

Physical Properties of Vinyl Chloride-Propylene Copolymers

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Synopsis

The polymerization conditions that control the physical properties of vinyl chloride-propylene copolymers have been examined, and the interaction between these polymerization conditions and the melt rheology, intrinsic viscosity, and bound propylene level of the copolymer have been quantified into a series of process control relationships. The interaction between primary and secondary suspension systems have been optimized for these copolymers to maximize the resin porosity. Binary initiator systems have been identified to overcome the degradative polymer kinetics associated with propylene comonomer.

INTRODUCTION

The melt flow-intrinsic viscosity relationship of polyvinyl chloride resin is a well-documented fabrication process parameter for this material.¹ In a rigid application polyvinyl chloride resin of a rather modest molecular weight (0.64 dL/g) can be injection molded with some care and the use of efficient thermal stabilizers. Copolymers of vinyl chloride-propylene have rather remarkable melt flow characteristics² and demonstrate outstanding thermal stability.³ These characteristics make the vinyl chloride-propylene copolymers attractive materials for injection molding of rigid containers for food application. Precise control of the polymer melt rheology and resin with low residual vinyl chloride monomer are essential for commercial acceptance of these materials by the packaging industry.

The melt flow characteristics of the vinyl chloride-propylene copolymers have been shown qualitatively to be related to the propylene content of the resin and the molecular weight of the resin,² but no quantitative relationships have been identified relating process conditions to polymer rheology or particle porosity.

EXPERIMENTAL

Polymerization Equipment

All polymerizations were run in a 3¹/₄-gal stainless steel reactor manufactured by Pressure Products of Hatboro, Pennsylvania. Temperature control during the polymerization was held to $\pm 0.1^\circ\text{C}$. The heat of polymerization was measured using experimental procedure previously described.⁴

Raw Material

1. Water, deionized and distilled under nitrogen purge
2. Vinyl chloride (Air Products and Chemicals, Specialty Gas Division; 99.9% pure), used as received
3. Propylene (Air Products and Chemicals, Specialty Gas Division; 99.9% pure), used as received
4. Sodium bicarbonate (Fischer, reagent grade), used as received
5. *t*-Butyl peroxyneodecanoate (Lucidol Chemical grade L-10 initiator, 75% active in OMS), used as received
6. α -Cumyl peroxyneodecanoate (Lucidol Chemical grade L-188 initiator, 75% active in OMS), used as received
7. Hydroxypropylmethylcellulose (Dow Chemical Co., both F-50 and K-35 grade), used as received
8. Polyvinyl alcohol (Sigma Chemical Corporation S-202 grade, 40% hydrolysis, 25% active material in methanol), used as received

Charging Procedure

The water, sodium bicarbonate, and primary and secondary suspending were added to the reactor under a nitrogen stream with the agitator at 250 rpm and the reactor walls at 15°C. The reactor was closed and evacuated with a water aspirator to 30 MM absolute pressure and held for 5 min. Vinyl chloride monomer was added and then propylene monomer. The agitation was increased to 500 rpm, and the reactor contents was heated to polymerization temperature. The initiator(s) were then added through a minicharge pot with 200 mL water. Where indicated subsequent initiator was added with water at the indicated time. The reactor pressure and heat of polymerization were measured continually during the polymerization. At the appropriate pressure rise the reactor content was cooled and vented into a 10-gal discharge vessel. The cooling and discharge took approximately 30 min. Samples of resin slurry used in stripping studies were stored in closed containers at 5°C.

Stripping Studies

Samples of resin slurry were heated to the indicated temperatures in equipment described previously.⁵

Recipes

Suspension system study:

Water, 4500 g
Vinyl chloride, 2775 g
Propylene, 225 g
Sodium bicarbonate, 1 g
Primary suspension agent,
either Methocel K-35
or Methocel F-50, 6.0 g
Secondary suspension agent,
either Sigma S-202

or nothing, 6.0 g (or 0.0 g)
t-Butyl peroxyneodecanoate,
 11.5 mL initially and
 5.5 mL at 3 and 4.5 h, 22.5 mL*
 Polymerization temperature, 55°C
 Pressure increase, 35 psi

Initiator study:

Water, 4500 g
 Vinyl chloride, 2775 g
 Propylene, 225 g
 Sodium bicarbonate, 1 g
 K35, 6.0 g
 S202, 6.0 g
 Initiators,
t-butyl peroxyneodecanoate and α -cumyl peroxyneodecanoate, variable
 Polymerization temperature, 55°C
 Pressure increase, 35 psi

Control equation study:

Water, 4500 g
 K35LV, 6.0 g
 S202, 6.0 g
 Sodium bicarbonate, 1.0 g
 Vinyl chloride and propylene, total of 3000 g
t-Butyl peroxyneodecanoate, 8.0 mL
 α -Cumyl peroxyneodecanoate, 5.0 mL
 Temperature, variable
 Pressure increase, variable

Test Methods

Property measured	Test method
Particle size distribution	ASTM A-1921-75
IPTU	ASTM D-3367
Inherent viscosity	ASTM D-1243-60A
Melt flow	ASTM D-1238-57-T at 190°C
Bound propylene	Proton NMR

DISCUSSION

Suspension System Development and Monomer Stripping

The use of a combination of a primary and secondary suspension agents is well documented for suspension-polymerized vinyl chloride.⁶ These combinations of primary and secondary suspension agents under ideal conditions increase the particle porosity of the polyvinyl chloride resin without

altering the particle size distribution. Cheng and coworkers^{7,7a} have examined the properties of hydroxypropylmethylcellulose suspension agents by both partition coefficient and interfacial tension procedures. These techniques have been employed to characterize and compare representative primary and secondary suspension agents. These are detailed in Table I. We have observed that for suspension grade polyvinyl chloride resin the resin porosity increases as the interfacial tension decreases and the partition coefficient increases for the suspending agent. In contrast, the suspension stability will decrease as the interfacial tension decreases and the partition coefficient increases for the suspending agent. In addition, suspension stability decreases if the suspending agent has a gel temperature (at 2% in water) less than the polymerization temperature.

Several screening runs demonstrated the advantage of the hydroxypropylmethylcellulose as a primary suspension agent. A 2² factorial design was run to determine the interactive effects of the hydroxypropylmethylcellulose primary suspension agent and a low-hydrolysis polyvinyl alcohol secondary suspension agent using the suspension system study recipe. These results are detailed in Table II. The K-35 and F-50 (runs 1 and 3) give rather low porosity resin. The binary combination of F-50 and S-202 demonstrates only a marginal improvement in resin porosity. By contrast, the binary combination of the K-35 and S-202 exhibit a large increase in resin porosity. The possible explanation for this unexpected increase in porosity is that the F-50 primary suspending agent in the presence of propylene, at temperatures close to its gel temperature T_{gel} , cannot interact with the S-202 secondary suspending agent to maintain the intraparticle structure. The K-35 primary suspending agent with the higher T_{gel} is capable of maintaining its intraparticle structure. These intraparticle structural properties are detailed in a recent patent.⁸

The rate at which vinyl chloride monomer can be removed from a polyvinyl chloride resin and the equilibrium level that can be achieved in

TABLE I
Suspension Agent Characterization

Suspension agent ^a	T_{gel} (°C) ^b	Interfacial tension (dyn/cm) ^c	Partition coefficient ^d
Hydroxypropylmethylcellulose			
F-50 grade ¹	56	4.0-6.0	1.57
K-35LV grade ²	70	6.0-7.5	1.00
Polyvinyl alcohol (87% hydrolysis) ³	100	8.0-9.0	0
Polyvinyl pyrrolidone ⁴	> 70	19-20	0
Polyvinyl alcohol (40% hydrolysis) ⁵	100	1-2	> > 100

^a Manufacturers: (1) Dow Chemical; (2) Dow Chemical; (3) Air Products, Vinol 540 Grade; (4) GAF Chemical Co., K90 Grade; (5) Sigma Chemical Co., S202 Grade.

^b Temperature at which 50% of the suspension agent (as a 2% water solution) phase separates from the water.

^c Determined in a spinning drop tensiometer with water-vinyl chloride at 25°C. Measurement based on at least three different lots of material.

^d Determined in an ethylene dichloride-water mixture as ratio of % in EDC phase to % in water phase.

TABLE II
Effect of Suspension Systems on the Physical Properties of Vinyl Chloride
Propylene Resins

	Suspension system			
	K-35	K-35 S-202	F-50	F-50 S-202
Porosity	13.2	22.0	12.0	16.0
IV (dL/g)	0.578	0.579	0.570	0.575
Particle size distribution, % on (μm)				
600	0.2	0.2	0.6	0
425	0.2	0.4	2.8	0
250	10.4	3.6	29.2	4.6
180	33.8	14.6	30.0	20.6
150	30.0	28.4	10.4	17.8
106	20.0	36.6	14.6	25.6
90	3.4	9.6	6.6	14.4
75	1.0	4.0	3.4	9.0
<75	1.0	2.6	2.4	8.0
Median particle size (μm)	172	143	185	139

a given time-temperature regime are vital to the commercial utilization of the resin. Berens⁹ has described the effects of time-temperature and resin morphology on the rate and equilibrium level of residual vinyl chloride monomer in polyvinyl chloride resin. The overall diffusion of vinyl chloride monomer out of the primary particles should be the rate-determining step in the process in the case of polyvinyl chloride resin. In the case of vinyl chloride-propylene copolymer, the effect of unreacted propylene monomer dissolved in the primary particles, the presence of propylene bound into the polymer backbone, and the lower molecular weight offer possible factors that could affect the rate and equilibrium level of residual vinyl chloride. A laboratory batch monomer stripping procedure developed by Chan and coworkers⁵ was used to compare a laboratory homopolymer slurry (IV = 0.95 dL/g IPTU = 24.8) to the K-35-S-202 binary suspension-based vinyl chloride-propylene copolymer slurry. Both resins, when tested at 80 and 100°C for vinyl chloride removal rate, exhibit the similar residual monomer levels (Fig. 1). At 80°C the residual vinyl chloride level as a function of time shows the expected two-stage curves: initial decrease from time zero to time 30 min represents the liquid-vapor diffusion regime; from 30 to 90 min represents the solid-liquid diffusion of the vinyl chloride out of the primary particles. The observed similarity in slope for homopolymer and vinyl chloride-propylene copolymer over the 30–90 min time regime is indicative of the same size to the primary particle with very little effect of either the resin molecular weight or the presence of propylene in the copolymer. At 100°C the vinyl chloride removal rates are superimposable for both the homopolymer slurry and the vinyl chloride-propylene slurry. At 30 min both materials are under 10 ppm. This similar behavior at 100°C in a batch

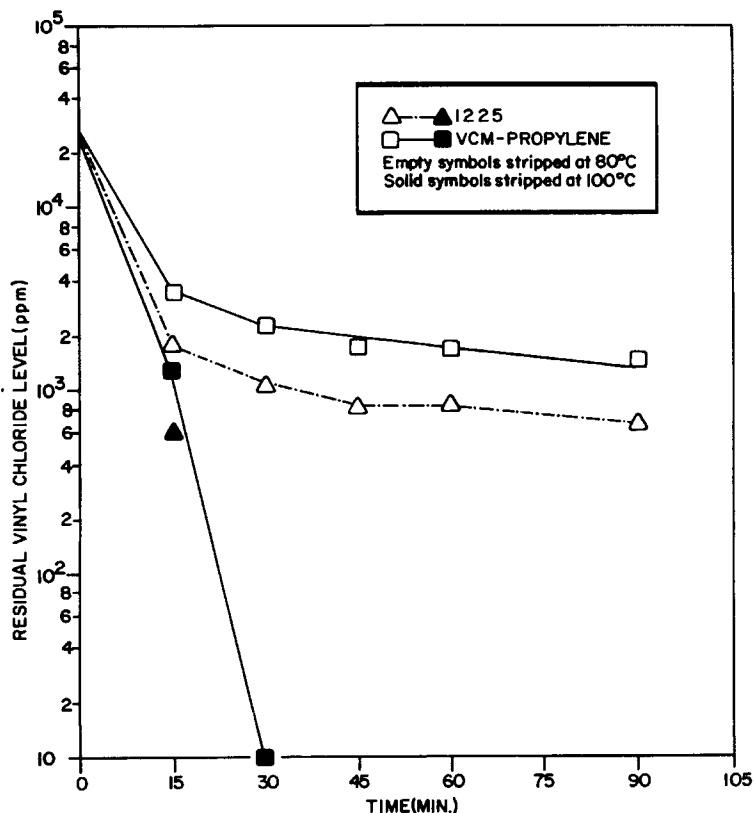


Fig. 1. Stripping profiles versus polymer type.

stripping process indicates that low levels of residual vinyl chloride can be obtained from this copolymer in a commercial scale continuous stripping column.

Initiator System Development

The copolymerization of vinyl chloride and propylene, because of the relatively high reactivity ratio of vinyl chloride versus propylene [R_1 (vinyl chloride) = 2.90, R_2 (propylene) \simeq 0.0], results in an overall increase in the mole fraction of propylene in the unreacted comonomer phase as the mixture copolymerizes. This is illustrated for an initial 92.5:7.5 weight ratio polymerization (Fig. 2). The propylene is a degradative chain transfer monomer,² and the increase in the mole percent propylene in the unreacted comonomer leads to a decrease in the polymerization rate with conversion.

Several different strategies were examined to overcome this decrease in polymerization kinetics:

- Step increase in polymerization temperature
- Multiple injection of initiator
- Multicomponent initiator system

All these techniques were directed at maximizing the rate of polymerization while staying within both the heat transfer limits and the maximum op-

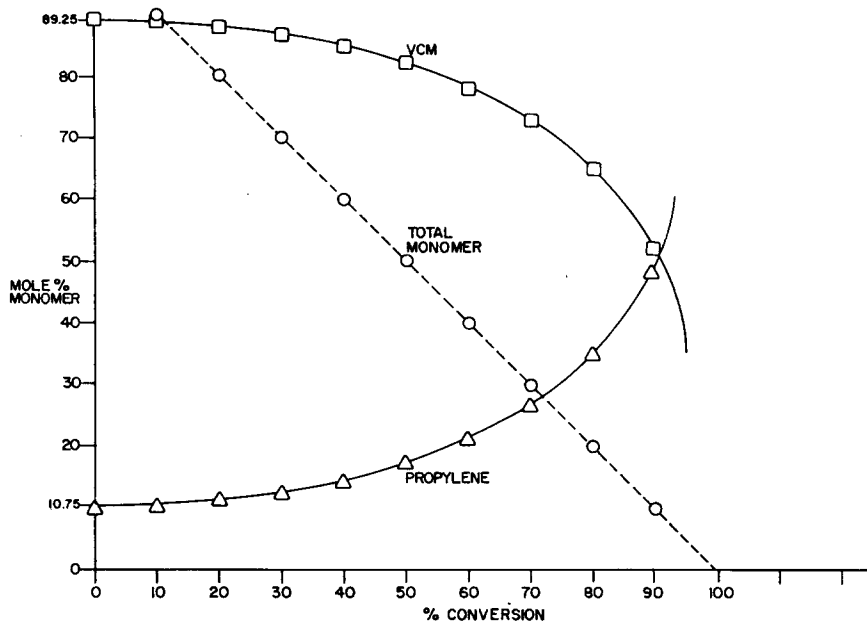


Fig. 2. Mole percent of monomers versus conversion.

erating pressure of a small commercial stainless steel reactor. The heat transfer coefficient for a small commercial reactor has been shown to decrease over the course of a vinyl chloride batch polymerization.¹⁰ This decrease in heat transfer capacity needs to be considered in any initiator study.

The step increase in polymerization temperature has been used to control polymerization kinetics of vinyl chloride.¹¹ When applied to a vinyl chloride-propylene copolymerization, the increase in temperature leads to an increase in the vapor pressure of the unreacted comonomer mixture because of the ever-increasing mole fraction of propylene in the unreacted monomer. The pressure limitations on most commercial vinyl chloride reactors are about 225 psia, and this temperature increase procedure quickly reaches these limits and is therefore unacceptable.

A multiple injection of initiator based on *t*-butyl peroxyneodecanoate was successful in achieving overall polymerization kinetics that closely matched the estimated heat transfer limits of a small commercial stainless steel reactor. The disadvantage to this approach was the need for multiple injections, which have the potential for misadventure and tend to impair the total thermal stability of the resin.

A binary initiator based on a mixture of α -cumyl peroxyneodecanoate (L-188) and *t*-butyl peroxyneodecanoate (L-10) was developed that, for an 92.5:7.5 vinyl chloride-propylene comonomer at 55°C, also demonstrates a kinetic profile close to that of the theoretical heat transfer limits of a production reactor. A U.S. Patent is pending on this subject; a European patent publication has been issued.^{11a} Other binary initiator systems for both higher and lower polymerization temperatures and initial propylene levels have been identified and, although not used in the subsequent process study, will be the topic of a future publication.

The binary initiator (Fig. 3) has the advantage of a single addition along with a slight improvement in the resin thermal stability. This binary initiator system was used in all subsequent process control studies.

Process Control Relationships

We have demonstrated that, for vinyl chloride-vinyl acetate copolymers, the resin properties can be predicted from the polymerization conditions.⁴ This technique was used to develop predictive polymer property equations for the vinyl chloride-propylene copolymers. For this study we used a fixed initiator recipe as detailed in the control equation study recipe in the Experimental Procedures section. A 2^3 factorial experimental design was chosen using the criteria established by Box et al.¹² The experimental program was intended to determine how the input (or independent) variables of

Level of charged propylene (5–10%), denoted weight percent P_c

Polymerization temperature (50–60°C), denoted T_p

Change in reactor pressure (20–50 psi), denoted ΔP

would affect the output (or dependent) resin properties of

Inherent viscosity (IV)

Bound propylene (% P_b)

Melt flow (MF)

The results of this 2^3 experimental study are detailed in Table III. The factorial design (with replicated center points) permitted development of models containing both linear and interactive terms for each output resin property. This allowed multiterm modeling of vinyl chloride-propylene co-

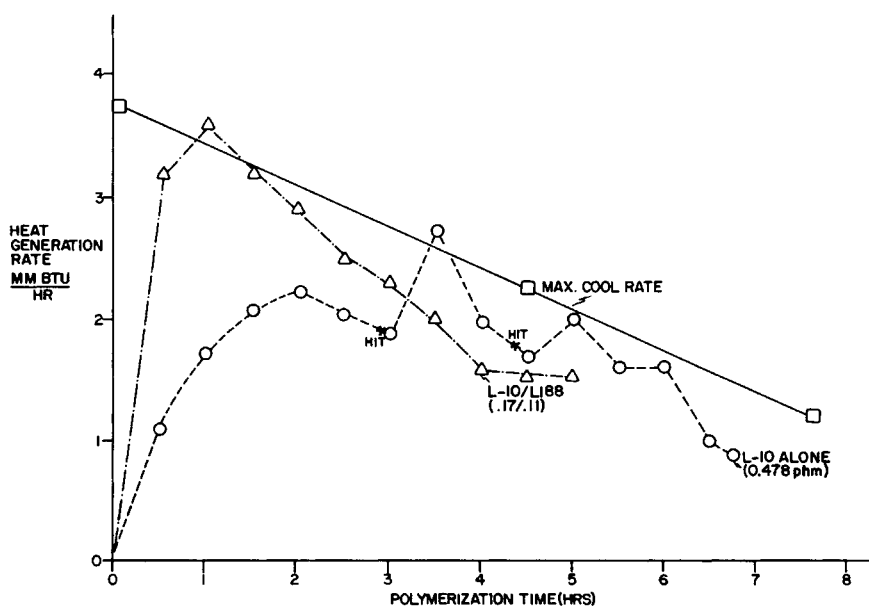


Fig. 3. Heat generation of initiator system versus time.

TABLE III
 Process Control Experimental Design

Run no.	Input parameters				Output parameters			
	Propylene (g)	Charged (%) ^a	T_p (°C)	ΔP (psi)	Yield (%)	IV (dL/g)	MF (gr per 10 ft)	% Propylene bound
1	225	7.5	55	35	73.0	0.579	46.7	5.08
2	225	7.5	55	35	75.0	0.570	53.9	5.32
3	150	5.0	50	20	72.4	0.733	6.3	3.63
4	300	10.0	50	20	58.7	0.607	45.1	6.46
5	150	5.0	60	20	72.5	0.588	32.3	3.39
6	300	10.0	60	20	61.6	0.503	112.8	6.54
7	150	5.0	50	50	82.7	0.712	8.9	3.61
8	300	10.0	50	50	76.4	0.574	62.5	6.45
9	150	5.0	60	50	80.2	0.581	42.7	4.19
10	300	10.0	60	50	75.5	0.459	190.2	7.13

^a Percentage of total monomer.

polymer properties. The resin property response surfaces have been graphically interpreted using contour plotting.

A summary of statistically significant terms for the various dependent resin properties is included in Table IV.

Predictive Model for Inherent Viscosity

In a free radical polymerization the interaction between the radical end and the monomer to form either an addition product or to transfer to monomer to form a new active site is the major factor controlling the molecular weight of the polymer. In the case of polyvinyl chloride the molecular weight can be controlled by the polymerization temperature,¹³ the presence of chain transfer agents,¹⁴ and the presence of comonomers.^{2,4} We have expanded on the work of Ravey and Waterman¹⁵ and have shown that the inherent viscosity of vinyl chloride-propylene copolymers can be predicted from our experimental data with a linear equation of the form

$$IV = K_1 - K_2[P_c] - K_3[T_p] - K_4[P_c \cdot \Delta p] \quad (1)$$

The square of the correlation coefficient R^2 for the predicted versus actual values for inherent viscosity is 0.9805.

 TABLE IV
 Summary of Statistically Significant Terms for Vinyl Chloride-Propylene Model Equations^a

Input variables	Inherent viscosity	Bound propylene	Melt flow
Polymerization Temperature (T_p)	*	*	*
Charged propylene (P_c)	*	*	*
Change in pressure (Δp)		*	*
$T_p \times P_c$			*
$T_p \times \Delta p$		*	
$P_c \times \Delta p$	*		

^a In this study the symbol (*) denotes an α of ≤ 0.10 in a stepwise multiple linear regression analysis.

The predictive equation for inherent viscosity [eq. (1)] indicates that, as the process parameters of charged propylene P_c , polymerization temperature T_p , and the cross product of charged propylene and pressure rise $P_c \cdot \Delta p$ are increased, the inherent viscosity of the copolymer will decrease. These mathematical relationships are consistent with our understanding of the effects of temperature and propylene level on the molecular weight of a vinyl chloride-propylene copolymer. Increasing polymerization temperature will decrease the molecular weight of the polymer.¹³ Propylene, which is a degradative chain transfer monomer because of the allylic hydrogens, will also decrease the molecular weight of the polymer.¹ The third component, the cross product of propylene charged and pressure rise (where the pressure rise is a measure of conversion) [$P_c \cdot \Delta p$] also is a factor that will reduce the inherent viscosity of the resin. This cross product term is consistent with current understanding of the polymer properties. It has been shown that increasing the conversion [Δp] for a vinyl chloride-propylene copolymerization decreases the inherent viscosity.² The interactive effects of conversion [Δp] with the charged propylene load [P_c] were not anticipated, and therefore this is an added advantage to this form of modeling study.

A comparison of the actual and predicted values for inherent viscosity based on predictive eq. (1) is noted in Table V. Graphic representation of the interaction between polymerization temperature T_p and charged propylene P_c on inherent viscosity at a pressure rise ΔP of 50 psia is shown in Fig. 4.

The inherent viscosity model equation demonstrates that increasing all the input process variables (i.e., T_p , Δp , and P_c) will decrease the inherent viscosity of the vinyl chloride-propylene resins. The inherent viscosity contours in Fig. 4 indicate the range of polymerization conditions (i.e., T_p and P_c at a Δp of 50 psia) that can be used to achieve a particular inherent viscosity. For example, an inherent viscosity of 0.5755 (contour C) can be achieved over the extremes of conditions from 60°C and 5% charged propylene to 50°C and 10% propylene. The choice of conditions depends on the balance of better copolymer physical properties achieved at high propylene level and low polymerization temperature compared with the better manufacturing costs achieved at high polymerization temperatures and low propylene levels.

TABLE V
Actual and Predicted Values of Inherent Viscosity According to Model Eq. (1)

Run no.	Actual	Predicted	Residual
1	0.579	0.590	-0.011
2	0.570	0.590	-0.020
3	0.733	0.721	0.012
4	0.607	0.611	-0.004
5	0.588	0.596	-0.008
6	0.503	0.489	0.014
7	0.712	0.703	0.009
8	0.574	0.575	-0.001
9	0.581	0.578	0.003
10	0.459	0.453	0.006

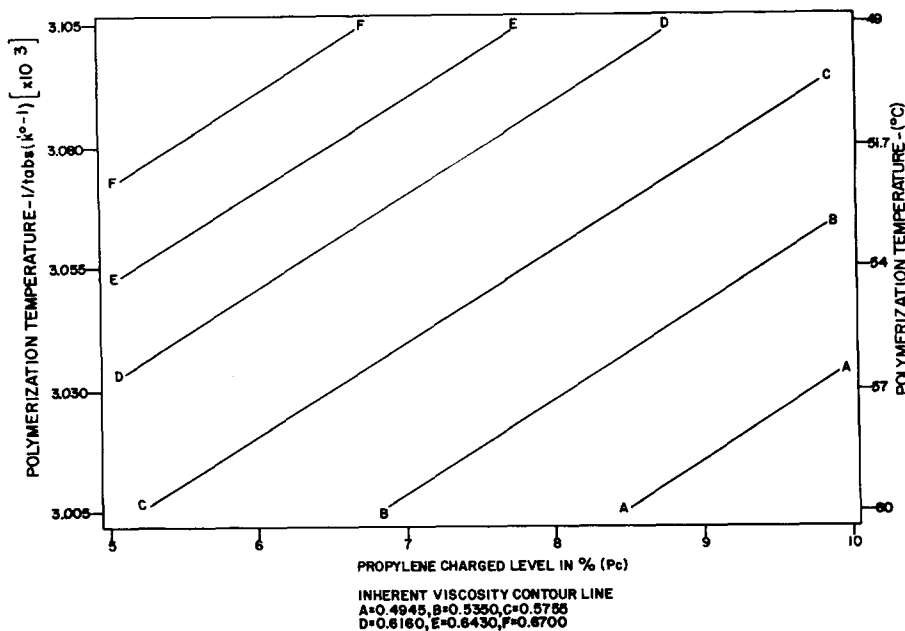


Fig. 4. Inherent viscosity contours as a function of polymerization temperature and charged propylene.

Predictive Model for Bound Propylene

The bound propylene P_b level in these copolymers was measured by proton NMR spectroscopy using the calculated ratios of



to calculate the composition of the copolymer. A similar procedure using ^{13}C NMR has been reported for the vinyl chloride-propylene copolymers.¹⁶ We found this NMR technique superior to a density gradient technique¹⁷ in overall reproducibility.

The bound propylene content of these copolymers was found to fit the relationship

$$\%P_b = K_1 + K_2[\%P_c] - K_3[T_p] - K_4[\Delta p] + K_5[T_p \cdot \Delta p] \quad (2)$$

with an $R^2 = 0.9965$.

Comparison of the actual and predicted values for bound propylene based on predictive eq. (2) is noted in Table VI. The predictive equation includes both polymerization temperature and pressure rise terms, which were not important in the study of vinyl chloride-vinyl acetate study.⁴ The bound propylene level decreases with increasing polymerization temperature K_3 because of the relatively low boiling point of propylene (-43°C); the higher the polymerization temperature the more propylene (relative to vinyl chloride) is driven into the vapor space and therefore out of the liquid phase where the polymerization occurs. The higher conversion K_4 results in a decrease in the expected bound propylene level. This occurs because the vinyl chloride monomer has a higher reactivity ratio than the propylene and the unreacted comonomer composition shifts to higher propylene content as the copolymer is formed. The reduction of vinyl chloride monomer in the unreacted comonomer phase reduces the relative solubility of the propylene monomer in the liquid unreacted comonomer phase and therefore results in a lower than expected propylene content in the polymer at higher conversions.

The effect of polymerization temperature and charged propylene on the level of bound propylene is illustrated in Fig. 5 at a pressure rise of 50 psia.

Predictive Models for Melt Flow Properties

The melt rheological properties of the vinyl chloride-propylene copolymers are controlled, in part, by the molecular weight and molecular weight distribution as well as the comonomer content and distribution. In this batch copolymerization we measured the expected¹ M_w/M_n of 2.1 ± 0.10 . The melt flow properties of these copolymers were determined in a Tinius-Olsen melt index device using a standard ASTM procedure. This melt index device is a simple capillary extrusion apparatus used extensively throughout the plastics industry to characterize the flow properties of resins and compounds. The device is designed to give a single point determination at a fixed shear rate and temperature. The primary purpose of this test device is to determine qualitative flow properties between different materials. Predictive mathematical models can be developed that will relate the melt flow properties to either the process parameters (T_p/P_c and, Δp) or product

TABLE VI
Actual and Predicted Values of % Bound Propylene

Run no.	Bound propylene		
	Actual	Predicted	Residual
1	5.08	5.18	-0.10
2	5.32	5.18	0.14
3	3.63	3.58	0.05
4	6.46	6.52	-0.06
5	3.39	3.50	-0.11
6	6.54	6.44	0.10
7	3.61	3.57	0.04
8	6.45	6.51	-0.06
9	4.19	4.20	-0.01
10	7.13	7.14	-0.01

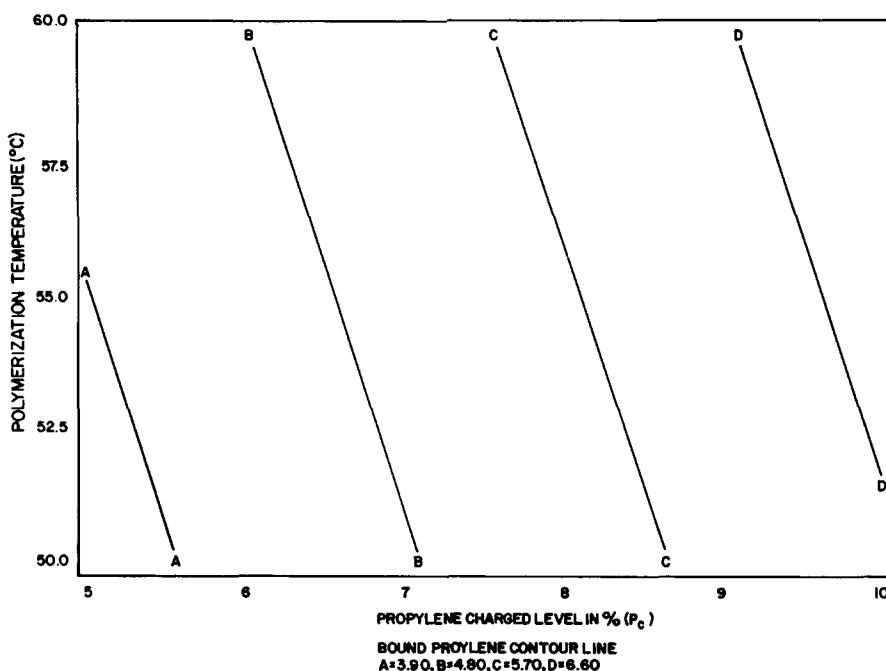


Fig. 5. Bound propylene contours as a function of polymerization temperature and charged propylene.

parameters (IV and P_b). This has already been demonstrated for the vinyl chloride-vinyl acetate copolymers.⁴ The melt flow property of these resins can be modeled in the natural log form¹ for the process relationship as

$$\ln(\text{MF}) = K_1 + K_2[P_c] - K_3 \left[\frac{1}{T_{\text{abs}}} \right] + K_4 [\Delta p] + K_5 \left[P_c \times \frac{1}{T_{\text{abs}}} \right] \quad (3)$$

with an $R^2 = 0.9859$.

The predictive model equation for melt flow based on process parameters indicates that increasing the charged propylene level [P_c] or the conversion [Δp] will increase the melt flow of the copolymer. This is in agreement with previously established literature² and indicates that increasing the propylene content of the resin by either higher charged propylene [P_c] or higher conversion [Δp] will increase the melt flow of the resin.

The polymerization temperature appears in terms 3 and 5 of eq. (3). In term 3, increasing the polymerization temperature will increase the melt flow by an overall effect of reducing the molecular weight of the copolymer. By contrast, in term 5, increasing the polymerization temperature will decrease the cross product of [$P_c \cdot 1/T_{\text{abs}}$] and therefore decrease the melt flow of the resin by forcing the propylene monomer out of the liquid phase and into the vapor phase. The overall dominant effect is that increasing polymerization temperature will increase melt flow.

A comparison of the actual and predicted melt flows are tabulated in Table VII. A contour plot of melt flow as a function of polymerization temperature and charged propylene content (Fig. 6) indicates the varying

TABLE VII
Actual and Predicted Values of Melt Flow According to Model Eq. (3)

Run no.	Actual	Predicted	Residual
1	46.70	40.79	5.91
2	53.90	40.79	13.11
3	6.30	6.55	-0.25
4	45.10	46.47	-1.37
5	32.30	32.56	-0.26
6	112.80	128.40	-15.60
7	8.90	9.47	-0.57
8	62.50	67.17	-4.47
9	42.70	47.06	-4.36
10	190.20	185.60	4.60

reaction conditions needed to achieve a particular melt flow. In combination with Fig. 4 the interaction between IV and MF contours as a function of polymerization temperature and charged propylene can define the unique resin properties that could be expected at a fixed pressure rise. The predictive melt flow equation based on the product parameters of composition ($\% P_b$) and molecular weight (IV) can be constructed in a fashion previously described.⁴ In the case of vinyl chloride-propylene copolymers, a two-term model of the form

$$\ln(\text{MF}) = K_1 + K_2[P_b] - K_3[\text{IV}]^2 \quad (4)$$

achieves an R^2 of 0.9986 in the comparison of predicted to actual values. This two-term model indicates that the melt flow of a vinyl chloride-pro-

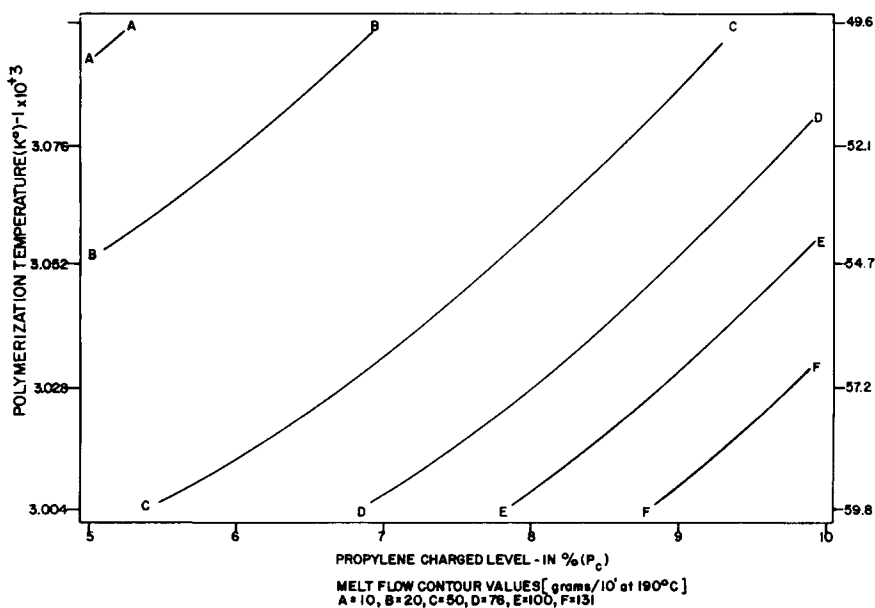


Fig. 6. Melt flow contours as a function of polymerization temperature and charged propylene.

pylene will increase as the level of bound propylene [P_b] is increased and will decrease as the molecular weight increases. The form of this equation is in agreement with basic understanding of melt flow properties. The presence of increased levels of bound propylene P_b in the copolymer will reduce the polar-polar interaction between the polymer chains and therefore increase the melt flow.² The negative effect of inherent viscosity raised to the second power $[IV]^2$ on melt flow is an unexpected effect, which may be unique for this experimental range of vinyl chloride-propylene copolymers.

A comparison of the actual and predicted values of melt flow are detailed in Table VIII. The very close agreement between the actual and predicted values indicates that a prediction of melt flow from polymer characteristics of inherent viscosity and bound propylene content should be very accurate. The contour plot that would be used for this analysis is detailed in Fig. 7. The contour lines in Fig. 7 indicate that small changes in inherent viscosity have major effects on the melt flow and variations in the level of bound propylene cause rather small changes in the melt flow.

CONCLUSIONS

1. Model equations that will predict the resin properties of copolymer composition and inherent viscosity can be developed for vinyl chloride-propylene copolymers.

2. The Tinius-Olsen melt flow of vinyl chloride-propylene copolymers can be predicted from model equations based on the process conditions of polymerization temperature, initial propylene monomer level and pressure rise, or the product parameters of bound propylene level and inherent viscosity. These model equations based on statistical experimental design procedures are consistent with established theories relating polymer and process properties to melt flow and in addition offer insights into the relationship between interactive terms that cannot be derived from established literature citations.

3. The particle morphology of the vinyl chloride-propylene copolymers can be controlled by the choice of both primary and secondary suspension agents.

4. The copolymerization kinetics can be optimized by the use of a properly chosen binary initiator system.

TABLE VIII
Actual and Predicted Values of Melt Flow According to Model Eq. (4)

Run no.	Actual	Predicted	Residual
1	46.70	47.17	-0.47
2	53.90	53.51	0.39
3	6.30	6.64	-0.34
4	45.10	43.99	1.11
5	32.30	33.12	-0.82
6	112.80	119.90	-7.10
7	8.90	8.60	0.30
8	62.50	61.37	1.13
9	42.70	40.28	2.42
10	190.20	189.10	1.10

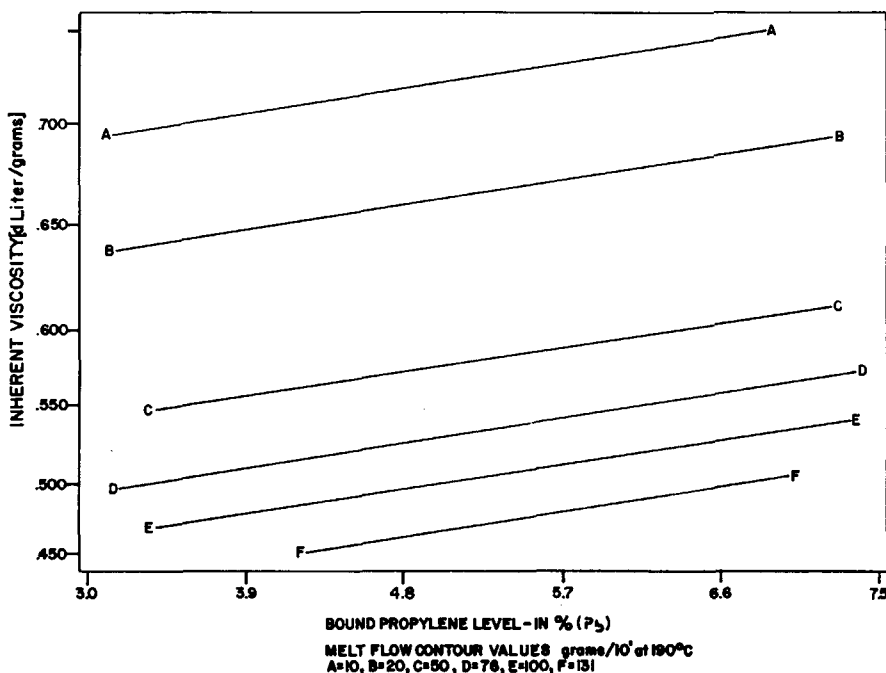


Fig. 7. Melt flow contours as a function of polymer inherent viscosity and bound propylene.

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