

# SAE Technical Paper Series

**880353**

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Reprinted from SP-743—  
Automotive Exterior Body Panels

International Congress and Exposition  
Detroit, Michigan  
February 29 — March 4, 1988



*The papers included in this volume  
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**ISSN 0148-7191**

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# Polyurea RIM in Exterior Body Panel Applications

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## ABSTRACT

Commercialized use of the reaction injection molding (RIM) process first involved polyurethane elastomers. Improvements to this RIM elastomer system were soon made by the use of a new aromatic-amine chain extender, diethyltoluenediamine (DETDA). New insights on the commercial usefulness of RIM elastomers were provided by these new systems classified as polyurethane/urea RIM elastomers. Recently, a further refined system has begun to make strong headway in the RIM elastomer market. Amine-terminated polyether resins along with the amine chain extender are incorporated into these systems which are referred to as polyurea RIM elastomer.

Polyurea RIM elastomer systems, which require no catalyst, are extremely fast and capable of high productivity. Incorporation of internal mold release agents allow for fast and easy release of parts from molds without external spraying of a release agent. Specific end use requirements can also be met by redesigning the polyurea RIM system. Speed and physical properties of the polyurea RIM systems allow for creative designing in automotive applications. Polyurea RIM elastomers are making significant contributions in automotive fascia material.

To further improve styling uniqueness in automobiles, polyurea RIM elastomers can be used to produce exterior body panels. A wide processing latitude, superior properties and cost advantage of the system make polyurea RIM a good candidate over polyurethane/urea and injection molded thermoplastics. Polyurea RIM elastomers are extremely tough and are not prone to corrosion as are the conventional stamped steel body panels. In this paper, recent advances in polyurea RIM elastomer technology as it relates to exterior body parts will be discussed.

## INTRODUCTION

The development of polymeric material systems that can be processed via The Reaction Injection Molding or RIM process has been an active field of industrial research for more than a decade.<sup>1,2</sup> Polyurea RIM materials are one of the most recent developments to result from this effort.<sup>3-5</sup> In this paper we will discuss some recent advances in exterior body panel applications using polyurea RIM technology and spray-in-mold applications. In order to allow the reader to fully appreciate the contribution that polyurea RIM materials have made to our industry, we will first review the history of RIM material development. The focus of our review is to enable the reader to understand how polyurea RIM materials address the processing and property needs of the RIM industry.

### The Evolution of RIM Materials

The first polymers to be used in the RIM process were polyurethane materials. These systems consist of polyether polyols, glycol chain extenders, catalysts and aromatic polyisocyanates. Processing problems such as low mold filling viscosity (which causes entrapment of air bubbles), long cycle times and the lack of a workable internal mold release capability along with property limitations such as poor high temperature dimensional stability caused these polyurethane materials to be replaced by polyurethane/urea materials. Today, polyurethane/urea RIM materials dominate the automotive RIM market in the United States. These systems consist of polyether polyols, diamine chain extenders such as diethyltoluenediamine (DETDA), catalysts and aromatic polyisocyanates.<sup>6</sup> While these are improvements over the old polyurethane technology, they still suffer from relatively poor high temperature dimensional stability and internal release capabilities. Polyurea RIM materials, developed at the Austin Laboratories of Texaco Chemical Company, answer these

needs.<sup>7-16</sup> These systems consist of polyether polyamines, diamine chain extenders such as DETDA and aromatic polyisocyanates. The evolution of RIM material technology is summarized in Table I. It is important to note that in polyurea RIM technology, polyether polyols are replaced by polyether polyamines. Also, no catalysts are used in polyurea RIM systems.

#### Polyurea RIM

When a RIM system is comprised of polyether polyamines, a diamine chain extender such as DETDA and an isocyanate, the reactions which occur in the mold are amine/isocyanate reactions to yield urea linkages. The RIM polymer that is produced from such a formulation has come to be known as polyurea RIM. The amine/isocyanate reaction is very fast and consequently the cycle time of polyurea RIM systems is also very fast. Closed mold times as short as 5 seconds or less have been reported. Also, the reactions of amines with isocyanates occur so readily that no catalysts are needed to speed them up. Catalysts have the benefit of promoting the desirable polymerization reaction, however, when they remain in the polymer they can promote decomposition (as is the case with RIM-produced products). This is especially evident at elevated temperatures. Since polyurethane and polyurethane/urea RIM polymers contain catalysts, they have poor resistance to high temperature. Even at relatively mild temperatures, for instance 120°C, catalysts promote poor dimensional stability in RIM products. In Table II, we see the effect of catalysts on the heat sag of a polyurea RIM material. The heat sag is doubled when the catalyst is added. Another performance property deficiency ethylene oxide capped polyols induce into a RIM polymer is poor moisture resistance. In Table III, the comparison between polyurea RIM fascia material and a conventional polyurethane/urea RIM fascia is made. The polyurethane/urea RIM fascia, which contains ethylene oxide capped polyols, absorbs significantly more water than the polyurea RIM material. In Table IV water absorption of soft polyurea RIM versus polyurethane/urea RIM is compared. Since the level of ethylene oxide capped polyol is higher in these soft materials than in typical RIM fascia products, the lower moisture resistance deficiency of materials based on ethylene oxide capped polyols is especially dramatic. An interesting note on the subject of water absorption is the effect low temperature has on moisture resistance in these materials. In Table IV we report the effect of nine freeze/thaw cycles on a polyurea RIM material and a polyurethane/urea RIM material. This cycling causes a very dramatic increase in the water absorption of the ethylene oxide capped polyol containing

polyurethane/urea RIM elastomer and no change in the water absorption of the polyurea RIM elastomer. Thus, application of polyurea RIM elastomers in outdoor uses such as gaskets for windows is clearly indicated by this study.

A critical characteristic of polyurea RIM materials which has precipitated the keen interest in these systems is their excellent release properties. By this we mean the ease of removal of a part from the core of the mold time after time. Polyether polyamines are excellent solvents for internal release agents such as acidic dimethylsiloxanes and zinc stearate. The excellent inherent release characteristics of polyurea RIM materials enhance the release characteristics of the aforementioned internal release agents. In fact, 500 or more moldings of a medium complexity fascia part have been made from an internal mold release containing polyurea RIM system. In addition, polyurea RIM materials do not require as much internal mold release agent as do polyurethane/urea RIM products.

Polyurea RIM materials also excel in other important performance properties. Excellent impact resistance and excellent high temperature dimensional stability are characteristic of them. In Table V, the comparison is made between a conventional polyurethane/urea high modulus RIM material and its polyurea RIM counterpart. Even though the conventional system is at a higher flexural modulus than the polyurea RIM material, the heat sag of the polyurea RIM material is much better. In fact, the polyurea RIM material will survive exposure to 205°C with some distortion, while the conventional system is totally decomposed under these conditions. The superiority in high temperature of polyurea polymers over polyurethane and polyamide polymers has been well known for some time.<sup>17</sup> This was best illustrated by Hill and Walker whose data is presented in Figure 1. With melting points as high as those given for crystalline polyurea materials it is not surprising that even the amorphous polyurea hard blocks in polyurea RIM polymers are so resistant to elevated temperatures.

Polyurea RIM materials are as versatile as conventional RIM systems in the diversity of products which can be made from them. Anything from soft elastomers in the 50 Shore A range to high stiffness elastoplastics in the 350,000 psi flexural modulus range can be made. Thus, polyurea becomes the RIM material of choice when a product designer has a high performance application.

#### Other Isocyanates

Polyurea RIM products can be made from isocyanates other than MDI-based isocyanates. As an example, TDI isocyanates have been used to make polyurea RIM materials. In Table VI we list the properties of some TDI-based polyurea RIM systems. TDI isocyanates make polyurea polymers which have a very high

density of urea linkages in the hard block. Consequently, these systems exhibit excellent high temperature dimensional stability and excellent flexural modulus ratio. Therefore, TDI-based polyurea RIM materials or systems which use a blend of MDI and TDI as the isocyanate may become materials of choice for certain high performance applications. The cycle time of TDI-based polyurea RIM systems is substantially longer than that of MDI-based systems because TDI reacts more slowly than MDI. The product typically has a closed mold time that is up to 5 times longer than MDI-based products.

Aliphatic isocyanates can also be used in polyurea RIM. We have studied aliphatic isocyanates such as tetramethylxylene diisocyanate and isophorone diisocyanate in polyurea RIM formulations. In Table VII, some of the properties of these materials are listed. The products studied are generally soft elastomers. There has been considerable interest in making weatherable RIM products in the soft elastomer area. At the present time, polyurea RIM systems based on aliphatic isocyanates are in their infancy. However, we wish to indicate that such products are possible and that with refinement these could find application in the manufacture of unpainted parts that require resistance to outdoor exposure.

#### Slower Polyurea RIM Systems

With slower polyurea RIM systems it is possible for molders to use conventional RIM machinery available in their plants today and still make excellent polyurea RIM parts. In previous work, we have shown that sterically hindered MDI isocyanates yield polyurea RIM products with excellent ultimate properties and longer mold filling times. Recently, we have discovered that certain modified amine chain extenders incorporated into polyurea RIM systems cause longer mold filling times. In Table VIII, we identify three of these modified diamine chain extenders. The first is Unilink® 4200 from UOP Corp., the second is N,N'-ditertiarybutyl ethylenediamine and the third is Ethacure® 300 from Ethyl Corp. The first two work by retarding the vitrification of the RIM polymer as it fills the mold. The third works by adjusting the chemical reactivity of the chain extender/isocyanate reaction in addition to retarding vitrification. All three materials give RIM polymers with excellent physical properties and increased mold filling times. Cycle times are somewhat longer when these slower polyurea RIM systems are employed. The ultimate property and certain processing gains polyurea RIM systems can bring to the RIM molding industry are realized only when the faster unretarded polyurea RIM systems are used. The heat sag of the slower polyurea RIM materials in particular are generally higher than for the faster reacting polyurea RIM systems.

#### Exterior Body Panels

The application of polyurea RIM in exterior body panels can now be fully appreciated since an overview of the technology has been given. Currently, steel fenders and door panels dominate the market for passenger cars and light trucks. Only a few American and foreign sports cars contain plastic exterior fascia and some body panels. Recently, the trend in the automobile industry has been toward an increase in the number of car models to meet consumer demand. This requires many presses and tools to stamp out the sheet metal parts for the different models and is therefore expensive. Costs have been reduced here by using the same basic framework for each model. Also, there has been a demand for improved warranty protection against corrosion and damage.

An economical way to solve this problem is extensive use of plastic exterior body panels instead of traditional sheet metal. High performance plastic, or "composite" body panels can deliver styling latitude and model uniqueness which have strong appeal to customers. This would also give creative automotive engineers an opportunity to design and produce products the consumer can easily distinguish and recognize. An example of this is the current use of RIM fascia. This development has dramatically changed automotive styling.

To be a successful candidate for exterior body panel applications, the material must meet certain requirements. The material must have sufficient flexural modulus or stiffness. To maintain quality fit, the material should have a low coefficient of linear thermal expansion (CLTE). For large ranges of environments and temperatures, the material must have good impact resistance and dimensional stability. Finished parts must have a Class A surface as well as good paint adhesion in order to appeal to customer needs. To meet high volume needs, the material must be capable of high productivity outputs, i.e. fast cycle times. Polyurea RIM, with the incorporation of an internal mold release and proper fillers, will fit all of these requirements. It also provides an especially attractive engineering material for accomplishing styling uniqueness.

For exterior body panel applications, polyurea RIM is competing with polyurethane/urea RIM and injection molding thermoplastics. The material itself has many advantages over thermoplastics currently available.<sup>19, 20</sup> Polyurea RIM inherently has very high thermal stability which enables it to survive "E-Coat" bake temperatures of 205°C.<sup>4, 22</sup> This is extremely important since polyurea RIM body panels will need to be mixed with steel in current automobile assembly operations for on-line painting. Polyurea RIM also has excellent compatibility with internal mold release agents<sup>5</sup> which facilitates the molding

of consistently high quality parts at high production rates. A big advantage associated with polyurea RIM is the lower tooling and press costs associated with the reaction injection molding of large exterior body panel and fascia parts. Not only would the tooling and equipment costs for polyurea RIM be lower versus steel stamping, it would also offer significantly lower tooling and equipment costs that are required for injection molding thermoplastics.

Exterior body panels made of polyurea RIM are usually reinforced with mineral fillers such as glass to give the stiffness and physical properties required. These resulting body panels will not rust or corrode and are very tough and resistant to damage.

#### Low Molding Temperature Polyurea RIM

Since polyurea RIM parts are handled by operators, hot molds are a problem for many of our customers. Heated molds, 120°C or higher, are needed to overcome brittleness at demold in high modulus, >70,000 psi, polyurea RIM systems which have high heat stability. Due to the speed and ease of mold release of polyurea RIM material, automation should soon be evident in reaction injection molding operations, negating high mold temperatures as an issue. Until then, lower mold temperatures around 75°C are desirable.<sup>18</sup> To meet this transitory requirement, high modulus polyurea RIM systems, based upon our JEFFAMINE® amines were modified so that they could be molded at these conventional temperatures. They are referred to as low mold temperature (LMT) high modulus polyurea RIM. In Table IX a comparison of the properties of the LMT system with a standard high modulus polyurea RIM material is made. The LMT material is tough at demold even at 75°C mold temperature. However, low and high temperature properties are somewhat sacrificed.

Recently, work has been done with the LMT polyurea system with our JEFFAMINE® amines in an effort to remedy the heat related problems. An improved system which operates at a lower mold temperature with good processing and no part brittleness has evolved. A comparison of this new LMT polyurea system to a polyurea HT system can be found in Table X. It should be noted that a sized glass which has been found to improve the properties of the polyurea RIM elastomer was used here.

This polyurea LMT system will further optimize thermal properties of RIM systems with respect to ease of processing and lower thermal distortion through on-line painting processes. Like the polyurea HT system, this system has a gel time of one second but it uses a mold temperature of 81°C, as compared to 115°C for the polyurea HT system. Better release from the mold is seen at 81°C than at 115°C. Repeated releases from a simple bare steel tool can also be achieved, as with

polyurea RIM fascia, through the use of IMR. Excellent part surface qualities can be obtained along with improved productivity and effectively lower part cost. Like current RIM systems, the polyurea LMT system can be processed on existing RIM equipment. The low heat sag value of 12.3 mm for a 150 mm overhang at 205°C for 60 min suggests that this system might be used for on-line painting processes where temperatures in excess of 150°C can exist.

Initial prototype work indicated this system processed extremely well at low mold temperatures even for the 300,000 psi flexural modulus. Exterior body panels went through the painting process with encouraging results. Good paintability was expected since it has been the case with polyurea RIM fascia materials using the same basic technology and the JEFFAMINE® amines.

#### Spray Polyurea Elastomers

To complement polyurea RIM systems, spray polyurea elastomer systems which have possible application for in-mold spraying of small exterior body panel parts have been developed. These spray polyurea elastomers use the same basic technology as polyurea RIM. They are based on similar JEFFAMINE polyetheramines. Spray system reactivities can be adjusted by the same means as the polyurea RIM systems. Optimum processing of the materials is achieved by the use of high pressure, impingement mixing equipment. Excellent mix of the material is demonstrated for these highly reactive systems which contain no solvents.

Typically, these systems have gel times of 1.2 sec to 1.8 sec with tack free times of less than 2.5 sec. The systems could then be sprayed into open molds which either have externally applied soap or with incorporated IMR. A glass chopper can be added to the equipment to dispense chopped fiberglass into the polyurea elastomer spray pattern. Flexural modulus, impact strength, heat distortion and CLTE can be improved with the addition of the fiberglass. Table XI gives the physical properties of selected spray polyurea elastomer systems.

This technique could be used to produce smaller exterior body parts without the expense of conventional RIM equipment. Snowmobile and jet ski cowlings, fenders and gas tank covers for the popular ATV's and motorcycles and other type parts can be prepared by in-mold spraying. Larger body parts and other aftermarket parts can also be produced in the same manner that spray fiberglass work is done. Reactive dyes along with UV stabilizers could be included to eliminate the separate painting processes for these parts. System reactivity and cure would allow for rapid production of these parts, as is the case with polyurea RIM.

#### Conclusion

As one can observe, polyurea RIM systems formulated with a wide variety of amine chain

extenders and isocyanates have an almost limitless degree of versatility. Formulations producing anything from soft elastomers to stiff, hard elastoplastics have been developed. This versatility of the polyurea RIM systems allows the design engineer to fully utilize his or her creative thinking in the automotive industry. Spray processing of polyurea elastomers also shows the advantages associated with polyurea RIM and adds to the creativeness of polyurea technology. The exceptional properties and processing of polyurea RIM material are useful in automotive fascia and exterior body panels. Toughness, corrosion resistance and styling freedom afforded by polyurea RIM high performance plastic is very appealing to consumers. The new LMT polyurea RIM materials will allow for greater processing latitudes and eventual on-line painting in the automotive industry. Polyurea RIM systems invite automation due to the material's superior processing characteristics.

#### Acknowledgements

The authors wish to acknowledge Ray Kruckemeyer, Dave Riffe and Milton Stark for their diligent work in preparing samples and operating our RIM equipment. We also wish to thank Texaco Chemical Company for their support of the RIM project.

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Table I. Evolution of RIM Materials

	<u>Isocyanate</u>	<u>Polyether</u>
1st Generation Polyurethane	MDI Based	Glycols EO Capped Polyols Catalysts
2nd Generation Polyurethane/Urea	MDI Based	Aromatic Diamine EO Capped Polyols Catalysts
New Generation Polyurea	MDI Based	Aromatic Diamine Polyether Polyamine

Table IV

Water Absorption of Polyurea and  
Conventional RIM Soft Elastomers

<u>Weight increase (%) after</u>	<u>Polyurea</u>	<u>Conventional</u>
1 day @ 25°C	1.65	3.15
7 days @ 25°C	2.07	5.08
7 days @ 25°C plus 9 freeze/thaw cycles	2.07	10.30

Table II

The Detrimental Effect of Catalysts on a  
Polyurea RIM Polymer

<u>Properties</u>	No Catalyst	With Catalyst
Flexural modulus, psi @ 25°C	32600	34000
Heat sag, mm 1 hr @ 120°C, 150 mm overhang	12.5	25

Table V

Polyurea RIM vs. Conventional High Modulus Materials

<u>Properties</u>	<u>Polyurea<sup>1</sup></u>	<u>Conventional<sup>1</sup></u>
Tensile strength, psi	3200	3450
Elongation, %	50	20
Flexural modulus, psi @ 25°C	170000	225000
Heat sag, mm 1 hr @ 120°C, 150 mm overhang	<1	8
1 hr @ 205°C, 150 mm overhang	30	Melts/decomposes
Impact resistance energy at break, <sup>2</sup> ft-lbs	18	6

<sup>1</sup> 20% by wt flake glass  
<sup>2</sup> 5 mph test

Table III

Water Absorption of Polyurea and  
Conventional RIM Fascia Products

<u>Weight increase (%) after</u>	<u>Polyurea</u>	<u>Conventional</u>
1 day @ 25°C	1.57	2.36
7 days @ 25°C	2.13	3.61
7 days @ 25°C plus 9 freeze/thaw cycles	2.21	4.02

Table VI

TDI vs. MDI Based Polyurea RIM Materials

<u>Properties</u>	<u>TDI</u>	<u>MDI</u>
Flexural modulus, psi @ 25°C	34000	34000
Flexural modulus ratio -30°C/70°C	1.5	2.0
Heat sag, mm 1 hr @ 120°C, 150 mm overhang	4	10



Table VII  
Polyurea RIM Materials Based on  
Aliphatic Isocyanates

Properties	IPDI	TMXDI
Tensile strength, psi	2500	1000
Elongation, %	580	470
Tear strength, pli	400	260
Flexural modulus, psi @ 25°C	12300	9400

Table VIII  
Slower Polyurea RIM Materials Based on DETDA

Properties	Retarder			
	Unilink 4200	N,N'-DTBEDA	Ethacure 300	None
Tensile strength, psi	4350	3900	4350	4130
Elongation, %	210	185	210	190
Tear strength, pli	530	475	490	500
Flexural modulus, psi @ 25°C	57200	60100	53600	58700
Heat sag, mm 1/2 hr @ 155°C	15	14	12	12
Gel time, sec	1.7	1.8	1.7	1.4

Table IX  
Low Mold Temperature (LMT) High Modulus  
Polyurea RIM vs. Conventional Polyurea RIM  
Materials

Properties	LMT Polyurea	Conventional Polyurea
Tensile strength, psi	3700	3900
Flexural modulus, psi @ 25°C	228000	219000
@ -30°C	420000	356000
@ 155°C	124000	176000
Flexural modulus ratio -30°C/70°C	2.6	1.95
Heat sag, mm 1/2 hr @ 155°C 150 mm overhang	6.5	2.0
Izod impact, ft-lbs/in., notched	1.78	2.25
Mold T, °C	75	135

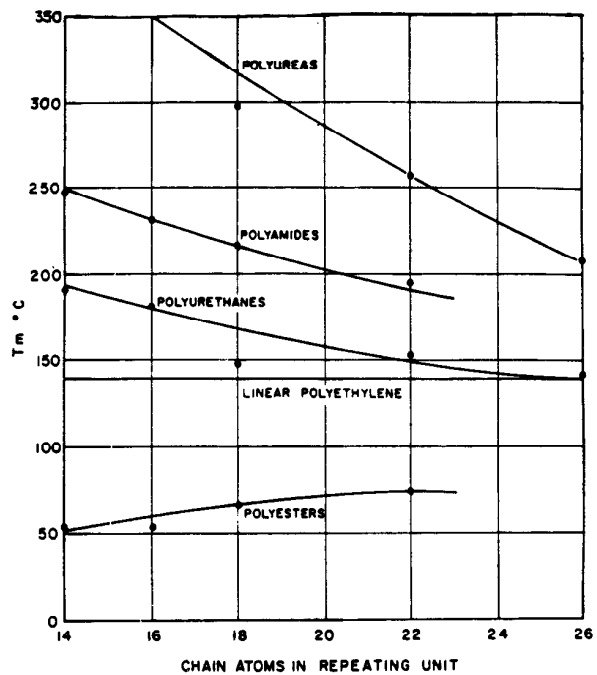
Table X  
New Polyurea LMT vs. Polyurea HT

	LMT	Polyurea HT
Flake glass, %	20 <sup>a</sup>	20
Tensile, psi	5507	3950
Ultimate elongation, %	15	28
Flexural modulus, kpsi @ 25°C	289	252
@ -30°C	422	367
@ 70°C	191	156
@ 155°C	166	N.A.
Flexural modulus ratio -30°C/70°C	2.21	2.35
Heat sag, 150 mm 121°C/60 min	N.A.	0.4
155°C/60 min	1.75	N.A.
163°C/60 min	N.A.	2.5
177°C/60 min	2.0	N.A.
191°C/30 min	N.A.	11.4
205°C/60 min	12.3	N.A.
Post cure	155°C/30 min	163°C/60 min
Index	105	103
Mold temperature, °C	81	121

<sup>a</sup> Sized glass

Table XI  
Spray Polyurea Elastomers

	11-32	17-2
Tensile, psi	1892	2066
Ultimate elongation, %	97	113
Tear, pli	456	479
Flexural modulus, kpsi @ 25°C	57.2	43.4
@ -30°C	113	88.5
@ 70°C	39.5	28.5
Shore D hardness 0 sec	55	58
10 sec	50	51
Heat sag, mm 100 mm - 120°C/60 min	3.0	3.25
150 mm - 120°C/60 min	8.25	5.88
Sample thickness, mm	2.0	3.0
Index	105	105



TREND OF CRYSTALLINE MELTING POINTS IN HOMOLOGOUS SERIES OF ALIPHATIC POLYMERS

(MILL AND WALKER, REF 17)

FIG. 1