

No Postcure RRIM for Automotive Exteriors

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ABSTRACT

Reinforced reaction injection molding (RRIM) has re-emerged as an important method in automotive exterior applications. Presently composite applications demand higher productivity and improved part performance. Stability at higher heat to endure E-coat oven bake, improvements in fillers yielding easier processing at high loading, improved toughness at high modulus, and higher productivity have already been realized with RRIM in Europe and NAFTA.

Now the kinetics of one new material, Bayflex 190 is such that reaction is essentially complete at demold. In the past RRIM molded parts were required to be baked at 120°C and above to complete chemical reactions, attain complete physical properties, and de-gas parts prior to painting. In current E-coat applications postcure of 190°C is typical. Elimination of postcure means significant savings in energy, increased productivity, decreased handling and lower capital expense. Bayflex 190 polyurea attains virtually all properties at demold. After molding parts can be washed and primed directly. Dynamic mechanical analysis shows that further heating to 200°C anneals and strengthens the composite.

Several very sensitive analytical methods have been employed to characterize the degree of cure at demold. Differential scanning calorimetry (DSC) shows no exothermic chemical reaction up to 200°C. Thermal gravimetric analysis (TGA) shows no CO₂ loss from unreacted isocyanates. And Fourier transform infrared spectroscopy (FTIR) scans indicate no free isocyanate in freshly molded samples. Parts painted in production exhibit no defects associated with elimination of postcure.

INTRODUCTION

Reaction Injection Molding (RIM) is a long established process for molding thermoset composites. It has been employed for automotive body panels and fascia for 25 years. In this process two liquid monomers, a polyisocyanate and a polyol or polyamine slurry containing filler, are metered at a controlled volume ratio. A simple schematic for this process is shown in Figure 1 below. These components mix and react as they flow into a closed mold.¹ Temperatures, pressures, and flow are carefully controlled.

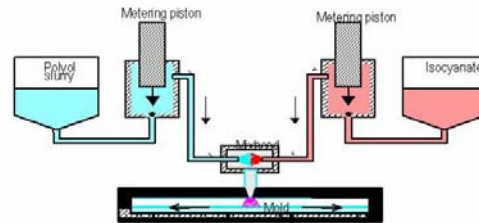


Figure 1. Simplified Schematic of the RIM Process.

Reinforced RIM has been exploited for the manufacture of fascia and body side moldings.²⁻³ It commands a high first run painted part capability and exhibits good impact performance. More recently, weight savings via thin wall stock technology have been established for rocker panels, fascia, and trim in Europe and in North America.⁴⁻⁷ The capability to withstand high temperature paint bake ovens has brought polyurea RRIM to application in pickup truck fenders.⁹⁻¹¹ Advances in the green strength of RRIM panels have yielded better release and cleaner mold surfaces. These improvements in processing lend themselves to improved cycle times. The application of a computerized Expert Process Control system^{8,11} has brought new levels of quality control and high productivity to RRIM molding. Higher productivity has already been realized in Europe.⁸⁻¹⁰

Currently, weight saving of RRIM molded parts compared to parts made of SMC or metal has been the main driving force for RRIM's growth. Additionally RRIM polyureas are capable of withstanding the high temperature paint bake typically found in OEM assembly plants. Bayflex 190, a new polyurea formulation, which allows high temperature post mold processing. It can withstand up to 200°C temperatures without loss of properties. Its density of 1.2 g/cc offers a substantial weight reduction. Thicknesses of 3.0 to 3.5 mm are typical. Without filler Bayflex 190 exhibits a flexural modulus of about 600 MPa. It exhibits rapid cure and excellent self-release from the mold. Especially important, this system exhibits excellent green strength at demold and excellent toughness in use. It is also very durable, both at demold and on the vehicle.

Another benefit of the rapid cure and green strength is found in the improved release of molded parts at demold. The mold remains cleaner longer. The flash is tougher and tends to demold with the molded part. Thus the mold maintenance frequency can be improved. This can significantly improve the cycle time for molding and the economics of RIM part manufacture.

Thus today's applications demand higher performance in processing, productivity, and part performance. The chemistry of Bayflex 190 can meet these new criteria. It is stable at higher heat to endure E-coat oven bake, it has improved compatibility with fillers yielding easier processing at high loading, and it exhibits improved toughness even at high modulus. It is also a candidate for elimination of postcure prior to prime. This paper describes this breakthrough in RRIM for automotive body panels, the elimination of postcure with Bayflex 190.

NO POSTCURE RRIM

Like SMC RRIM has required postcure to complete chemical reactions, attain complete physical properties, and de-gas parts prior to painting. In the past, RRIM molded parts were required to be baked at 120°C and above to accomplish this. More recently RRIM has been used for pick up truck fenders where it replaced SMC and steel. In these cases the RRIM material is required to be cure at 190°C prior to prime and assembly. This was necessary to improve properties such as modulus and sag⁸ and to prevent out-gassing during paint processing.

Bayflex190 is a polyurea RIM material suitable for automotive exterior body panels such as car and truck fenders. It is capable of replacing SMC and metal due to its stability at high temperatures. It also exhibits remarkable toughness. In addition it seemed completely cured at demold. Because of this work was begun to evaluate whether post cure could be eliminated or significantly reduced. Elimination of postcure would have several benefits. These include lower energy consumption, decreased handling, and lower capital investment for new high heat body panel applications. Overall this would increase productivity and improve costs.

Table 1 shows the properties achieved with Bayflex 190 with 20% wollastonite filler measured after various post cure times and temperature. This data indicates that mechanical properties of Bayflex 190 do change slightly with postcure temperatures ranging from 120°C to 190°C. All values tend to improve slightly as temperature or time of cure increase. Modulus increases from 1800 to 2200 Pa and impact test values improve. Mold shrink continues during postcure, but stops at 170°C.

At demold parts molded with Bayflex 190 have already attained modulus over 1000 MPa and are very durable. But in order to eliminate postcure,

Certain questions then arise. Can the degree of cure be measured? Are the changes seen in Bayflex 190 after postcure due to chemical reaction or to annealing of the polymer network? Would subsequent high heat exposures in the assembly plant promote paint defects of un-postcured parts via outgassing? To answer these questions a series of analytical tests were conducted. Their purpose was to determine 1) if any unreacted isocyanate is present in un-postcured parts, 2) if further chemical reactions are carried out in postcure, and 3) if gases are evolved. It is also of interest to characterize the changes that do take place in Bayflex 190 during postcure.

In addition to these analyses, the molding and painting of actual automotive fenders was also carried out. The results of these investigations are described below.

DIFFERENTIAL SCANNING CALORIMETRY

This analysis was made to determine the extent of cure of the molded panels. It is well known that unreacted isocyanate in molded parts can combine with itself, water or unreacted polyol. Reaction of isocyanate with itself or with water generates carbon dioxide. This gas might be trapped in the curing paint causing defects if parts were primed without postcure.

Figure 2 below shows the result of differential scanning calorimetry (DSC) performed on a sample of Bayflex 190 with 20% mica filler directly after molding and after 190°C cure for 45 minutes. The samples were scanned from -30°C to 210°C. The y-axis indicates heat flow. Each sample was scanned, cooled, and scanned a second time. Neither sample exhibited an exothermic peak (downward), which would indicate reaction of isocyanate. Both samples did exhibit a small, broad endothermic peak (upward). This is due to a small amount of water released from the mica filler. This peak is easily removed by warming to 100°C briefly.

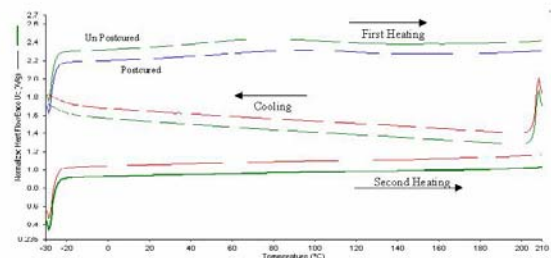


Figure 2. DSC of Bayflex 190 Postcured and Un-Postcured

This data reveals no further detectable chemical reaction in the sample when heated up to 200°C. Were unreacted isocyanate present, an exothermic peak (downward) would be evident between 150°C and 200°C. In this region isocyanates react to form carbodiimide and isocyanurates. Nor does there seem to be any exothermic peaks for any other reaction under 200°C.

This data suggests that the Bayflex190 is virtually cured at demold since no exothermic peaks are evident.
THERMAL GRAVIMETRIC ANALYSIS

Gravimetric analysis is useful to determine weight loss of a material during heating. Release of gas would indicate evolution of CO₂ from isocyanate reaction. Figure 3 shows the weight loss for samples of Bayflex 190 with 20% mica reinforcement from 0 to 600°C. The trace for the un-postcured and postcured samples are nearly identical. Only the loss of 0.3% moisture, coincidental to the DSC above, is found between 50 and 100°C. No weight loss is found between 150 and 200°C where unreacted isocyanate would generate CO₂. Small differences in weight loss are seen above 300°C, but these are well into the decomposition of the material. Thus there is no weight loss ascribed to isocyanate reactions up to 200°C for either postcured or un-postcured Bayflex 190.

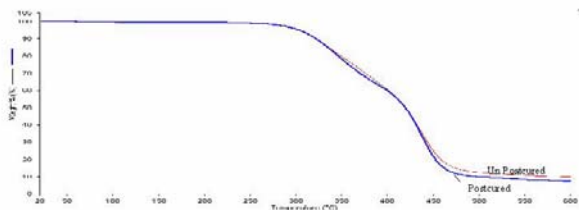


Figure 3. TGA of Bayflex 190 Postcured and Un-Postcured

FOURIER TRANSFORM INFRARED SPECTROSCOPY

Analysis via infrared spectroscopy was carried out, in order to determine whether unreacted isocyanate were still present in parts after demold,. Normally the isocyanate group when present exhibits a very strong peak in the infrared absorbance spectrum near 2300 cm⁻¹. Using FTIR each molded surface and the interior of a molded plaque were analyzed (Figure 4). Only very weak absorbencies were detected. It is known that other moieties containing functionality similar to isocyanate are found in this region such as carbodiimides. Such species are expected as existing already in the sample and account for a portion of the peak observed.

Thus from FTIR analysis there remains little or no isocyanate present. Generation of CO₂ during paint processing is expected to be minimal. Paint defects due to out-gassing are not expected.

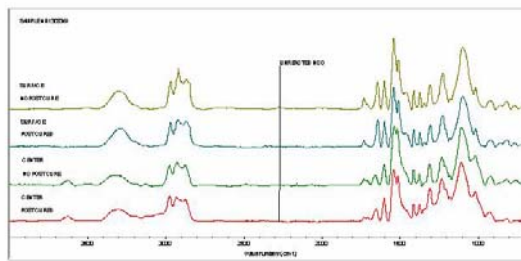


Figure 4. FTIR Spectrum of Bayflex 190 Postcured and Un-Postcured

PAINT LINE TESTING

Automotive front fenders were molded and painted using a variety of heat treatments. Groups of 10 fenders were used for each test. This included post cure at 190°C, post cure at 120°C, and no post cure. Parts were washed via conventional 5 step acid wash consistent with that of RRIM parts in production. All parts were painted with a conductive prime, base coat and clear coat. Paint bake from 120°C to 170°C was applied, and a post bake of finished parts at 190°C was included for some parts. In all cases no defects such as porosity, pinholes, yellowing or blistering were found.

These results are consistent with the analytical results discussed above. Since no significant reaction occurs after demold, parts are safely painted without postcure. No evidence of out-gassing was evident. This work was performed at Venture Industries in Grand Rapids, MI.

DYNAMIC MECHANIC ANALYSIS

Two observations of this work are yet inconsistent. First, the properties of Bayflex 190 with mica or wollastonite filler do change upon heating. Second that no further chemical reaction can be detected by several sensitive analytical tests. Table 1 indicates that the modulus increases and that elastomeric properties improve with heating up to 200°C.

Dynamic mechanical analysis (DMA) was used to explain these inconsistencies. Figure 5 and 6 show the DMA trace of samples of Bayflex 190 with 20% mica reinforcement un-postcured and postcured, respectively. Shown for each sample are three traces – the storage modulus (G'), the loss modulus (G''), and their ratio Tan δ.

Both curves show a glassy state below -50°C and a broad rubbery region from 0°C to 200°C. No melt transition is seen beyond 200°C because the material is a thermoset network. Thermoset materials such as Bayflex 190 are networks, which upon heating above 250°C decompose rather than melt.

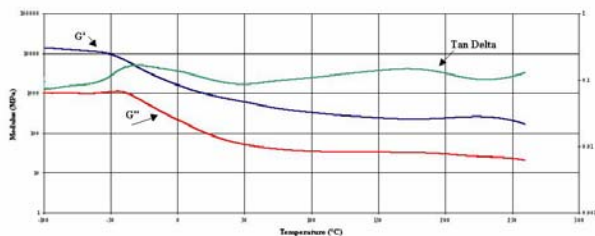


Figure 5. DMA of Bayflex 190 Un-Postcured

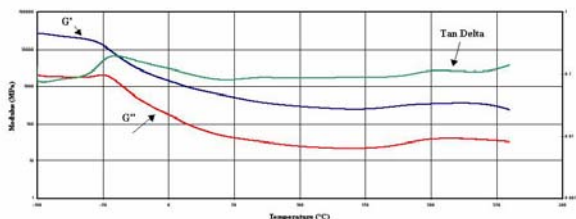


Figure 6. DMA of Bayflex 190 Postcured

These data are nearly identical for un-postcured and postcured samples. Postcured samples show a slight increase in modulus below -50°C and a small increase in modulus between 100°C and 200°C . This is consistent with a re-ordering of hard and soft segments within the polymer. After high temperature treatment the hard and soft segment separate further into more defined domains. This causes a more crystalline state at low temperature and thus higher modulus below -50°C . There is also a slight flattening in the rubbery region consistent with improvements to impact values shown in Table 1. This is supported by comparison of the $\text{Tan } \delta$ curve for each sample. After postcure the $\text{Tan } \delta$ shifts its low temperature peak at about -50°C to lower temperature. A broad peak near 200°C shifts to higher temperature.

CONCLUSION

The kinetics of Bayflex190 RRIM polyurea result in a virtual cure of molded parts when demolded. DSC, TGA and FTIR analyses indicate no further chemical reaction after demold. No detectable NCO is found by infrared spectroscopy, no release of gases is detected via TGA, and no further detectable exothermic chemical reaction are detected in DSC. Further heating up to 200°C does, however, yield improvements in mechanical and thermal properties such as flexural modulus, ultimate elongation, high temperature sag, and impact strength. These subtle changes are due to hard and soft segment domain separation in the polymer. Thus it is possible to omit postcure of parts molded with Bayflex 190.

ACKNOWLEDGMENTS

The author would like to thank Bob Rowley, Dan Allman, and Dell Pifer of Venture Industries for their help in the molding and painting of fenders from un-postured Bayflex 190; Dr. Chu Shih-Chien, Joe Dettorre, George Pastor, and Dr. Farhad Cama for their analyses of Bayflex 190 samples; and Bill Keller, Les Hamilton Jr.

and Rosemary Quader for the molding and determination of physical properties.

REFERENCES

- Oertel G., Polyurethane Handbook, Carl Hauser Verlag, Munich, Vienna, (1985).
- Ludwico W.A. and Taylor R.P., "The Bayflex® 110 Series - The New Generation of RIM Materials," paper no. 770836, SAE Automotive Engineering Congress and Exposition, Detroit, MI, Sept. 26-29, 1977.
- Lau C.J. and Suddaby B.R., "Opportunities for Mineral Fillers in Polyurethane/Urea RIM for Automotive Applications," Functional Fillers, Intertech Conferences, Chicago, IL, Sept. 22-3, 1993.
- Kogelnik H.J., Rains R.C., Haradzin R.L., and Groenen J., "Novel Polyurethane RIM Approach for Cost Reduction and Productivity Enhancement," SAE International Congress and Exposition, paper no. 930541, Detroit, MI, March 1-5, 1993.
- Kratz H.S. and Milewski J.V., Handbook of Fillers and Reinforcements for Plastics, Van Nostrand Reinhold Co., New York, 1978. pp. 301-10.
- Hurley, M.F., et al., "New Competitive Polyurethane Materials for Automotive Fascia," Proceedings of the SPI 36th Annual Technical/Marketing Conference, (1993).
- Hurley M.F. et al., "Advances in Competitive Polyurethane Materials for Automotive Fascia," 950551SAE International Congress and Exposition, Detroit, MI (1995).
- Expert Process Control is a trademark of Bayer AG.
- James, A., 1999, "ELPO Capable Polyurea RIM: A Breakthrough Material for Composite Body Panel Application," presented at the SAE International Congress and Exposition, February 1999-01-3225.
- McLaren, J., and Arnold, K. 1998, "Infrared Post-Cure of RIM Body Panels: A Significant Cost Savings," technical paper presented at the SAE International Congress and Exposition, February 23-26, 1998 (980988).
- Hurley M.F., Meiners H-J. and Doerner K-H., "High Performance Reinforced Reaction Injection Molding for Body Panels," 99IBEC20, International Body Engineers Conference, Detroit MI (1999).
- Postcure at 375°F for 45 minutes prior to these experiments.
- These items are provided as general information only and are not part of the product specification

CONTACT

Thomas A. Petricko has been involved with RIM and RRIM technology for more than 20 years. He joined Bayer Corporation, then Mobay Corporation, as a technician in 1979. Since that time he has been involved with Applications and Process Development, Process Engineering, Marketing and Business

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