

Spray Polyurea Versatile High Performance Elastomer for the Polyurethane Industry

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ABSTRACT

Two-component spray elastomers and coatings have recently shown large increases in market interest, sales volume and use because of regulations which limit the volatile organic content of the coating, i.e., solvent-based coatings. Also, new improvements in spray application equipment have contributed to the interest and use of these high-performance type systems which have very good physical property characteristics. Typically, these elastomer-type systems include polyurethane, polyester, epoxy-urethane, acrylic-urethane and oil-modified urethane. A newer development in two-component elastomer and coating systems is the use of 100% solids systems based on amine-catalyzed polyurethane RIM technology. The advent of these type systems is due mainly to the superior performance of the polymer and the development of spray equipment capable of processing the systems. Recently, in order to keep on the leading edge of technology, a further-refined 100% solids spray elastomer system, based upon polyurea RIM technology, has also been demonstrated. Amine-terminated polyether resins along with amine chain extenders are incorporated into these systems which are referred to as spray polyurea elastomers.

Polyurea spray elastomer systems, which require no catalyst, are extremely fast in reactivity and cure. This leads to higher productivity and fast turnaround time. Also, the systems are virtually unaffected by moisture due to this fast reactivity. Improved physical properties and better hydrolytic and thermal stability can be obtained with the spray polyurea elastomer systems. Spray elastomer systems based upon this polyurea technology are good candidates for both coating and noncoating-type applications, which makes this a very versatile technology. In our changing world of technology, we are always seeking better ways of accomplishing our objectives. Recent advances in spray polyurea elastomers and coatings will be discussed in this paper.

INTRODUCTION

The development of two-component spray elastomer and coating systems has been an active field of research

and interest for many years. This research has evolved from typical polyurethane systems to high performance, 100% solids polyurethane elastomers based on RIM technology. Further evolution brought forth two-component spray elastomer systems incorporating high molecular weight polyols, amine chain extenders and amine catalysts. Processing of these high performance materials was made possible by improved refinements in spray application equipment. Recent advances in RIM technology, namely polyurea RIM, have produced a new evolution in spray elastomer technology. Polyoxyalkylene diamines and triamines have replaced the polyols; amine chain extenders are utilized; and catalysts have been eliminated. This leading edge technology gives rise to versatile high performance elastomer systems herein referred to as spray polyurea elastomers.

CHEMISTRY AND CONCEPT

Some of the first polymers used in two-component spray processing were polyurethane materials. These systems consisted of polyether polyols, glycol chain extenders, catalysts and aromatic polyisocyanates. The need for higher performance elastomer materials, coupled with new advances in RIM technology [1], replaced the current technology with polyurethane/urea spray elastomer systems. These systems consist of polyether polyols, diamine chain extenders such as diethyltoluenediamine (DETDA), catalysts and aromatic polyisocyanates. Showing improvements over polyurethane technology, these polyurethane/urea spray elastomer systems seemed to satisfy the needs of the industry. As RIM technology evolved to polyurea RIM materials, developed at the Austin Laboratories of Texaco Chemical Co. [2-10], so has the two-component spray elastomer technology. Two-component, 100% solids spray polyurea elastomer systems seem to be just on the horizon.

Polyureas are defined as polymers formed by the reaction of isocyanates with primary or secondary amine-terminated materials, wherein the linkages thus formed are urea groups. These systems consist of the key ingredient, JEFFAMINE® polyetheramines, diamine chain ex-

tenders such as DETDA and aromatic polyisocyanates. It is important to note that in spray polyurea elastomer systems, polyether polyols are replaced by polyether polyamines. Also, no catalysts are used in the spray polyurea elastomer technology. This evolution of the two-component spray elastomer technology can be summarized in Table 1.

The amine/isocyanate reaction in the spray polyurea elastomer systems is normally very fast, proceeding to completion within a few seconds without any catalysts. Typically, working times or system "gel times" are less than three seconds. This fast reaction is very consistent and predictable, unlike many fragile systems which depend on the life of a sensitive catalyst package for reactivity.

The key to the advantages of the spray polyurea elastomer technology is in the JEFFAMINE® polyetheramines from Texaco Chemical Co. As mentioned previously, the products are amine-terminated polyethers, generally having polyoxypropylene backbones. Suitable JEFFAMINE amines for use in spray polyurea elastomer technology include, but are not limited to, those presented in Table 2.

The isocyanate component of this emerging technology is a soft block quasi-prepolymer based on methylene diphenyl diisocyanate. In the quasi-prepolymer preparation, high molecular weight, high performance polyether diols and triols are used. JEFFAMINE® polyetheramines have also been used as the soft block constituent in the MDI quasi-prepolymer. However, high pressure mixing and caution should be exercised in their preparation. A wide variety of spray polyurea materials are possible, ranging from soft elastomers to hard polymers, by varying the soft block content in the quasi-prepolymer and the amine chain extender in the resin, maintaining an A-component to B-component volume ratio of 1 to 1.

SPRAY EQUIPMENT

In order to process this exciting new technology, heralded as "An Entrepreneur's Dream" in a recent editorial in *Plastic Trends* [11], some consideration should be given to processing equipment. Due to the fast reaction rates, conventional static mix, solvent flush equipment cannot be used. In order to insure good mixing and fast dispersion of the material, impingement mixing by high pressure, two-component spray equipment is required. This is very similar to the impingement mixing technique used in the RIM process. Use of relatively low cost, commercially available high pressure proportioning units, coupled with either spray or pour guns available from Gusmer® Corp. opens up many opportunities for polyurea elastomer materials outside of molded RIM parts.

Table 1. Evolution of two-component spray elastomer technology.

	Isocyanate	Polyether
Polyurethane	MDI Based	Glycols EO capped polyols Catalysts
Polyurethane/Urea	MDI Based	Aromatic Diamine EO Capped Polyols Catalysts
Polyurea	MDI Based	Aromatic Diamine Polyether Polyamine

Table 2. JEFFAMINE® polyetheramine.

	Functionality	Approximate molecular weight
JEFFAMINE T-5000	3	5000
JEFFAMINE D-4000	2	4000
JEFFAMINE T-3000	3	3000
JEFFAMINE D-2000	2	2000

TECHNOLOGY

As previously discussed, spray polyurea elastomers result from the high pressure, impingement mixing of a soft block quasi-prepolymer based on MDI with a resin component made up of polyetheramines and amine chain extenders, to yield this highly reactive elastomer system. Elastomers with excellent physical properties result from these self catalytic systems. A comparison of a typical spray polyurea elastomer system to a polyurethane/urea and a polyurethane system can be found in Table 3.

It should be noted that for both the polyurethane and the polyurethane/urea, catalysts are required to promote the reaction of the hydroxyl materials in the resin with the quasi-prepolymer of MDI. The green strength of the polyurea elastomer system was superior to those of the other two. In addition to these reported physical properties, it has been well known that polyurea materials have superior high temperature performance over polyurethane, polyurethane/urea and polyamide polymers [12]. Also, elastomers prepared from JEFFAMINE® polyether amines would have better hydrolytic resistance compared to systems based on polyether polyols. A graphical depiction can be seen in Figure 1.

Due to the fast reaction rates and cure of the polyurea elastomer systems, sloped or vertical surfaces can be sprayed without forming runs or drips. Surfaces can be walked on within seconds after spraying and in the case of open mold spray production, parts can be stacked without fear of sticking together. This fast, preferential reaction of the polyether amine and amine chain extender compared to hydroxyl materials yields spray polyurea elastomer systems which are relatively insensitive to water during processing. While processing of the system described in Table 3, damp substrates were sprayed upon in order to evaluate adhesion and moisture effect on the resulting polymers. No elastomer foaming was noted in the polyurea elastomer system while slight and moderate elastomer foaming was noted in the polyurethane/urea and polyurethane systems, respectively.

As mentioned previously, soft, elastomeric to hard polymer systems can be obtained, suggesting wide formulation flexibility of the polyurea elastomer systems. Since these polyurea elastomer systems are 100% solids and processed at a 1:1 volume ratio, the range of elastomer systems hardnesses is affected by the composition of the soft block quasi-prepolymer isocyanate. The particular quasi-prepolymer utilized determines the content of the amine chain extender in the resin. The MDI content in the quasi-prepolymer plus the chain extender level determines the elastomer's hard block content. The soft block content arises from the polyether polyol or polyether amine in the quasi-prepolymer plus the polyether amine content of the resin. Table 4 gives the physical properties of selected spray polyurea elastomer systems over a range

Table 3. Spray elastomers. Polyurethanes vs. polyurethane/urea vs. polyurea.

	Polyurethane	Polyurethane/ urea	Polyurea
Chain extender	Ethylene glycol	DETDA	DETDA
Gel time, sec.	2.5	2.2	1.8
Tensile strength, psi	640	1700	2220
Elongation, %	200	200	190
Tear, pli	140	390	440
Impact resistance (5 mph) notched, ft-lbs/in.	3.0	3.9	5.2
Abrasion resistance, wt loss mg (1000 gm, 1000 rev, H-18 wheels)	250	180	195
MVT, perms at 30 dry mils	0.077	0.034	0.023

of material hardnesses. Note that the effective gel times of the soft polyurea elastomer systems are slower than those of the harder polyurea spray elastomers. This is due to the lower ratio of the amine chain extender to the polyether amines in the resin component.

It has also been demonstrated that less reactive spray polyurea elastomer systems can be prepared and still yield excellent physical properties. Incorporation of modified amine chain extenders in the spray polyurea elastomer system slows down the effective gel times and allows for a wider application window. Examples of these modified amine materials are UNILINK® 4200 from UOP Corp., N,N'-bis(tertiarybutyl)ethylenediamine from Virginia Chemicals and ETHACURE® 300 from Ethyl Corp. Table 5 gives examples of each of these materials in spray poly-

urea elastomer systems. The vitrification of the spray polyurea elastomer system is slowed by the first two materials while the reaction between chain extender and isocyanate as well as the vitrification is affected by the ETHACURE 300 [13]. Note in Table 5 that the secondary aliphatic amine chain extender has adverse effects on the heat stability of the polyurea elastomer as indicated by poor heat sag values in comparison to the other aromatic amine chain extenders.

The incorporation of increasing amounts of modified amine chain extenders relative to the DETDA content yields slower systems that can be processed either by spray or pour techniques. Complete replacement of the DETDA with these modified amine chain extenders gives systems with extremely slow gel times compared to the all DETDA extended spray polyurea elastomer systems. An example of a spray polyurea elastomer system utilizing UNILINK 4200 as the chain extender can be found in Table 6. Note that while this system is much slower than the other spray polyurea elastomer discussed (Tables 3, 4 and 5) elastomer physical properties are very good.

Added reinforcement can also be incorporated into the spray polyurea elastomer technology by two methods. It has been demonstrated that WOLLASTOKUP® 10012, aminosilane treated wollastonite from NYCO, can be incorporated in the resin side of the polyurea elastomer

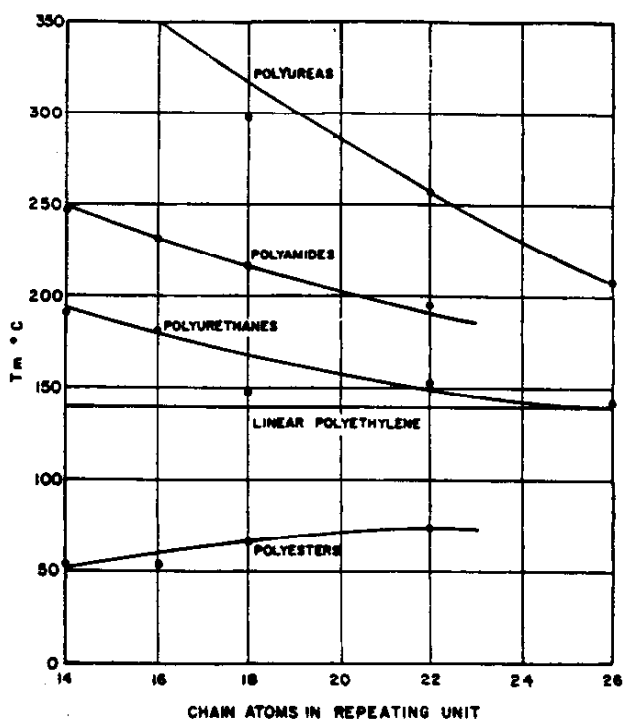


Figure 1. Trend of crystalline melting points in homologous series of aliphatic polymers.

Table 4. Spray polyurea elastomer systems.

	Soft	Medium	Hard
Gel time, sec	2.5	2.0	1.8
Hardness, Shore A, 0 sec	70	—	—
Hardness, Shore D, 0 sec	24	43	55
Tensile strength, psi	880	1600	1890
Elongation, %	240	220	100
Tear, pli	230	360	456
Flexural modulus, psi			
77°F	7200	20100	57170
158°F	6860	19850	39490
-20°F	18450	56200	113160
Abrasion resistance, wt loss mg (1000 grn, 1000 rev, H-18 wheels)	770	450	400
MVT, perms at 30 dry mils	0.087	0.061	0.035
Water absorption, % wt gain (immersion for 24 hrs, 25°C)	8.35	3.13	2.74

Table 5. Slower spray polyurea elastomers based on DETDA.

	Unilink 4200	N,N'-DTBEDA	Ethacure 300	None
Gel time, sec	2.2	2.5	2.5	1.5
Tensile strength, psi	1850	1750	1870	1920
Elongation, %	120	140	130	120
Tear, pli	425	385	425	405
Hardness, Shore D, 0 sec	48	41	53	50
Flexural modulus, psi				
77°F	42230	41540	43690	42900
158°F	29640	33480	33860	36820
-20°F	95640	74990	84850	83240
Heat sag, mm				
100 mm-250°F/60 min	1.5	2.0	1.0	0.3
150 mm-250°F/60 min	3.1	15.1	4.0	1.9

systems with no adverse effects on system processing. Flake or milled glass as well as other reinforcing fillers can be incorporated. Internal mixing components made of carbide were installed to eliminate deterioration of the spray equipment. An example of this application is illustrated in Table 7. Note that while elastomer elongation was lowered, improvements were noted in elastomer stiffness and heat sag characteristics. Use of sized calcium metasilicate improves the adhesion of the polymer material by forming a chemical bond to the filler material. This system had a gel time of 1.8 sec.

Another method of providing reinforcement is by use of a glass chopper and externally adding chopped glass roving into the spray pattern of the polyurea elastomer systems. Due to the fast reactivity of the polyurea elastomer technology, there is no time to "roll" the glass into the polymer material, as is done with polyester type systems. However, sufficient "wet-out" of the chopped glass roving is obtained to yield improvements in key physical properties. Table 8 depicts a spray polyurea elastomer system with a gel time of 2.5 secs incorporating the FIBERGLAS® roving from Owens-Corning Fiberglas Corp.

The technique of incorporating filler material in the spray polyurea elastomer systems could be useful in the production of small automotive and other applications of spraying into open molds. The fast reactive rates, cure and superior physical properties would yield high productivity with minimal equipment investments. Reactive dyes from

Milliken, pigments from PDI and other filler type materials can easily be incorporated into this spray polyurea elastomer technology.

ALIPHATIC SYSTEMS

A more recent advancement in the spray polyurea elastomer technology is the development of 100% solids, aliphatic elastomer systems. Aromatic MDI's have been replaced by meta-tetramethylxylene diisocyanates, m-TMXDI® from American Cyanamid Company, in the quasi-prepolymer preparation. Also, the high molecular weight polyols normally used have been replaced by JEFF-AMINE® polyether amines to give polyurea quasi-prepolymers. Resins are based on JEFFAMINE® polyether amines and aliphatic amine chain extenders. System processing is like the aromatic polyurea elastomer systems and gel times from 1.5 to 15 secs are possible. Good weatherable spray polyurea elastomer systems could find broad applications in coating areas. Examples of some selected aliphatic spray polyurea elastomer systems can be found in Table 9.

It is interesting to note that the low temperature proper-

Table 6. Spray polyurea elastomer—UNILINK 4200 extended.

Gel time, sec.	45
Surface tack free, sec	90
Tensile strength, psi	1715
Elongation, %	150
Tear, pli	450
Hardness, Shore D, 0 sec	56
Flexural modulus, psi	
77°F	45620
158°F	13100
-20°F	103080
Abrasion resistance, wt loss mg (1000 gm, 1000 rev, H-18 wheels)	1/0
MVT, perms at 30 dry mils	0.014
Water absorption, % wt gain	1.74

Table 7. Spray polyurea elastomers incorporating sized mineral particles.

	Neat	WOLLASTOKUP 10012
Filler in polymer, %	0	4.6
Tensile, psi	2520	2060
Elongation, %	125	30
Tear, pli	505	515
Hardness, Shore D, 0 sec	62	57
Flexural modulus, psi		
77°F	48120	70705
158°F	42170	42940
-20°F	110970	15090
Impact, notched, ft-lbs/in.	9.15	3.43
Heat sag, mm		
100 mm-250°F/60 min	3.0	0
150 mm-250°F/60 min	15.0	4.0
100 mm-311°F/60 min	*	4.0
150 mm 311°F/60 min	*	18.5

*Complete sag.

Table 8. Spray polyurea elastomers containing chopped glass roving.¹

	Neat	Filled
Glass content, % ²	0	3.4
Gel time, sec	2.5	2.5
Tensile strength, psi	1980	1760
Elongation, %	190	5
Tear, pli	460	480
Hardness, Shore D, 0 sec	56	54
Flexural modulus, psi		
77°F	35140	94550
158°F	24770	73090
-20°F	91990	123480
Impact, notched, ft-lbs/in.	6.92	6.12
Heat sag, mm		
100 mm-250°F/60 min	11	1
150 mm-250°F/60 min	20	1.5
100 mm-311°F/60 min	38	1.5
150 mm-311°F/60 min	³	17

¹Glass incorporated into elastomer using Venus R-84 Glass Chopper.

²1.25 inch chopped glass roving.

³Complete sag

ties of the aliphatic spray polyurea elastomer systems are so good. Green strengths of these systems are superior to those of the aromatic spray polyurea elastomer systems. This all indicates that phase separation of the hard and soft blocks in the polymer is not occurring as with the aromatic systems. A variety of dyes, pigments and reinforcements can be incorporated in the aliphatic spray polyurea elastomer systems also.

CONCLUSION

As one can observe, spray polyurea elastomers have potential for limitless degrees of application and versatility. The advantages of both the aromatic and aliphatic spray polyurea elastomers will widely revolutionize the spray industry. These advantages have been summarized in Table 10. Spray processing of polyurea elastomers also shows the advantages associated with polyurea RIM and adds to the creativeness of polyurea technology. The exceptional properties, processing characteristics, toughness and processing freedom afforded by spray polyurea high

Table 9. Aliphatic spray polyurea elastomers.

Index	1.05	1.05	1.07*	1.10
Gel time, sec	3.0	3.0	3.0	3.0
Tensile strength, psi	1195	970	1295	1245
Elongation, %	520	425	420	480
Tear, pli	255	210	250	210
Hardness, Shore A, 0 sec	74	—	—	—
Hardness, Shore D, 0 sec	—	39	36	38
MVT, perms at 30 dry mils	0.05	0.05	0.06	0.06
Abrasion resistance, wt loss mg (1000 gm, 1000 rev. H-18 wheels)	305	320	470	460
Low temperature properties (20°)				
Tensile strength, psi	—	1330	1665	1560
Elongation, %	>250	310	350	350
Tear, pli	—	595	600	605

*2% Titanium dioxide in the spray polyurea elastomer.

Table 10. Advantages of spray polyurea elastomers.

- Fast Reactivity and Cure
- Relative Water Insensitivity
- Two-Component, 100% Solids (1:1 Volume Ratio)
- Excellent Physical Properties
- High Thermal Stability (up to 350°F)
- Wide Formulation Flexibility
- Reinforcement Incorporation Capability
- Easily Pigmented
- Ease of Application (spray or pour techniques)

performance elastomers is very appealing to consumers. Formulations producing anything from soft elastomers to stiff, hard elastoplastics to aliphatic systems have been developed. Spray polyurea elastomers are truly an entrepreneur's dream material.

ACKNOWLEDGEMENTS

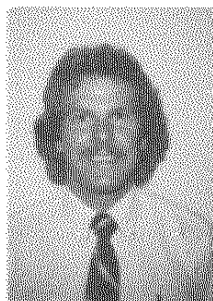
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BIOGRAPHY

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development and application development of amine catalysts in polyurethane foam.

Dudley J. Primeaux II received an M.S. degree in Organic Chemistry from Lamar University in Beaumont, Texas in 1984. He joined Texaco USA that same year. In 1985, he transferred to Texaco Chemical Co. where he was involved in polyurethane foam development. He then joined the Performance Polymers Group where he has been involved in RIM and spray polyurea elastomer develop-