Scale-up Synthesis of Diallyl Phthalate Prepolymer

Bendix Kansas City Division

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By D. A. Carey
Department 814

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Quarterly Report on 705438
FY84-4 July to September 1984
G. K. Baker, Project Leader

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SCALE-UP SYNTHESIS OF DIALLYL PHTHALATE PREPOLYMER

BDX-613-3147, UNCLASSIFIED Quarterly Report, Distributed October 1984

Prepared by D. A. Carey, D/814, under 705438

This project was initiated to develop processes for the synthesis of diallyl phthalate (DAP) prepolymer in the Bendix Chemical Polymer Facility. Thus far, five scale-up reactions have been carried out in a 100-gallon reactor and fourteen have been conducted in the 15-gallon resin kettle. The synthesis of diallyl isophthalate prepolymer (DAIPP) was also investigated; eight scale-up reactions of this prepolymer have been carried out. Aging studies on DAIPP were also conducted.

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SCOPE AND PURPOSE

The purpose of this project is to develop scale-up processes for the synthesis of diallyl phthalate prepolymer (DAPP) in the Bendix Chemical Polymer Facility. A specific objective is to synthesize a prepolymer that is a replica of Dapon 35, which is no longer commercially available in the United States, in order to support the WR production requirements of Bendix, Monsanto Research Corporation, Mound Facility, and Martin Marietta Corporation, the Oak Ridge Y-12 Plant.

SUMMARY

Two scale-up syntheses of diallyl phthalate prepolymer (DAPP-26 and 27) were conducted in a 100-gallon resin kettle. These prepolymer reaction products were used to establish the feasibility of using the recently installed rotary vacuum vessel to recover large quantities of DAPP. The first batch of prepolymer was overheated during the drying process by frictional heat from the agitator. Examination of this prepolymer indicated that it was slightly crosslinked. In the second batch (DAPP-27) 117 pounds of diallyl phthalate prepolymer was successfully extracted. This was accomplished with the aid of 1500 ppm of stabilizer (A02246). Also, during this quarter a 50/50 blend (recovered/virgin) of monomer was used to produce a batch of DAPP which had similar chemical properties to that made from 100% virgin monomer.

The evaluation of stabilizers (Irganox 1010 and A02246) for solid diallyl isophthalate prepolymer (DAIPP) was completed during this quarter. Both stabilizers have improved the stability of DAIPP; however, no marked difference was observed in the degree of stability obtained from either stabilizer. Mound Facility has obtained preliminary favorable test results from fiber glass molding compound made on a laboratory scale using DAIPP resin produced at Bendix Chemical Polymer Facility. The DAIPP molding compound showed enhanced thermal and physical properties as compared to DAPP molding compound. Mound is presently evaluating a larger batch of DAIPP which was made from a blend of batch 21 and batch 23B.

ACTIVITY

Synthesis of Diallyl Phthalate Prepolymer (DAPP)

In the synthesis of diallyl phthalate prepolymer, only approximately 25 percent of diallyl phthalate monomer is converted to prepolymer. The remaining 75 percent of unreacted monomer is removed by methanol extraction. During the previous quarter, the rotary vacuum vessel was

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used as a still to remove the methanol from the monomer-methanol solution. One scale-up reaction (DAPP-28) was prepared in the 15-gallon resin kettle using a 50/50 (recovered/virgin) monomer blend. The diallyl phthalate prepolymer obtained was similar to prepolymer which was made from virgin monomer. Also, when compared to earlier batches synthesized from virgin monomer, no noticeable time change in the polymerization rate was observed.

In addition, two scale-up reactions (DAPP-26 and 27) were prepared in the 100-gallon resin kettle. The purpose of the scale-up syntheses was to produce prepolymer for a large scale DAPP extraction evaluation. The prepolymer reactions were terminated when the viscosity of the reaction mixture was 50 centipoise at a temperature of 65°C. The purpose of this viscosity target was twofold: Firstly, reaction mixture under this condition contains DAPP product which has the desired bimodal molecular weight distribution; and secondly, this condition also allows a "wide operational window" which would accommodate some further polymerization during the extraction and drying processes without any detrimental effect on the final product.

Scale-up of Prepolymer Recovery Using Methanol Extraction

The solid prepolymer was separated from the monomer in the reaction mixture by extracting the monomer with methanol in three stages. Approximately 600 pounds of diallyl phthalate reaction product was placed in the rotary vacuum vessel. Seventy-three gallons of methanol were added and the mixture agitated at 37°C for 30 minutes. The mixture was cooled to room temperature and allowed to settle overnight. During this time, two phases were formed. One was methanol-monomer phase and the other was the prepolymer phase. The prepolymer phase had some monomer still not extracted. The upper layer (methanol-monomer phase) was syphoned from the reactor. The process was repeated in the second and third stages with the same amount of methanol as in the first stage; however, the extraction temperature was raised to 65°C in the second and the third stages. After the third extraction and the removal of the methanol-monomer phase, the prepolymer was vacuum dried in the same vessel at 65°C. Batch 26 (DAPP-26) was agitated during the drying process. Unfortunately, frictional heating increased the temperature of the prepolymer significantly and this resulted in the formation of a crosslinked product. Batch 27 (DAPP-27) was dried, but the agitator was used only to grind the prepolymer to a powdered form. That is, the agitator was used only after the product was considered fairly dried. Also, 1500 ppm of A02246 stabilizer was added prior to the drying process. This time, the prepolymer product was acceptable. The total yield of DAPP after grinding was 117 pounds, and the final product after drying had 5.0 percent residual monomer and a $\overline{M}_w$ of 31,000.

Solid DAIPP Aging Studies

As discussed in an earlier report, DAIPP is apparently less stable than DAPP(1). Therefore, an investigation to improve the stability of DAIPP was initiated. Two uni-modal molecular weight prepolymer batches (DAIPP-23A and 24) were manufactured for this evaluation. Since DAIPP-23A

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and DAIPP-24 had similar properties, they were combined to provide the desired quantity of material for the stabilization investigation. The aging studies were conducted at 40°C and 50°C using Irganox 1010 and A02246 as the stabilizers at different concentration.

The molecular weight of the samples was monitored as a function of time and temperature. The information obtained from this evaluation is tabulated in Tables 1 and 2. For comparison purposes, earlier work done with unstabilized prepolymer is also included in the tables. As can be seen, samples which had stabilizers underwent a slower rate of solid state polymerization. As would be expected, the prepolymer aged at 40°C showed less solid state polymerization than those samples aged at 50°C. The $\overline{M}_w$ measurements, however, did not differentiate between the type and level of stabilizer used. On the other hand, the $\overline{M}_w$ measurements clearly indicate that either stabilizer would be effective in retarding the solid state polymerization. Actually, after 34 days at 50°C, it is essentially impossible to measure the molecular weight of the sample without stabilization. At this point, the DAIPP had crosslinked.

Mound Facility Characterization of DAIPP Molding Compounds

The three samples of DAIPP (DAIPP-21AC, 18BC, and 21/23 blend) sent to Mound were selected because of the wide ranges in molecular weights. Table 3 shows the molecular weights and monomer content for all samples. Of those samples, Mound has recently evaluated DAIPP-21AC on a laboratory scale. The formulations used in preparing the molding compound are shown in Table 4 along with an Osaka diallyl phthalate prepolymer used as a comparison. The formulations used are comparable in all respects, except that a lower amount of monomer was used with DAIPP-21AC, due to its higher initial monomer content.

Differential Scanning Calorimetry (DSC) and Thermogravimetric Analyses (TGA) were used to determine thermal properties of the two molding compounds after "B-Staging" (See Table 5). Mound determined that the DSC curing properties of the two molding compounds were similar; however, TGA data showed the DAIPP molding compound exhibits a higher decomposition onset and a slightly higher inflection point which is interpretated as an inherently better thermal stability. The physical properties of both molding compounds were also examined. The results are given in Table 6. Based on this limited evaluation, the DAIPP molding compound produced parts which surpassed all the properties required for certification for DAPP molding compound. The heat distortion tests (HDT) results were of particular interest to Mound personnel because the DAIPP showed enhanced thermal stability over DAPP as already determined. This enhanced thermal stability is probably due to an inherent difference in the basic structure of this prepolymer. These initial results with DAIPP are encouraging and work with this prepolymer will be continued.

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Conclusions

Large quantities of DAPP can be produced using the recently installed process equipment for handling solid polymers in the BKC Chemical Polymer Facility. It has been demonstrated that A02246 or Irganox 1010 can be used to retard the solid state polymerization of diallyl isophthalate prepolymer. Initial evaluations conducted at Mound on a molding compound using DAIPP resin have shown enhanced thermal and physical properties as compared to DAPP molding compound.

Planned Activity for Next Quarter

Three hundred and fifty pounds of diallyl phthalate prepolymer will be produced in BKC Polymer Chemical Facility for Monsanto Research Corporation, Mound Facility, to evaluate on a production-type scale.

REFERENCE

1. D. A. Carey, Scale-up Synthesis of Diallyl Phthalate Prepolymer, Quarterly Report, Bendix Report Number BID-A542, December 1983.

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TABLE 1. MOLECULAR WEIGHTS OF DAIPP WITHOUT AND WITH STABILIZER AGED AT 50°C

Stabilizer Type	Concentration Weight Percent	$\overline{M}_w$	$\overline{M}_n$	Aging Time,Days
without stabilizer	0	17,271	5,616	0
without stabilizer	0	19,099	5,879	6
without stabilizer	0	96,336	7,580	27
without stabilizer	0	195,715	7,680	34
Irganox 1010	0.5	20,321	7,751	6
Irganox 1010	0.5	31,631	8,992	27
Irganox 1010	0.5	33,871	8,949	34
Irganox 1010	0.5	42,585	9,670	77
Irganox 1010	0.06	20,782	7,751	6
Irganox 1010	0.06	33,201	8,651	27
Irganox 1010	0.06	37,909	9,455	34
Irganox 1010	0.06	43,751	9,720	77
A02246	0.5	20,650	6,981	6
A02246	0.5	33,165	8,731	27
A02246	0.5	36,740	8,066	34
A02246	0.5	43,851	9,060	77
A02246	0.06	21,320	7,321	6
A02246	0.06	34,135	9,501	27
A02246	0.06	40,061	9,560	34
A02246	0.06	44,850	9,963	77

[redacted]

TABLE 2. MOLECULAR WEIGHTS OF DAIPP WITHOUT AND WITH STABILIZER AGED AT 40°C

Stabilizer Type	Concentration Weight Percent	$\bar{M}_w$	$\bar{M}_n$	Aging Time, Days
without stabilizer	0	19,203	6,384	13
without stabilizer	0	26,954	6,412	55
without stabilizer	0	105,161	9,872	94
Irganox 1010	0.5	19,301	7,561	13
Irganox 1010	0.5	22,156	7,050	55
Irganox 1010	0.5	31,988	8,971	94
Irganox 1010	0.06	21,300	6,560	13
Irganox 1010	0.06	21,583	7,693	55
Irganox 1010	0.06	33,802	9,594	94
A02246	0.5	20,356	6,970	13
A02246	0.5	22,122	7,352	55
A02246	0.5	32,949	9,884	94
A02246	0.06	20,681	7,009	13
A02246	0.06	23,982	6,958	55
A02246	0.06	34,721	9,771	94

[redacted]

TABLE 3. MOLECULAR WEIGHTS AND MONOMER CONTENTS OF DIALLYL ISOPHTHALATE PREPOLYMER (DAIPP)

Prepolymer	Type of MW Distribution	$\overline{M}_w$	$\overline{M}_n$	MWD	Monomer, Wt.%
BKC-DAIP 21-AC	Bi-modal	63,700	7,300	8.76	5.6
BKC-DAIP 21-D	Bi-modal with high mol. wt. shoulder	143,400	7,600	18.95	4.4
BKC-DAIP 18-BC[a]	Tri-modal	542,600	9,200	59.1	5.1
BKC-DAIP 2123[b]	Bi-modal	43,750	7,700	5.69	3.2
Osaka-o-DAP 29061-RT1	Bi-modal	45,600	6,600	6.89	2.8

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[a] Not completely soluble in THF - insolubles filtered off.

[b] 20-pound BKC-DAIP prepolymer sample.

[redacted]

TABLE 4. DAIPP AND DAPP MOLDING COMPOUND FORMULATIONS

Materials	Formulation No.	
	625	609
Prepolymer		
Type	DAIPP(#21-AC)	o-DAPP(Osaka)
Wt.%	38.5	37.0
Fiber Reinforcement		
Type	Fiberglass, 1/8 inch	Fiberglass, 1/8 inch
Wt.%	44.0	44.0
Other		
Hydrous Alumina (Techfil 106)	10.0	10.0
Kaolin Clay (ASP-400)	1.0	1.0
o-DAP Monomer	1.5	3.0

Remainder - Calcium stearate, t-Butyl perbenzoate, hydroquinone

Procedure - Dissolve prepolymer in acetone in 2-gallon sigma blade mixer; add other materials; remove acetone by vacuum and mill on 2-roll mill to 100°C, "B-Stage"/15-45 min./100°C, vented oven.

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TABLE 5. THERMAL PROPERTIES OF FIBERGLASS DAIPP AND DAPP MOLDING COMPOUNDS

DSC Results	#625 (DAIPP-FG)	#609 (DAPP-FG)
Exotherm		
Peak, °C	165.9	164.8
H_R, J/g	97.5	94.3
Endotherm		
Peak, °C	103.7	113.8
H, J/g	0.6	2.75
TGA Results		
1) Wt.% Volatiles (to 300°C) (incl. monomer/catalyst)	1.6	2.2
2) Polymer Decomposition		
Extrapolated Onset	377	348
Inflection	407.5	400.4
Wt.%	44.6	45.0
Wt.% Residue at 900°C	53.3	53.4

[redacted]

TABLE 6. PHYSICAL PROPERTIES OF FIBERGLASS DAIPP AND DAPP MOLDING COMPOUNDS

	Results and Number of Test Specimens		
Physical Test	Minimum Acceptable Value	#625% (DAIPP-FG)	#609 (DAPP-FG)
Rheometer			
Min. Torque, in.-lb.	4-15	4.5	3.5-4
% of Max./3 min.	90%	99%	94
Tensile Strength			
lb./in.^{2} - ASTM D-651	4500	7672 (2)	6797 (3)
Notched Izod Impact Strength			
ft.-lb./in. notch ASTM D-256A	0.30	0.594 (2)	0.487 (2)
Compressive Strength			
lb./in.^{2} - ASTM D-695	16,000	18,420 (4)	17,150 (2)
Arc Resistance			
sec., ASTM D-495	115	125 (4)	122 (5)
Heat Distortion Temp.			
°C, ASTM D-648	160	180 (1)	164 (1)
Mesa Spiral			
Flow, in.	varies	----	20

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