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REACTION INJECTION MOLDING AND FAST POLYMERIZATION REACTIONS

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REACTION INJECTION MOLDING AND FAST POLYMERIZATION REACTIONS

PREFACE

The emergence of reaction injection molding (RIM) has been followed by the industry with mounting interest. RIM technology has brought to polymer processing a new flexibility and savings in both energy and capital investment. The new developments and the number of engineers and scientists working in RIM is growing at so fast a rate that there is need for sharing information on progress in this area.

This book is based on papers presented at the International Symposium on Reaction Injection Molding which was held in 1981 in Atlanta, Georgia, and was sponsored by the American Chemical Society, Division of Organic Coatings and Plastics Chemistry. The book is divided into four parts covering different areas of RIM development.

The first part is devoted to the future trends of RIM development in the United States and Japan.

The structure-properties relationship and effects of annealing on properties of RIM elastomers are covered in the second part.

New non-urethane polymers such as polyamides, polyisocyanurates and polystyrene suitable for RIM processing are discussed in the third part.

In the last part the engineering and technological aspects of RIM, such as glass reinforcement, mixing, flow and moldability are covered in detail.

Finally I would like to thank Mrs. Iris Glebe for typing this book and for help with editing, and K. Zielinski for his assistance

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FUTURE OF RIM DEVELOPMENT IN THE U.S.A. IN THE 1980's

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INTRODUCTION

This paper covers the development of RIM in the U.S.A. to the present, as well as the future of RIM and RRIM in the U.S.A. in the 1980's.

RIM molded urethane elastomers for automotive bumper (fascia) covers were first commercially produced in the 1975 model years on the General Motors' Monza, Skylark and Starfire series. This introduction of commercial RIM molded articles has been followed by a steady growth in use, particularly with elastomeric RIM, resulting in the use of some 50 million lbs. of RIM elastomer, most of which went into the automotive market in 1980 (Table I).¹ Rigid RIM use amounted to approximately 20 million pounds (Table I) and along with non-automotive elastomeric RIM represents a new area of growth for RIM.

This paper discusses some of the details of the above markets (Section II) since they act as the stimuli for the present and future developments which are discussed in Sections III, IV and V.

RIM AND RRIM MARKETS IN THE U.S.A.

The projected RIM usage for 1985 shown in Table I can be further examined not only by the type of RIM material (rigid vs. elastomeric) but also by the market and use, such as automotive market. Table II shows that although the average weight of American cars will be further downsized from 4200 lbs. in 1979 to 3000 lbs. in 1985, total plastic usage will increase (since plastic usage plays a key role in

Table I. Projected RIM Usage by Type¹

	<u>Millions of Pounds</u>	
	<u>1980</u>	<u>1985</u>
Rigid RIM	15	40
Elastomeric RIM	50	110

weight reduction). Total urethane usage² also is expected to increase by 1985. The breakdown for the various types of urethanes is given in Table III.² The designation foam in Table III includes slabstock, molded seating, bumpers and head restraints. Some of these may be RIM molded but others (e.g., slabstock) most likely are produced using low pressure equipment. Note the predicted large growth in RIM elastomer and the appearance of RRIM (scheduled for the 1981 Sporty Omega as RRIM molded front fenders.³ Thus RRIM automotive body paneling parts represent a new application area for RIM. The automotive elastomeric parts consist of bumper covers, full front fascia steering wheels, sight shields, air dams, deflectors and spoilers of which bumper covers and fascia account for approximately 90% of the poundage (as of 1980).

Some of the elastomeric RIM and most of the rigid RIM reported in Table I goes into non-automotive applications. Some of these applications are described in Table IV. Many of these applications are expected to contribute significantly to the growth of RIM in 1985 and the latter part of the 1980's.

THEORETICAL UNDERSTANDING

As in so many other areas, large scale commercial use of RIM preceded a full understanding of the technology from a theoretical point of view. However, as the surge into new applications contin-

Table II. Plastics Usage vs. Car Weight²

<u>Model Year</u>	<u>1979</u>	<u>1985</u>
Average Weight, lbs.	4,200	3,000
Total Plastics, %	4.86	7.66
Total Urethane, %	1.03	1.83

Table III. Present and Future Use of RIM²

Urethane Elastomers and RRIM in American Automobiles

<u>Model Year</u>	<u>Millions/Pounds</u>	
	<u>1979</u>	<u>1985</u>
RIM Elastomer	37.4	116.8
RRIM	-	69.8
Foam*	269.2	250.4

*Includes production via low pressure processes as well as RIM.

Table IV. Non-automotive RIM Applications

<u>Application</u>	<u>RIM Type</u>
Business machine housings	rigid
Recreational (ski boots, golf carts)	elastomeric
Recreational (ski cores, water skis)	rigid
Shoes (soling)	elastomeric
Agricultural	elastomeric
Appliances	elastomeric/rigid

ued, researchers at various academic and industrial labs began to examine the RIM process from a more fundamental point of view. This research can generally be divided into a study of the RIM process itself and a study of the polymer produced.

The RIM process itself has been divided into three component parts, impingement mixing,⁴ mold filling,⁵ and curing (kinetics).^{6,7} These have recently been reviewed.⁸ The results of these and other investigations show that a Reynolds number of 200 will give good mixing and that the mold should be filled before large pressure buildup occurs. This has become more critical in recent years with the faster

reaction systems, some of which are discussed in Section IV.

The above studies were conducted primarily on elastomeric or non-rigid type RIM materials which may be only slightly blown ($sp \sim 1.0$)? Rigid RIM generally has been involved in more highly blown systems ($sp \sim 0.6$)? and in these instances the foaming process is also a critical part of the analysis.⁹

The understanding of the RIM process gained through the above studies has helped to contribute towards further improvements in RIM equipment, some of which are discussed in Section V.

Since RIM produced elastomeric polyurethanes are segmented two phase polymers, the basic studies which have been done of the morphology of TPU's and cast materials apply as well to RIM elastomers. A good review of these results can be found in Reference 8. In order to achieve complete reaction and yet useful properties, the right balance of compatibility and incompatibility between the chemicals and the resulting polymer must be achieved.^{10,11} For rigid RIM one of the key factors is the balance between the foaming process and the chemical reaction.⁹ Each of the types of RIM materials demands special attention to the balance between processing and properties.

Because of the variety of formulating possibilities, a range of products can be achieved. This range of materials possible is listed in Table V. As shown in Table V, the newer applications in the future will be coming from the high modulus materials which are not true elastomers.

CHEMICAL DEVELOPMENT

Currently, commercial RIM produced articles are based on isocyanates, polyols, extenders, catalysts and blowing agents. The extenders are either glycols or amines or some combination of the two. The major chemical producers of isocyanates and polyols for RIM use are listed in Table VI. The total urethane market in North and South America is expected to be 3.6 billion pounds in 1983 (of which elastomers account for 363 million pounds).¹² Isocyanate expansion has kept pace, and MDI (crude and pure) capacity in 1983 will be approximately 800 million pounds. The pure MDI types are used in elastomeric RIM and some higher modulus RIM, while the crude MDI types are used in rigid RIM. It is expected that MDI will still be the prime isocyanate for isocyanate based RIM in the near future, with the aliphatics being used for light stable materials.¹³ Some efforts are being put into non-phosgene routes to MDI, although these have met with limited success to date.¹⁴

Because isocyanate technology lends itself to the production of a variety of MDI based materials, and since polyols themselves are

Table V
General Properties of Isocyanate Based RIM Systems

	Low Flexural Modulus	Intermediate Flexural Modulus	High Flexural Modulus
Flexural modulus, kpsi @ RT	20 - 75	75 - 150	200 - 400
Tensile elongation, % @ break	100 - 300	50 - 200	< 50
Izod impact, ft-lb/in	10 - 15	5 - 15	< 5
Impact strength	high	medium - high	low
Material description	elastomer	pseudo-plastic	plastic
Application (automotive)	fascia	fender	hood or deck lid

Table VI. Major Producers of Isocyanates and Polyols

	Isocyanate (MDI)	Polyol
BASF Wyandotte Corporation	yes	yes
Dow Chemical Company	-	yes
ICI (Rubicon)	yes	-
Mobay Chemical Corporation	yes	yes
Olin Chemical Company	-	yes
Texaco Chemicals	-	yes
Union Carbide Corporation	-	yes
The Upjohn Company	yes	-

available in a variety of types, polyurethane materials will be further developed in the future. The next two sections discuss future developments in urethanes and other isocyanate based materials. The final section concludes with a discussion of non-isocyanate based RIM.

Polyurethane Development

The present state of polyurethane development has been a result of efforts by isocyanate, polyol and extender suppliers. Over the past several years various liquid versions of MDI have been developed for use in RIM.¹⁵ Polyol development has centered on the end-capping of polypropylene glycol with EO to yield high primary OH terminated polyols with good reactivity.¹⁶ Recent polyol developments have been the grafted types¹⁷ and those with other "hard segment" blocks internal to their structure.^{18,19} Further development in polyols would appear to involve further efforts related to incorporating various types of "hard segments" into the polyol backbone.²⁰

Although the use of aromatic amine extenders would give aromatic urea "hard segments," traditionally these extenders have been considered along with glycol as "urethane" extenders.²¹ Although their use in urethanes was well established in other areas (cast elastomers and foams,^{22,23}), the use of amine extender in elastomeric RIM is relatively new.²⁴ Said to impart fast demolding and good green strength,²⁴ it is expected that further developments with amine extenders will occur, as is evident from the volume of recent patents on the subject.^{25,26,27,28,29,30}

The very reactive isocyanate function also can react with itself in a trimerization reaction to produce the isocyanurate structure.³¹ This technology can be combined with urethanes to produce very high temperature resistant plastics.³² Although these are brittle plastic materials because of their high crosslinking density,³³ they may find use as suitable binders for long-fiber reinforcement in a mat-molding type of process.³⁴

Non-urethane Isocyanate Based Polymers

Isocyanates can undergo other reactions besides the ones described above. Often used in combination with glycol extenders, or polyols, these reactions can produce new structures such as polyamides using the presently developed RIM process.^{35,36} Additionally, as newer types of equipment are produced (see Section V), other reactions of isocyanates may be put to further development in RIM type processing.³⁷

Non-isocyanate Based RIM

Recently, a great deal of attention has been given to RIM processing non-isocyanate non-urethane systems. Chief among these have been polyester,³⁸ epoxy³⁹ and Nylon 6.⁴⁰

The processing of caprolactam based systems probably represents one of the more promising approaches because of the economics and the physical properties of the resulting polymer. Potentially polyester is the least costly; however, the styrene content may pose a problem, although it may be overcome by processing polyester with very low styrene contents.

MACHINERY DEVELOPMENTS

In general, the RIM process consists of the RIM metering equipment itself with its storage tanks, as well as clamps or presses to hold the tool in which the molding is to be made.¹

There have been recent developments in all of these areas, as well as new designs in RIM equipment. Improvements to conventional RIM equipment have included new mix heads^{41,42} both for unfilled and filler (RRIM) RIM. Following the lead of thermoplastic injection molding, microprocessors and other types of electronic instrumentation and controllers have been incorporated into the feature of the latest offerings in RIM equipment.^{43,44}

The advent of filled RIM, generally termed RRIM, was brought about through advances in equipment.⁴⁵ It appears just as likely that further advances in RIM design will give rise to new generations of systems such as the equipment development now going on with Nylon

6.⁴⁰ However, it should be pointed out that this new generation of equipment (heat traced lines, heated pumps, perhaps higher pressures, etc.) can also be used with chemical systems heretofore not possible with conventional RIM. Thus, there will be increasing numbers of candidate systems with perhaps economics being the decisive factor in the choice.

CONCLUSIONS

In summary, the future of RIM in the U.S.A. will continue to be fueled by automotive demand and applications. However, an increasingly large market will develop in non-automotive applications.

The types of materials will include not only the elastomer type but also the higher modulus types. These developments will be backed by an increasing use of new polymer types made possible by new and radical developments in the RIM equipment itself.

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