymers with Ethacure® 300 at an isocyanate index of 1.05 (see Table 3).
- The cast elastomers, sheets and buttons, were cured for one hour at 80 °C in a Carver hydraulic press.
- After demolding, the samples were conditioned for seven days at room temperature prior to testing.

Table 3: Formulation and casting considerations: PTMG based prepolymers with TDI

Ingredient (g)	Casting A (Control)	Casting B (90/10 blend)	Casting C (80/20 blend)
PTMG-TDI prepolymer	55.25		
PTMG-AP2001G-90/10 prepolymer		55.29	
PTMG-AP2001G-80/20 prepolymer			55.28
Ethacure® 300	4.75	4.71	4.72
Cure Temperature, °C	80	80	80
Gel time, s	360	344	304

PREPARING QUASI-PREPOLYMER AND CASTINGS USING MDI

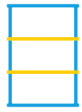
PREPARING QUASI-PREPOLYMERS WITH MDI

Preparing NORYL™ AP2001G polyol / polyol blends | **Preparing quasi-prepolymer with MDI** | Processing cast formulations

Preparing quasi-prepolymer

Polyol blend with NORYL AP2001G polyol

Diisocyanates used: MDI



Quasi-prepolymer (MDI)

Key Considerations:

Matching solution viscosities of all components by preheating may improve mixing characteristics.

- To identify highest workable concentrations in an overall formulation, consider the viscosity trend.
- Achieving a homogeneous solution will depend on solution temperature, time and overall formulation.
- To avoid potential phase separation with the polyol components, add polyol blend with NORYL AP2001G polyol in stages.

Ensure polyol water content is less than or equal to 0.06%. At lab scale, consider the following procedure:

- Homogenous polyol blends were dehydrated under vacuum of ~3 mmHg at 70 °C for at least 24 hours with continuous mixing in a round bottomed flask.
- Confirm water content after drying using ASTM D4672 (SABIC used Karl Fisher Titration).

Gentle heating (40-100 °C) of the resins may be required to obtain a uniformly mixed system.

PREPARING QUASI PREPOLYMER WITH MDI

Preparing NORYL™ AP2001G polyol / polyol blends | **Preparing quasi-prepolymer with MDI** | Processing cast formulations

Preparing prepolymer or quasi-prepolymer

Polyol blend with NORYL AP2001G polyol

+

Diisocyanates used: MDI

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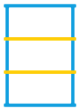


Quasi-prepolymer (MDI)

Prepare MDI quasi-prepolymers using an NCO:OH ratio of 1.05:1

Quasi-Prepolymer Procedure

1. Charge MDI to a 1L glass reactor equipped with mechanical agitator under N_2 sweep.
2. Slowly add the polyol blend as to maintain the reactor temperature at room temperature.
3. Flush with N_2 then close and store at room temperature overnight.
4. Monitor reaction by following the NCO % by the di-n-butylamine method (ASTM D-5155).
5. Determine final NCO % by the di-n-butylamine method (ASTM D-5155).
6. Store the quasi-prepolymer in a glass jar under N_2 at room temperature.

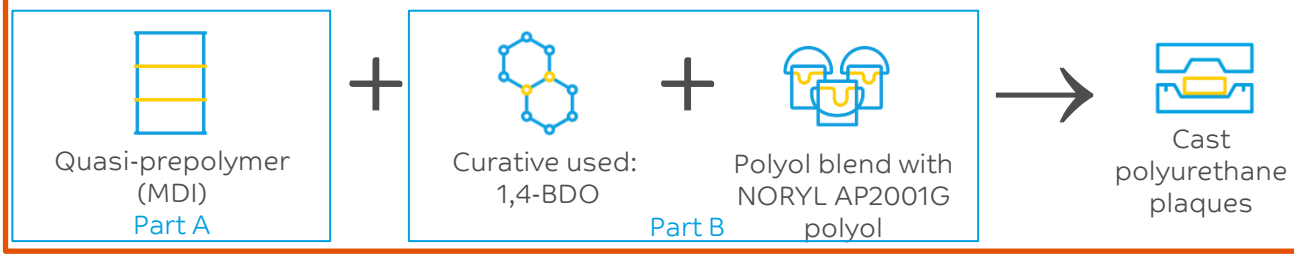
Table 4: Prepolymer formulations

		Ingredient	Qty. (g)	Measurement	Value
	**Polyol blend** with NORYL AP2001G (20% AP2001G)	PTMG 2000 NORYL AP2001G	1000.00 250.17	OH value (Troy Polymer Inc. method)	50.9
	Reference prepolymer	PTMG 2000 Lupranate® 81	61.34 300.76	Theoretical NCO% Final NCO%	23.03 22.73
	20% AP2001G prepolymer	**Polyol blend** Lupranate 81	55.41 234.66	Theoretical NCO% Final NCO%	23.03 21.59
	10% AP2001G prepolymer	**Polyol blend** PTMG 2000 Lupranate 81	27.83 27.80 234.63	Theoretical NCO% Final NCO%	23.03 21.92

PREPARING CAST FORMULATIONS WITH MDI

Preparing NORYL™ AP2001G polyol / polyol blends → Preparing quasi-prepolymer → Processing cast formulations

Processing cast formulations using quasi-prepolymer



Key Considerations

- To maximize loadings of NORYL AP2001G polyol in the formulation, the polyol may be used in both the part A (quasi-prepolymer) and part B of the final formulation.
- The part B solution is a blend of the PTMG polyol and NORYL AP2001G polyol (see “Preparing NORYL AP2001G Polyol / Polyol Blends” section) plus curative.
- Polyurethane cast elastomers are prepared by compression molding of the reactive mixture in a Carver press. Part A and Part B components are preheated at 40 °C and cured for 30 minutes at 80 °C as shown in the next page.

PREPARING CAST FORMULATIONS WITH MDI

Preparing NORYL™ AP2001G polyol / polyol blends | Preparing quasi-prepolymer | **Processing cast formulations**

CAST formulation and processing considerations

Formulation		Casting D (control)	Casting E (10% AP2001G-QPP)	Casting F (20% AP2001G-QPP)
% AP2001G polyol in total system		-	5.6	11.0
Part B Ingredients (g)				
PTMG 2000		28.88	14.17	-
20% AP2001G polyol in PTMG 2000		-	14.16	27.63
1,4 Butanediol		4.55	4.49	4.53
Dabco T12		0.008	0.008	0.008
Part A Ingredients (g)				
Part A	NCO%			
Reference prepolymer	22.73	26.18	-	-
10% AP2001G prepolymer	21.59	-	26.80	-
20% AP2001G prepolymer	21.92	-	-	27.45
Sheet Synthesis Details				
Part B and Part A, temp., °C		40	40	40
Mold and Carver press, temp. °C		80	80	80
Speed mix time, s		20	20	20
Gel time (avg), s		67 ± 12	80 ± 9	87 ± 12
De-mold time, min		30	30	30

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