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D. Feldman[a]; M. Macoveanu[a]; G. Robila[a]
[a] Polytechnic Institute, Jassy, Romania

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Suspension Polymerization of Vinyl Chloride with Programmed Temperature: Morphological Characteristics and Thermal Stability of Poly(vinyl Chloride)

D. FELDMAN, M. MACOVEANU, and G. ROBILĂ

Polytechnic Institute
Jassy, Romania

ABSTRACT

Poly(vinyl chloride) obtained by intermittent polymerization in suspension with temperature programming, has been characterized from the point of view of morphological properties and of thermal stability. The data have been compared with the values of the morphological characteristics and thermal stability for the PVC samples obtained under identical polymerization conditions, but at constant temperature. The poly(vinyl chloride) obtained by polymerization with temperature programming has the same properties as the poly(vinyl chloride) obtained by simple polymerization at constant temperature, with an identical average molecular weight. However, the former polymer shows improved thermal stability, as well as a decrease in the volumetric properties.

DEPENDENCE OF THE CHARACTERISTICS OF PVC POWDER ON POLYMERIZATION CONDITIONS

In industrial practice, reactor design can be tackled from more than one view point. One starts from the desired properties one wishes to impart in view of the subsequent use of the product.

Numerous papers have been published dealing with the influence of polymerization conditions on the properties of the formed poly(vinyl chloride). Recently, there has been increasing interest in methods of obtaining polymers with identical properties in different reactors, which is extremely important in scaling up laboratory runs to industrial production.

A thorough study of the effect of the reactor design on product quality in suspension polymerization of vinyl chloride was reported by Hedden [1].

The usual stages for getting different products based on PVC-S, starting with the raw material up to the final product, are shown in Fig. 1.

The polymer properties are not determined immediately after polymerization, but after washing and drying of the polymer.

The polymerization reaction is checked in the first test, in which a baseline is established for the behavior of the PVC powder used in the subsequent processing.

In the second test, the effect of further processing used to obtain the semi- or final product is ascertained.

In suspension polymerization of vinyl chloride, macromolecular chains are formed from drops of monomer dispersed in the aqueous phase. The polymer formed at the beginning has the same molecular weight distribution as the final product [2].

An increase in intensity of stirring causes an increase in the polymerization rate [3], but it also leads to a narrowing of the granulometric spectrum, as well as to an increase in the size range of the PVC particles [1].

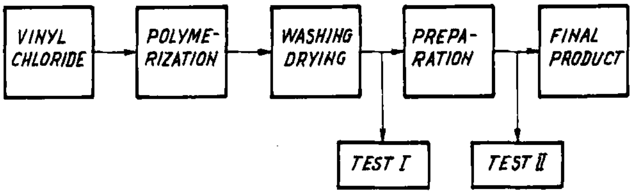

FIG. 1. Steps in obtaining final product from PVC-S.

The structural characteristics of the PVC particles of vital importance in establishing the subsequent processing properties of the polymer.

Two principal processes are taking place in the process of interaction between the PVC powder and the plasticizer [4]. Adsorption of the plasticizer is a phenomenon based on surface and capillarity forces; these forces help the plasticizer to occupy the free accessible volume existing in the PVC powder, both as a free volume between the particles and as a free accessible volume existing as pores within the particles. This phenomenon depends on the porosity of the polymer powder, being predominant at low temperatures, when the diffusion of the plasticizer in the polymer is not marked. The absorption of the plasticizer in the polymer is a diffusion process depending upon temperature, average molecular weight of the polymer, chemical nature both of the polymer and of the plasticizer, and the physical structure of the PVC particles.

The PVC-S particles, both the porous and the compact type, are made up of component microparticles which form holes (pores) of different shapes and sizes and which are surrounded by a "pericellular film" having a thickness of several Angstroms. The degree of aggregation of these microparticles differentiates the porous type from the compact one. The pericellular film plays an important part in the process of interaction between polymer and plasticizer.

Bort et al. [5] showed, on the basis of electron microscopy studies, that the compound structure of the PVC particles depends, especially upon the polymerization rate, which determines their size, number, and component.

Some papers in the specialized literature deal with the evolution of some characteristics of PVC-S powder during polymerization [5, 6], but the polymerization temperature has always been taken as constant.

The purpose of this paper is to characterize the PVC-S powder obtained by carrying out the polymerization at a constant rate by use of a temperature program [7]; the characterization is made from the viewpoint of processing behavior of the powder, establishing the most important characteristics being the aim of the first test. The results have been interpreted by comparing them with the corresponding data for PVC samples obtained under the same polymerization conditions except at constant temperatures of 45, 52, or 60°C.

EXPERIMENTAL

The polymerization of vinyl chloride in suspension was carried out in a 0.5 liter reactor from V_4A, equipped with a combined propeller-anchor agitator (45 rpm).

The polymerization recipe was the following: 130 g vinyl chloride, 324 g distilled water, 0.84 g Methocell HG 75/50 (Dow methoxypropylcellulose) and 0.43 g diisopropyl peroxydicarbonate.

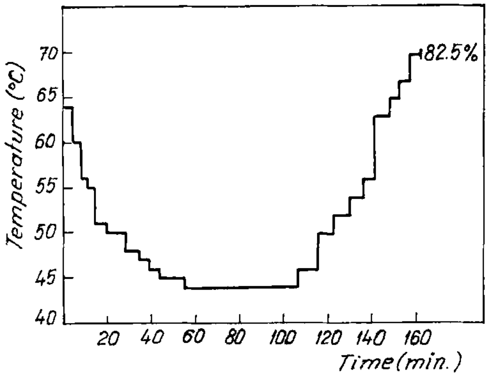

FIG. 2. Temperature program necessary for a constant rate vinyl chloride polymerization in suspension [7].

The polymerization temperature was of 45, 52 or 60°C, variable in time, according to the temperature program shown in Fig. 2.

The characteristics of the PVC powder determined were evaluated by the following procedures: K value, according to Romanian Standard STAS 6321-61 and 7614-66; moisture and volatile contents, according to STAS 7798-67; ash content, according to STAS 7308-65.

The optical microscopic examination was carried out as proposed by Prokopova and Pelzbauer [8]. The principle of the method is the following: if the PVC particles are immersed in a liquid with an optical index of the light identical to that of the poly(vinyl chloride), for instance, cedar oil, the porous particles seem to be opaque, while compact particles are transparent.

The size range of the granules was established by use of a mesh screen with vibration, as described in STAS 6641-74.

The unsagged and sagged density was determined according to STAS 5875-58, and STAS 7309-65, respectively.

The flow properties and the angle of natural slope of the powder were established by passing the powder through a funnel having an aperture angle of 60° and an aperture of 9 mm [9].

Real density was determined by a pycnometric method, according to STAS 5886-58.

Irreversible adsorption of plasticizer in the cold ($S_{\text{irrev-cold}}$) was determined by centrifuging [10] a mixture of 1 g PVC and 2 g DOP (dioctyl phthalate) in a glass vial equipped at the lower part with a filtering surface. Centrifugation was carried out for 10 min at

6000 rpm. The amount of plasticizer remaining in the polymer was determined gravimetrically.

The specific surface was determined from adsorption of nitrogen in an Areameter (Ströhlein GmbH, West Germany).

The absorption time of the plasticizer at 75° C (sorption time), was evaluated according to STAS 6641-74.

Swelling in ethyl acetate was measured at normal temperature, according to the method given by Glück et al.

The total porosity of the PVC (ϵ_T) and the inaccessible porosity of the PVC particle (ϵ_{inacc}) were calculated by Eqs. (1) and (2) [11].

$$\epsilon_T\ (\%) = \left(1 - \frac{\text{sample density}}{\text{structural density of the constituents}}\right) \times 100 \qquad (1)$$

$$\epsilon_{inacc.}\ (\%) = \left(1 - \frac{\text{real density (pycnometric)}}{\text{structural density of the constituents}}\right) \times 100 \qquad (2)$$

where the structural density of the constituents was considered to be 1.400 g/cm^3, while the sample density (unsagged density) and the pycnometrical density were determined as described above.

The absorption rate V_A was computed by means of Eq. (3).

$$V_A = \frac{(66 - S_{irrev\text{-}cold})}{t_{sorption,\ 75^\circ C}} \qquad (3)$$

as parts DOP per 100 g PVC/min.

The thermal stability of the PVC samples was determined by three different methods: (a) the Congo red method, according to STAS 6032-59; (b) a Brabender Plastograph method of a mixture consisting of 100 g PVC sample, 1.5 g lead dibasic stearate (PbH_2 stearate), 0.5 g lead dibasic phosphite, 1 g calcium stearate, and 1.7 g glycerin monostearate; and (c) with the use of a Paulik-Paulik-Erdely derivatograph (MOM Budapest) under the following conditions: rate of heating, 12° C/min, in air; 50 mg sample; maximum temperature 900° C; DTA 1/10, DTG 1/10.

The evaluation of the activation energy and of the order of destruction reaction was performed as described by Freeman and Carrol [12].

The labile chlorine content (Cl_L) was determined by means of a phenolization reaction [13]. The atoms of labile chlorine in the polymer are replaced (by reaction of PVC samples with phenol) with phenolic structures substituted in the para-position; these groups show characteristic absorption in the 250-300 nm region of the UV spectrum [14]. The phenolization of the PVC samples was carried out by heating 1 g of polymer in 30 g phenol at a temperature of 60°C for 98 hr. After reaction, the excess of unreacted phenol was removed by a thorough washing of the samples with methanol and by repeated resettling from different solvent-nonsolvent systems [13]. The UV measurements were made with a Pay-Unicam-SP 700 spectrophotometer.

The determinations have been performed on tetrahydrofuran solutions of phenolized polymer by using 10 mm containers. Solutions of the same polymer which had not been phenolized but had an identical concentration were used as reference materials. The solvents and the nonsolvents were characterized spectroscopically before usage.

The quantity of labile chloride existing in the polymer per 100 structural units was calculated by means of Eq. (4),

$$Cl_L(\%) = 100[(F + 62.5)/C] \tag{4}$$

where C is the concentration of the solution expressed in grams polymer/100 ml THF and F is the concentration of measure solution expressed in equivalents of reacted phenols/100 ml THF (tetrahydrofuran); this value is determined by using a calibration curve constructed for PVC reacted with phenol [13].

RESULTS AND DISCUSSION

Some characteristics related to the geometry and morphology of PVC particles are presented in Table 1. These characteristics were obtained by polymerization in suspension at constant temperature as well as at a temperature variable in time according to the program established for conducting the process at constant rate. As is known, the K value has a determinant role and must be known in order to choose the most suitable processing and the gel temperature.

As a rule, the larger the value of K, the better are the mechanical characteristics of the products obtained from a given PVC type, but, at the same time, the processing will be more difficult.

TABLE 1. Physical and Morphological Characteristics of the PVC-S Powder

		Polymerization temperature			
No.	Characteristic	45°C	52°C	60°C	Program
1	K value	74.7	66.9	59.1	71.7
2	Content of moisture and volatiles (%)	0.18	0.20	0.28	0.30
3	Ash content (%)	0.014	0.020	0.039	0.028
4	Unsagged density (g/cm^3)	0.450	0.360	0.320	0.295
5	Sagged density (g/cm^3)	0.520	0.410	0.385	0.330
6	Relative compression (%)	16.0	13.9	11.9	11.9
7	Natural slope angle (degrees)	61	59	53	57
8	Pycnometrical density in CH_3OH (g/cm^3)	1.180	1.265	1.280	1.260
9	Rate of flow (g/sec)	5.1	3.1	3.6	3.7

As one can see from Table 1, the poly(vinyl chloride) obtained by polymerization with temperature program has a K value identical to that of a PVC obtained by suspension polymerization at a constant temperature around 49°C.

As shown in a previous paper [7], the average molecular weight and K value, can be computed by calculus on the basis of the temperature program used and by taking into account the dependence of the PVC molecular weight on temperature in the given temperature range. The agreement with the experimental data is very good.

In PVC processing, the unsagged and sagged densities become increasingly important as continuous processes or big capacity processes are involved, the monomer feed being in most cases volumetric.

The existing studies show that both the unsagged and the sagged densities depend on the following factors: pellet size (in identical conditions when the pellet size is bigger and the degree of dispersion smaller, the unsagged density will increase), pellet shape (powders having spherical and regular pellets have an unsagged and sagged

TABLE 2. Granule Size Distribution for the PVC Samples

	Residue (%)			
	45°C polymerization	52°C polmerization	60°C polymerization	Programmed temperature
Sizer 315 μm	71.5	64	88	76
Sizer 250 μm	11.5	13	2.8	10
Sizer 160 μm	7.0	9	3.0	6.6
Sizer 100 μm	4.0	5	2.0	2.4
Sizer 63 μm	2.8	4	2.2	4.0
Cover	3.2	5	2.0	1.0

density, respectively, greater that those with coarse particles of irregular shape); structure and condition of the pellet surfaces; electrostatic loads; and working conditions.

As shown in Table 2, the majority of the PVC particles obtained has dimensions betwen 250 and 350 μm. The range of particle size can be quite large.

The studies by optical microscopy led to an average diameter for PVC particles of 330 μm. The presence of particles of quite large dimensions the relatively wide range of particle sizes (for all the samples) are attributed to the small speed of stirring (45 rpm). The fact that the values of the unsagged and sagged densities are relatively small can be explained by the coarse structure of the particles, with big dimensions for approximately 85% of particles. On the other hand, the values of the pycnometric density are small enough for all the samples. It seems that, because the polymerization temperature is higher at the beginning of the process, the values of the unsagged and sagged densities are smaller in the case of the poly(vinyl chloride) obtained with programmed temperature.

Generally speaking, as Bort shows [5], for polymers having the same K value, the structures of the microparticles constituting the PVC particle have to be similar.

The synthesis temperature, which determines the K value, influences the structure of the component microparticles as follows. With the increase in temperature, the number of microparticles constituting the particles is reduced, also decreasing their degree of interpenetration. When the temperature becomes higher, a "hollower" structure of the macromolecules which form the microparticles is achieved.

This is why poly(vinyl chloride) obtained with the programmed temperature has the same K value as a PVC obtained by polymerization at constant temperature around 49° C, but its unsagged and sagged densities are comparable with those of a PVC obtained at a constant temperature of 60-65° C, which corresponds to the starting point in the programmed polymerization.

An important technological property of PVC is the rate of flow as a powder. This complex characteristic depends upon the shape of the pellets, internal friction, the condition of the pellets surface, the particle size distribution, density, and moisture content. As can be seen from Table 1, the PVC obtained with a temperature program has a rate of flow comparable to that of the PVC obtained at a constant temperature around 49° C, a temperature which is supposed to lead to polymer having the same K value.

This assertion is valid also for the value of the angle of natural slope, which represents the acute angle between the generatrixes of the cone formed by the free flow of the powder and the plane surface.

Some morphological particularities of the PVC-S particles have been made evident with the help of optical microscopy (Fig. 3), by using the method proposed by Prokopova and Pelzbauer [8].

From an examination of Fig. 3b and 3c the existence of porous particles and of some particles which are closer to the compact type may be noted. Both the particles in polymer obtained at a temperature of 52° C and those in PVC obtained with the programmed temperature are heterogeneous from a morphological point of view, both compact and porous particles being present, the latter in a greater proportion.

Often, the porous PVC and PVC obtained in rapid processing are considered equivalent. Actually, a linear dependence has been established between porosity and the saturating speed of the plasticizer [16]. However, the saturating speed of the plasticizer may vary for polymers having the same porosity and distribution of pore sizes.

Butucea et al. [15] explain this apparent contradiction by considering the process of interaction between plasticizer and polymer particle as consisting of two stages: in the first stage, the plasticizer reaches the level of the microparticles composing the particle by the action of adsorption, these phenomena being directly determined by porosity, in the second stage, the plasticizer breaks into microparticles by diffusion, of this process depending upon the determinant factor and the magnitude of the microparticle surfaces.

In the case of the PVC samples studied, it is noted (from Table 3)

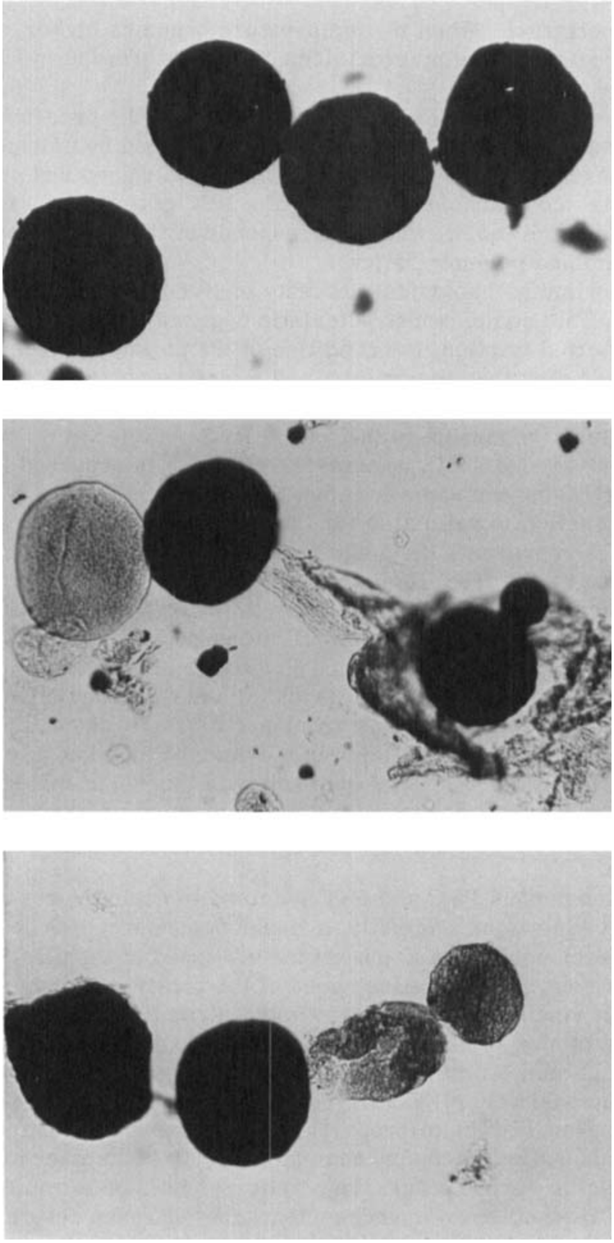

FIG. 3. Differentiation of the type of PVC particles by optical microscopy: (a) PVC particles obtained at 52°C (in air); (b) PVC particles obtained at 52°C (in cedar oil); (c) PVC particles obtained with programmed temperature (in cedar oil).

TABLE 3. Characteristics Related to Porosity and Sorption of Plasticizer

No.	Characteristic	Polymerization temperature 45°C	52°C	60°C	Program
1	Sorption time at 75°C (min)	120	33	17	28
2	Irreversible plasticizer adsorption in cold (%)	52.6	48.8	37.5	50.4
3	Absorption rate, (parts DOP/100 parts PVC/min)	0.1	0.5	1.1	0.3
4	Specific surface (m^2/g)	1.8	2.8	2.8	2.6
5	Total porosity ϵ_t(%)	67.9	74.3	77.2	79
6	Inaccessible porosity of the particle (%)	16.5	9.7	8.6	10

TABLE 4. Swelling of PVC Samples in Ethyl Acetate

Polymerization temperature (°C)	Increase of swelling volume with time (cm^3) 0	1 min	2 min	3 min	5 min	10 min	20 min
45	1.90	2.20	2.35	2.50	2.75	3.25	3.40
52	2.80	3.10	3.30	3.50	3.65	3.80	3.90
60	3.85	4.50	5.30	5.40	5.50	5.55	5.55
Program	2.70	3.20	3.45	3.60	3.75	3.80	3.80

that the sample obtained by polymerization with programmed temperature corresponds in porosity and sorption characteristics of the plasticizer to the poly(vinyl chloride) obtained at a constant temperature, which is supposed to indicate the same value K. Examination of the data on swelling of the PVC samples in ethyl acetate presented in Table 4 leads to the same conclusion.

The data on the thermal stability of the PVC samples are shown in

TABLE 5. Thermal Stability of PVC Samples

Method	Polymerization temperature			
	45°C	52°C	60°C	Program
Congo Red (sec)	38	42	45	43
Brabender Plastograph				
Total stability (min)	14.7	15.5	13.5	19
Elongation strength, (kg-f)	1.44	1.28	1.10	1.50
Duration constant couple (min)	12	13	11	14.5

Tables 5 and 6. The results obtained by using the Congo Red method and the Brabender thermal stability values are shown in Table 5. The values found by means of the Congo Red method for the PVC obtained at 52°C and for that PVC obtained with temperature programming, lead to the conclusion that both PVC samples have the same thermal stability. On the other hand, the Brabender plastograph data indicate that the poly(vinyl chloride) obtained with temperature programming has better thermal stability. As it is known, the Brabender thermal stability method is the most reliable of those used for the estimation of PVC workability.

Analysis of the percent weight loss data from Table 6, indicates that the poly(vinyl chloride) obtained with the programmed temperature (conversion C = 80%) has a better thermal stability than the other samples.

The activation energy and the order of the reaction of dehydrochlorination are in agreement with the literature data for PVC. The results of the activation energy measurements and of the temperature of dehydrochlorination of the model compounds [17] demonstrate that the PVC stability is determined by the concentration of the labile groups, by the number of the units connected in syndiotactic chains, and the position of the labile groups, in comparison with the syndiotactic sequences from the macromolecule.

The thermal stability of the PVC is also influenced by the particle size [18]. Since the stereoregularity of all PVC samples examined is similar [19], we have tried to establish the content of labile groups (Table 7) in the samples obtained by polymerization at constant temperature and in the sample obtained with the temperature program.

TABLE 6. Thermal Degradation Behavior of the PVC Samples

No.	Sample	TGA			Loss in weight at T_m (%)	Order of degradation reaction n	Activation energy (kcal/mole)
		T_i (°C)	T_m (°C)	T_f (°C)			
1	PVC obtained at 45° C, C = 80%	220	282	370	29.6	0.9	44.43
2	PVC obtained at 52° C, C = 80%	200	282	370	34.0	0.8	38.35
3	PVC obtained at 60° C, C = 80%	198	275	368	33.0	1.3	44.73
4	PVC obtained with temperature program, C = 9%	210	282	370	30.0	0.6	44.92
5	PVC obtained with temperature program, C = 30%	210	275	380	35.0	0.5	43.26
6	PVC obtained with temperature program, C = 55%	200	275	370	34.3	0.7	35.38
7	PVC obtained with temperature program, C = 80%	210	280	375	24.7	0.0	40.46

TABLE 7. Percentage of Labile Chloride in PVC

Polymerization temperature (°C)	F_{EF}/100 ml THF	C (g/100 ml THF)	Cl_L(%)
45	2.475×10^{-5}	1.444	0.108
	1.950×10^{-5}	1.050	0.107
52	2.425×10^{-5}	1.271	0.121
	1.275×10^{-5}	0.625	0.129
Program	2.125×10^{-5}	1.315	0.101
	1.325×10^{-5}	0.800	0.102

Some of the chloride atoms in PVC with a greater reactivity (called labile chloride) are, to a certain extent, responsible for polymer degradation [20]. Analysis of the data presented in Table 7 shows that the PVC sample obtained by temperature programmed polymerization has the smallest content of labile chloride. The labile chloride content is practically identical in the sample obtained with temperature programming and in the PVC sample obtained at 45°C. On the other hand, Caraculacu et al. [13] found that there is an inverse relation between the average molecular weight and the labile chloride content.

Because the average molecular weight of the PVC sample obtained at the programmed temperature is smaller than that of the sample obtained at 45°C (Table 1, [7]), the labile chloride content should be greater in the case of the former sample, but this was not found to be so.

Consequently, it can be said that carrying out a polymerization process with a constant rate for the entire duration, of reaction by means of a temperature program supposed to ensure, at the same time, a constant rate of evolution of reaction heat, determines a decrease in the labile chloride content. This fact has, as a final result, a slight improvement of the thermal stability, as compared to the polymer having the same K value but obtained by polymerization at constant temperature.

It is noted (from Table 2) also that the sample obtained with the programmed temperature reactions contains 76% particles with dimensions greater than 315 μm as compared to 71.5% in the sample obtained at 45°C.

According to the data of Guyot and Bert [18], the difference, in the dimensions of PVC particles can be one more factor to partially contribute to the explanation of the slightly improved thermal stability of the PVC obtained at programmed temperature.

CONCLUSIONS

The analysis of the experimental data suggests that the poly(vinyl chloride) obtained with the programmed temperature is equivalent to the poly(vinyl chloride) obtained at the same constant temperature having the same K value. However, it seems that the volumetric properties are slightly poorer, while the thermal stability is slightly better. A thorough study of these values based on a greater number of samples is necessary in order to permit final conclusions.

Depending on the temperature program used and consequently the magnitude of the constant rate of polymerization, a K value of the polymer can be pre-established, if one can anticipate the plasticization and gelation behavior, as well as the melt flow under the conditions of optimal use of the reaction volume over the whole duration of the polymerization process.

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