

On the Rheology of Molten Binary Blends of Polyolefins. X. Homogeneity and High Shear (Poiseuille's) Melt Flow of Polypropylene-Polyethylene Blends

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Synopsis

Statistical analysis of inherent viscosities (LVN), shear modulus (G^*), and melting temperature (T_m) interval data for isotactic polypropylene-linear polyethylene (HDPE) blends was performed in order to verify their microheterogeneity. High shear measurements in viscometric (Poiseuille's) flow were carried out on four replicated compositions of the blends. Least-squares treatment of the results yielded power law parameters for the blends differing in composition. The significance of differences between the blends of various HDPE content was tested using the multiple-range (Duncan's) test, and tentative conclusions are drawn on the composition dependence of the melt flow viscosities of the blends.

INTRODUCTION

Increasing industrial importance^{1,2,3,30,78,96} of the blends of polymers, resulting from their advantageous processability⁴ and versatility of end-use performance inspired numerous reviews devoted to the compositions of homopolymers. The majority of the research was done on blends of elastomers (e.g., Corish⁵) and three-component ABS-type blends.⁶⁻¹⁰ Only a few papers are devoted to melt flow of blends of crystalline polymers,^{4,11,12,13} and none of these covers the high-shear melt flow behavior of the blends.

Thermodynamic description of the state of aggregation for polymer blends, in spite of marked advances in thermodynamics of mixtures of liquids,¹⁴⁻¹⁶ is in the early stages of development.^{17,18} Because of the high consistency of polymer blend components, their "thermodynamic" immiscibility, as predicted by thermodynamic excess functions, yields little practical information on the actual state of aggregation of a blend of polymers.

Similarly, the actual theories of laminar mixing for very viscous, non-Newtonian liquids^{19-24,95} offer but a semiquantitative criterion for adequacy of mixing in form of the striation thickness concept.²⁰

Significant dependence of the melt flow behavior (even in homopolymers) upon test sample preparation and shearing history,²⁵⁻²⁹ as well as the

above-mentioned inadequacies of thermodynamic and engineering mixing theories for polymer-blend state of aggregation, render the melt rheometry of those systems particularly prone to errors. Before considering ways for minimizing these, it seems pertinent to recapitulate commonly employed criteria for the homogeneity of polymer blends. (The homogeneity, "single-phasedness," of a blend is often an undesirable characteristic from the standpoint of either end-use performance or processability of polymer blends.^{5,6,10,91})

Thermodynamic Criteria. These consist of functions of state for undiluted blends,^{17,18,31,32} interaction parameters in dilute solutions for blends and for components,³³⁻³⁵ and phase equilibrium at melting, and breadth of melting temperature interval.^{36,45}

Viscoelastic Criteria. These are criteria based upon the viscoelastic response of blends, i.e., temperature (or frequency) dependence for complex (shear or elongation) moduli of the blends in the linear viscoelasticity range; permanence of characteristic relaxation processes for the blend components as envisaged in a three-dimensional modulus (frequency—temperature—composition space).⁵⁸⁻⁶¹ This "relaxation spectrometry criterion"^{43,46-61} is usually supplemented with auxiliary data from stress relaxation,⁴⁸ tribometric,⁶² and rheoptical^{39,46,48} measurements. In view of the findings of Ferry⁶⁴ and Kuleznev et al.^{65,66} that the property—composition graphs are not necessarily linear even for homopolymers (e.g., blends of polymer fractions) the "additivity criterion" approach in estimating the homogeneity of a blend could be dismissed as inadequate in spite of its widespread use in the past.^{14,39,41,42,63,65-68} It is perhaps worth underscoring here that, because of the prominent dependence of the linear viscoelastic behavior of crystalline polymers upon the thermal history of the test sample, the "relaxation spectrometry criterion" applied to blends of crystalline polymers at temperatures below T_m may lead to erroneous conclusions.

Optical Criteria. These criteria encompass a wide range of tests from gross uniformity tests (i.e., based on naked-eye comparison with a reference sample), to microscopic examination for persistent spherulitic forms of components in a blend,^{6,39,48,62,69} to the composition dependence of the refractive index for dilute solutions and blends.⁷⁰ Infrared and ultraviolet light transmission spectra at selected bands^{4,6,39,46} as well as IR dichroism and x-ray scattering from the foils made from blends should be considered as an important extension of optical criteria.

There was also an attempt to employ the *extractability* of a component from the blend as a measure of the components' compatibility.⁷¹

Numerous attempts to formulate the phenomenological approach in describing the composition dependence of the viscoelastic behavior for polymer blends, i.e., using models describing the interaction of components within a blend,^{12,54,55,56,72-77} are applicable only at the linear viscoelasticity range. Hence these are of little value in the quantitative estimation or the shear rate dependence of melt flow behavior of crystalline polymer blends.^{12,13,75}

In spite of numerous industrial applications,^{2,4,78,96} the polypropylene-polyethylene blends were studied as such only in a few cases.^{4,11,36,39,46,48,62,92,93} These blends were commonly employed as model mixtures of crystalline polymers^{3,42,44,47,59,67,68,79} or as reference compounds in evaluating the state of aggregation of ethylene-propylene block copolymers.^{37,51,69} So far, the melt flow behavior of molten crystalline polymer blends was studied either in the low shear rate, quasi-Newtonian range^{11,13} or in low-frequency forced oscillation experiments.^{62,79} Studies into the viscoelastic behavior of polypropylene-polyethylene blends within the melting range were concluded with a simple supermolecular mechanism^{61,62} of "molten polyethylene reinforced with stiffer polypropylene."¹¹ However, a marked increase in the molten blend fluidity upon the introduction of a small amount of polypropylene,³⁰ as well as structural transitions observed for molten ethylene-propylene copolymers⁶¹ in Poiseuille's flow suggests that the shear flow of the blends, at least for a certain range of compositions, is better described with the Schuur-Vegt's hypothesis of shearing-induced "crystallization" in a molten blend.⁸²⁻⁸⁴ In view of the complex shear rate-composition dependence of the melt viscosity of polypropylene-polyethylene blends in the Poiseuille's flow,³⁰ it is surprising that apparently there were no attempts to evaluate the significance of differences in properties of blends of varying compositions.⁸⁵ The analysis of significant differences is a prerequisite for an assessment of the reproducibility of the blending method employed, as well as for the admissibility of the interpolation in melt viscosity-composition graphs. Hence, Poiseuille's melt flow of the polypropylene-polyethylene blends should be investigated for accurately standardized test samples, i.e., having the same uniformity and with exclusion of blends obtained via coprecipitation^{25,28} and employing strictly reproducible rheometric procedure.

The present work is intended as a check for the extent, reproducibility, and range of increase in fluidity of molten linear polyethylene resulting from the introduction of a small quantity of polypropylene.

It was also interesting to evaluate both shear rate and composition dependence of this melt viscosity suppression. The reproducibility of the blending method employed was checked by statistics of melt rheometry data for four replications of each of the blended compositions. Such a statistic is also important for other reasons: (a) the width of the fiducial limits for rheological parameters is an indication of the adequacy of the mixing,²⁰ and (b) the analysis of significant differences in melt flow characteristics for blends differing in composition is a necessary prerequisite for comparing the viscoelastic behavior of the blends in the transition zone, below T_m .

The latter results from a dependence of the complex modulus (G^*)-temperature relationships for crystalline polymers on the development of spherulitic texture. Apparently, the viscoelastic behavior of molten blends of crystalline polymers does not depend on the *thermal* history of the test sample. Hence, the melt flow properties of the blends are a resultant of temperature, shear, and macromolecular characteristics only.

EXPERIMENTAL

Evaluation of Structure Characteristics

Dilute solution viscosities were measured with an Ubbelohde viscometer at 120°C (viscosity number at 0.5 g/dl, tetralin, designated *T* 120) and with a Desreux-Bischoff viscometer at 135°C (limiting viscosity number, LVN, in decaline as solvent obtained according to ISO DR 754, designated *D* 135). Flow rate for the blends was measured according to ISO DR 1001 procedure N, i.e., at 190°C under a load of 10 kg.³ IR spectrophotometry (UR 10 spectrophotometer, C. Zeiss, Germany, at 840,900 and 1660 cm⁻¹ bands) was employed for comparing the IR spectra for blends and components, as well as for checking the effect of blending on blend degradation. Densities were measured using the M 309 (Davenport, London) density gradient column and standardized samples cut from extrudates obtained during the measurement of molten viscosities at $v_{hz} = 0.5$ cm/min. Such standardization of test samples meets the requirements of the nominal density test ASTM D 1298-65T. Melting behavior was studied for all the replications of the blends and for the components with a crossed polaroids microscope (ASTM D 2117-64) and for selected replications of blends and components with DTA.⁴⁴ A set of control measurements with a Perkin-Elmer differential scanning calorimeter was additionally performed for some of the replications and components. The heating rate was 1.8°C/min. Results of the above measurements together with other characteristics are listed in Table I.

TABLE
Structural and Performance Characteristics of

N _{o.}	Characteristics	AS	ASHos 15	ASHos 25
1	Av. mol wt $\bar{M}_v \times 10^{-3}$	620-580 ^c	410-460	162-178
2	Density, d_{23}^{40} , g/cm ³	0.9070	0.9127	0.9171
3	Flow rate	8.5	10.6	11.6
4	Melting temperature interval ΔT , °C	168-171	163.5-175	166.5-171
5	Tensile strength, R_t , kg/cm ²	350	252-350	326-368
6	Elongation at break ϵ_r , %	14-22	10-14	6.3-10
7	Storage modulus G' , kg/cm ² , at 20°C	6680	5990	6780
	0°C	10400	6840-10000	8500-12300
8	Stiffness in flexure, E_t , kg/cm ²	2220	2670	2841
9	No. of blend replications for rheometric evaluation	(\emptyset)	5(\odot)	8(\circ)

^a AS = 100% polypropylene; ASHos 15 = 85% (wt-%) polypropylene, 15% (wt-%) polyethylene, etc., Hos = 100% polyethylene.

^b R. Chiang, *J. Polym. Sci.*, **28**, 235 (1958). Average from four measurements.

^c J. B. Kinsinger, *J. Phys. Chem.*, **63**, 2002 (1959).

Mechanical Properties and Relaxation Spectrometry

The tensile strength behavior of the blends was evaluated according to the ISO R 527/66 method. Compression-molded, 2-mm-thick test samples were employed. Tensile tests were carried out at room temperature and elongation speed of $\dot{\epsilon} = 50$ mm/min. Stiffness in flexure according to ASTM D 747 was measured at 20°C with a Tinius Olsen stiffness tester on compression-molded test samples, 80 × 2 × 4 mm, cut out from plaques. Temperature dependence of logarithmic damping decrement, Λ (ISO DR 537),⁶⁷ was investigated for compression-molded foils, strips 60 × 10 × 0.5 mm, at temperatures of from -60° to +170°C. A AZ 450 torsion pendulum was used, in which the sample is weighted with an inertial disc. Unless otherwise specified, all test samples were used in the "as received" state, i.e., without additional thermal treatment.⁶⁷ Because of different sensitivities of the complex shear modulus (G^*) components toward particular molecular relaxation processes,^{57,59} both G' and G'' were calculated from Λ . Results of the torsional oscillation damping measurements were collected in Figure 1.

Melt Flow Rheometry

Melt flow rheometry was studied using a commercial constant shear rate viscometer (MCER) coupled to the TTM-type Instron universal testing machine at temperatures of 190° ± 0.5°C and 210° ± 0.5°C for selected replications of the blends. All the capillaries have conical entrance of 90°, and dimensions as shown in Table II.

I

Polypropylene-Polyethylene Blends and Their Components

ASHos 50	ASHos 75	Hos	Testing method
140-155	115-125	92-100 ^b	ISO DR 754 decalin, 135°C
0.9269	0.9364	0.9474	ISO DR 823 density gradient column
13.6	11.5	2.4	ASTM D 1238-65T Method N
170.5-176.5	165.5-166.5	128-130	ASTM D 2171-64 hot-stage microscope
248-301	232-289	300	ISO DR 527/66
6.3	6.3-9	120	
5664	5290	6680	ISO R 537
7300-8400	6400-7680	—	
2768	2223	2100	ASTM D 747
12 (○)	4 (○)	(○)	(points on graphs)

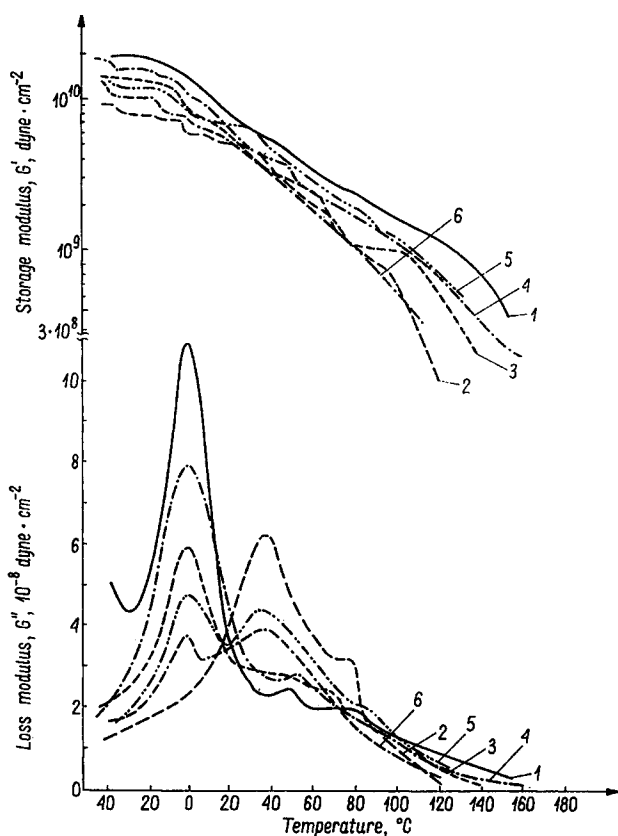


Fig. 1. Temperature dependence of storage (G') and loss (G'') moduli for polypropylene-polyethylene blends: (1) polypropylene; (2) polyethylene; (3) ASHos 15; (4) ASHos 25, (5) ASHos 50; (6) ASHos 75.

TABLE II
Capillary Dimensions

No.	Length l , mm	Diameter d $\pm 0.5\%$, mm	Ratio l/d	Material
1	25.501	0.7708	33.08	Tungsten
2	50.927	1.2827	39.70	Carbide
3	51.029	0.7683	66.41	
4	1.300	0.6850	1.89	Brass

A No. 2 capillary was employed in tentative measurements, and a No. 4 orifice in the evaluation of entrance effects.⁸⁶ From results of the tentative measurements, the importance of thorough cleaning of the rheometer barrel become apparent. The traces of the force of extrusion F_e for measurements with unclean reservoir were irregular, and in such cases the attainment of steady flow conditions (stationary force, F_e), especially at low piston speeds v_{hz} , was very slow (ca. 30 min at $V \cong 1 \text{ sec}^{-1}$).

Standardizing the Rheometric Procedure

Upon completing the tentative measurements with a No. 2 capillary, further measurements were performed in three stages.

The first, directed toward estimation of the piston height effect, encompassed measurements with capillaries Nos. 1 and 3. The reservoir of the rheometer was filled up to height $L = 200$ mm. Results of these measurements were used in the estimation of the dependence of piston height L on extrusion force F_e .

The results of the measurements (F_e -extrusion time graphs) plotted for whole reservoir length L as well as those at several "sections" of L (e.g., for the lowest v_{hz}) generally deviate from a linear F_e - L correlation. Ratios of the pressure drop in the reservoir, p_B , to that in the capillary, p_C , i.e., p_B/p_C , do not depend on v_{hz} ; $p_B/p_C \leq 1$ only at v_{hz} lower than 1 cm/sec, for $v_{hz} \geq 1$ cm/sec (p_B/p_C) increases. As indicated by Skinner, the p_B/p_C ratio should be a linear function of L .³⁷ In fact, it was found that p_B/p_C decreases with plunger descent down to $L = 50$ - 20 mm, when there is a minimum on the F_e -time graph (polypropylene, capillaries Nos. 1 and 3, whole range of v_{hz}). For orifice No. 4 and shear rates $V \geq 75$ sec⁻¹, force F_e does not depend on L . At higher shear rates (180-753 sec⁻¹), F_e decreases with decrease in L . At still higher shear rates, exceeding $V = 1880$ sec⁻¹, F_e increases (while L decreases) down to a maximum at $L = 100$ mm and then decreases linearly with L .

The extrusion of polyethylene is in general characterized by a linear piston height dependence of F_e , except for an increase of the force F_e at low values of L . Experimental values of the p_B/p_C ratio differ from those estimated from Skinner's formula³⁷: $p_B/p_C = (L/l) \cdot (r/R)^{3n+1}$.

The highest deviations were found during the flow of molten polypropylene through orifice No. 4. For the flow of molten polyethylene, the deviations are smaller: theoretical value of p_T/p_C is 1.8; actual values, 1.2 to 1.3, depending on the range of shear rates ($p_T = p_B + p_C$). Good agreement between experimental and theoretical values was found for polypropylene and the No. 1 capillary, though the dependence of F_e on L is nonlinear. In the case of capillary No. 3 and polyethylene, the measured decrease in extrusion force is $\Delta F_e/F_e = 7$ - 10% , as compared with a theoretical value of 2% .

The foregoing discussion necessitated a standardization of the sequence of shear rates and standardization of piston height increments ΔL over which forces F_e were to be measured.

The second stage of the rheometric studies consisted, therefore, of measurements of F_e at a set sequences of shear rates V performed for standardized height of reservoir filling, L_0 . At this stage, the least-squares treatment was employed in order to determine the flow curves for blends and the components, as well as for checking the significance of differences between the flow curves for replications of particular blends and for components. This check encompassed, of course, all pertinent levels of shear rate.

Also the initial height of melt in the reservoir was reduced to $L_0 = 70$ mm, and the sequence of shear rates programmed for the third stage of measurements was corrected.

At the last stage, the measurements were aimed at an estimation of melt flow activation energies, E_P . The sequence of plunger velocities was $v_{hz} = 0.5, 0.2, 0.1, 0.05, 0.02, 0.01, 0.005, 0.5,$ and 1.0 cm/min. As a result of the standardized procedure, the accuracy of measurements increased, i.e., the average error in melt viscosity was reduced from $E_\eta = 10\%$ (first series of measurements) to $E_\eta = 4\%$ (third series).

A tentative estimation of the entrance correction for the nominal shear stress P was carried out with a "zero length" capillary (i.e., orifice)⁸⁶ and yielded corrections within the error of melt viscosity determination (E_η).

Bagley's correction procedure could not be employed since the MCER rheometer used was not equipped with a continuous shear rate setting system, and hence the procedure would be admissible for a single shear rate ($V = 53$ sec⁻¹). The nominal shear stresses P were therefore employed throughout. This is perhaps justified, considering both the length⁸⁴ of the capillaries used ($l/d \geq 30$) as well as the fact that elastic effects associated with Poiseuille's melt flow of the blends were investigated simultaneously with the R 17 rheoniometer and via extrudate swell measurements.⁸⁸

Polypropylene-Polyethylene Blends

These were prepared on laboratory roll mills under standardized conditions of temperature ($190^\circ \pm 1^\circ\text{C}$), time (10 min), speed (16 rpm), and friction (1:1.15).^{3,4} Structural characteristics of the components and blends are presented in Table I. The blends are designated ASHos 15, 25, 50, and 75, the letters being short forms for the trade names of the components (Moplen AS—Montecatini S.p.A., Milan; and Hostalen GD2—Hoechst A.G., Frankfurt/Main) and the numbers corresponding to the wt-% content of polyethylene (Hos) in a blend.³ Corresponding volume per cent contents of polyethylene in the blends are 14.41, 24.13, 48.83, and 74.11%. All the blends were prepared in four replications of each composition.⁴

RESULTS AND ANALYSIS OF EXPERIMENTAL DATA

Qualitative evaluation of the uniformity of the blends via variance analysis for selected test data of properties was performed.

Although gross uniformity of the blends was ascertained during melt mixing and on 0.5-mm-thick compression-molded samples,¹⁹ a closer examination of this important characteristic was obviously pertinent.

Results of dilute solution viscosity measurements in a single concentration (VN) are presented in Table III. The statistics of VN data for all the blend replications indicate that the mixing procedure employed yields reproducible results. Nevertheless, considering the close proximity of \overline{VN} for ASHos 25 and ASHos 15 blends, these were compared using the total

significant difference (TSD) test.⁸⁹ This yielded $\bar{S}(\bar{X}) = 0.049$ and TSD $S(X) = 3.76$, hence TSD = 0.184. Since the difference between $\bar{V}N$ for the blends considered is $\Delta\bar{V}N = 3.639 - 3.521 = 0.118$, which is smaller than 0.184, this difference is insignificant.

TABLE III
Miscibility Estimation from the Statistics of Viscosity Number^a

Statistics	ASHos 15	ASHos 25	ASHos 50	ASHos 75
Number of measurements, n	15	16	16	16
Arithmetic mean, $\bar{V}N$	3.639	3.521	3.073	2.643
Standard deviation, S_{VN}	0.227	0.113	0.072	0.084
Error of a measurement, $S_{VN}/VN \times 100\%$	6.2	3.2	2.3	3.2
Confidence interval for a measurement, $\pm t_{0.05} \cdot S_{VN}$	± 0.497	± 0.241	± 0.153	± 0.179
Median, Me	3.53	3.51	3.07	2.63
Error of the mean, %	1.6	0.8	0.6	0.8
Standard deviation of the mean, $S_r \times 10^3$	59	28	18	22
Confidence interval for the arithmetic mean, $\pm t_{0.05} \cdot S_r$	± 0.127	± 0.060	± 0.038	± 0.046
Range, R_{VN}	0.71	0.36	0.26	0.31

^a I.e., reduced viscosity of solution; solvent, tetralin; temp., 120°C.

Analysis based on the temperature dependence of complex shear modulus G^* for the blends are collected in Table IV and presented in Figure 1. It is apparent from the graph that the characteristic relaxation processes (CRP) of the blend components are preserved: peaks of the loss modulus G'' for the blends appear at the same temperatures as those for the homopolymers (components). Differences in height of the peaks might be ascribed to minute differences in the development of spherulitic texture between test samples. Data represented in the graph confirm the findings that the polypropylene-polyethylene blends are microheterogeneous.^{36,30,42,47} Dependence of the viscoelastic behavior of the crystalline polymers on the degree of the development of spherulitic structure⁴³ markedly hinders attempts to estimate the significance of differences between the blends at temperatures below the melting range (Table IV).

TABLE IV
Miscibility Estimation from Statistics of Loss Modulus G''_{\max} ^a

Statistics	ASHos 15	ASHos 25	ASHos 50	ASHos 75
Arithmetic mean $G'' \times 10^{-8}$	8.76	10.08	8.05	7.55
Standard deviation for a measurement $S_{G''} \times 10^{-8}$	1.68	1.65	0.155	0.121
Error of measurements $E_{G''}$, %	19.29	16.37	1.93	1.60
Confidence interval $\epsilon_{G''}$, $\pm t_{0.05} \cdot S_{G''}$	± 7.09	± 5.03	± 0.49	± 0.39

^a CPR β at ca. 0°C.

Wide confidence limits for the CRP of the blends necessitate a check for the significance of differences. It was again performed using the TSD test, and the following results were obtained: $TSD \cdot S(\bar{X}) = 4.29$; for $S(\bar{X}) = 0.55$, $TSD = 2.36$. At this value of TSD only the differences between ASHos 25 and ASHos 75 are significant ($\Delta\bar{G}'' > TSD$).

An additional check of the significance of differences was therefore required. Student's *t*-test was employed for this purpose, yielding significant differences associated with errors of 13% for ASHos 25 and ASHos 50 and 20% for ASHos 50 and ASHos 75, and reaching 50% for the ASHos 15-ASHos 50 pair.

The melting behavior of the blends, i.e., both the composition dependence of the width of melting temperature interval⁴ as well as the DTA and DSC traces, yield qualitative^{43,44} confirmation of microheterogeneity of polypropylene-polyethylene blends.^{36,39,42,46,47,48,77} On the basis of melting temperature interval breadth⁷ (see also $E_{G''}$ in Table IV) one could speculate that the most homogeneous blend is ASHos 75, while ASHos 15 is the most heterogeneous.⁴⁸ Statistics of Poiseuille's flow data for the molten blends at 190°C and 210°C for some of the blend replications are presented in Tables V (first series of measurements), VI (standardized measurements at 190°C), and VII (standardized measurements at 210°C).

In order to check the significance of the differences between blends replication at all levels of shear rate studied, the analysis of variance (Bartlett's *F*-test) was employed. The limiting value of the test function F^0 (Table V) was chosen on a 0.95 confidence level. For the blends ASHos 15, 25, and 75, no significant differences *within* given composition (i.e., between the replications) were found. On the other hand, for ASHos 50, the differences in melt flow behavior could be considered significant at shear rates up to $V = 50 \text{ sec}^{-1}$. At higher V , there are differences between replications even at the 0.99 confidence level. Nonetheless, since values of η for two replications of ASHos 50 were close to the group (i.e., ASHos 50) average $\bar{\eta}$, one of them, No. 12, was selected for further investigation. The composition dependence of the melt viscosity for the blends was then studied using similarly selected representative replications for the remaining compositions.

On the replications as well as on the blend components, three series of measurements were performed (Table VI). The analysis of significance applied to the linear dependence of $\log P$ and $\log V$ indicate that at the range of shear rates employed, the correlation is significant at the 0.001 level and the coefficient of correlation $R > 0.99$ for all blends investigated. Therefore, least-squares treatment for the calculation of the flow curves and of the power law exponent n was admissible. Values of n were subsequently employed in correcting shear rates after Rabinowitsch.

A comparison of the flow curves indicates (Fig. 2) that the melt viscosities η of polyethylene are higher, in the whole range of shear rates, than the viscosities of the blends and of polypropylene. The flow curves for the latter, however, are so closely positioned that only by using statistical analysis could one resolve whether the differences between their placement

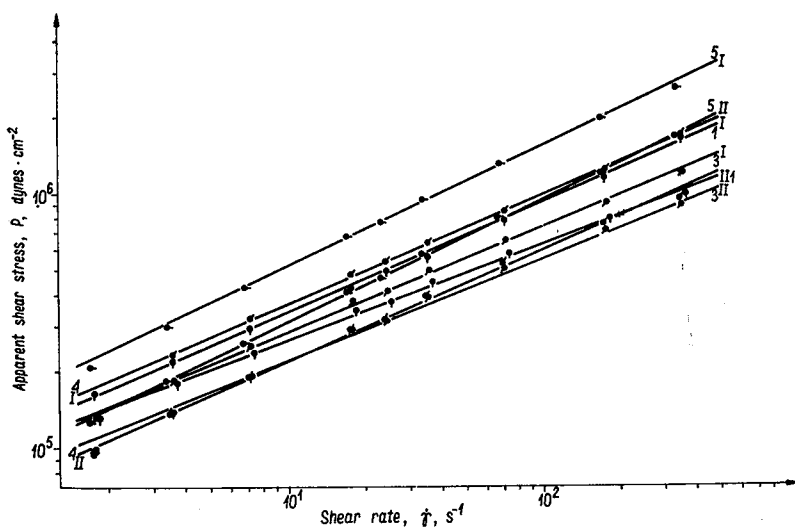


Fig. 2. Flow curves plotted using the least-squares method. See Fig. 3 for the description.

are within, or exceed, the experimental error. The multiple range (Duncan's test) was employed for this purpose.⁹⁰ Because, in general, the flow curves are not parallel to each other (differences in slope n), the conclusions would depend on the range of the shear rate considered.

Results of Duncan's test (D) reveal that within the whole range of shear rates, the melt viscosities η of polypropylene and of the ASHos 50 blend differ significantly from each other and the remaining blends. For ASHos 15, 25, and 75, however, at certain shear rate ranges differences in melt viscosities become insignificant. Hence, there are insignificant differences between melt viscosities for ASHos 25 and ASHos 75 at shear rates $V = 5 \sim 15 \text{ sec}^{-1}$. For $V = 15 \text{ sec}^{-1}$, all the three blends are undistinguishable; but at $V = 40 \sim 350 \text{ sec}^{-1}$, there are significant differences between the melt viscosities of all the blends and the components.

It is apparent from Figure 3 and Table VII that the introduction of a small amount of polypropylene significantly increases the melt fluidity of polyethylene. This effect, important from the standpoint of processability, ranges from 15% to 40% at $V = 1.35 \text{ sec}^{-1}$ to a 50% to 75% reduction of viscosity at $V = 530 \text{ sec}^{-1}$ for ASHos 75 and ASHos 50, respectively. The shear stress dependence of melt viscosities at 190° and 210°C is plotted in Figure 4. In this graph, the least-squares calculated (open circles) and experimental (filled circles) values are compared; the former were subsequently employed in estimating the constant shear stress melt flow activation energies, E_P , for some of the blends (Table VIII).

Composition dependence of the rheological melt flow equation exponent n is presented in Figure 5. In Figure 6, the composition dependence of the standardized melt flow viscosity η^0 is shown; η^0 is related to reference shear rate $\dot{\gamma}^0 = 1 \text{ sec}^{-1}$, hence $P = P^0(\dot{\gamma}/\dot{\gamma}^0)^n$ and $\eta^0 = P^0/\dot{\gamma}^0$, P^0 being the shear

TABLE V
 Rheometric Data for Selected Repetitions of Blends—First Series of Measurements: Accuracy of Measurements Standardized for $L_0 = 135$ mm and Data for Statistical Test of Significance of Among-the-Blend-Replication Differences^a

Piston speed v_{hz} , cm/min	Shear rate V , sec ⁻¹	Polypropylene			ASHos 15			ASHos 25		
		E_{η} , %	$\bar{P} \times 10^{-6}$, $\bar{\eta} \times 10^{-3}$	1^b	E_{η} , %	$\bar{P} \times 10^{-6}$, $\bar{\eta} \times 10^{-3}$	5^b	E_{η}	$\bar{P} \times 10^{-3}$	8^b
0.005	1.32	3.3	1.57	119.0	15.0	1.57	119.0	6.0	1.38	104.5
0.010	2.64	1.8	2.19	82.9	7.0	2.14	81.1	2.0	1.95	73.9
0.020	5.28	2.3	2.94	55.7	7.4	2.91	55.1	2.7	2.68	50.8
0.050	3.20	1.6	4.27	32.3	7.3	4.25	32.2	4.5	3.92	29.7
0.100	26.40	2.4	5.67	21.5	7.2	5.60	21.2	1.7	5.20	19.7
0.200	52.80	2.0	7.67	14.5	9.4	7.48	14.2	5.2	6.76	12.8
0.500	132	3.2	10.80	8.2	10.5	10.70	8.1	4.7	9.45	7.2
1.000	264	3.7	14.25	5.4	9.4	13.80	5.2	7.4	12.20	4.6
2.000	528	9.0	20.50	3.9	13.0	8.70	3.5	8.6	16.00	3.0
5.000	1320	—	—	—	14.0	29.20	3.2	—	24.60	1.9
Average error of a measurement, \bar{E}_{η} , %			3.9			10.2				4.8
Range of error R_{η} , %			1.8-9.0			7.3-15.0				2.0-8.6

Piston speed v_{hor} , cm/min	Shear rate V , sec ⁻¹	ASHos 50			ASHos 75			HDPE		
		E_{η}	$\bar{P} \times 10^{-5} \bar{\eta} \times 10^{-3}$	$\bar{\eta} \times 10^{-5}$	E_{η}	$\bar{P} \times 10^{-5} \bar{\eta} \times 10^{-3}$	$\bar{\eta} \times 10^{-5}$	E_{η}	$\bar{P} \times 10^{-5} \bar{\eta} \times 10^{-3}$	$\bar{\eta} \times 10^{-5}$
0.005	1.32	5.6	1.29	97.7	24.3	1.24	93.9	12.0	1.81	137.0
0.010	2.64	4.1	1.81	68.6	15.0	1.78	67.4	7.7	2.63	99.6
0.020	5.28	3.0	2.54	48.1	10.4	2.54	48.1	5.2	3.72	70.5
0.050	3.20	3.3	3.83	29.0	6.7	3.83	29.8	2.1	5.84	44.2
0.100	26.40	1.8	5.11	19.3	4.00	5.34	20.2	1.1	8.13	30.8
0.200	52.80	2.2	6.79	12.9	3.0	7.25	13.7	1.3	11.17	21.2
0.500	132	2.1	9.83	7.4	6.8	10.70	8.1	0.9	16.57	12.6
1.000	264	2.3	12.67	4.8	5.6	14.23	5.4	0.7	21.77	8.3
2.000	528	5.7	16.63	3.2	3.4	18.80	3.6	—	27.90	5.3
5.000	1320	—	23.60	1.8	2.0	26.53	2.0	18.0	32.80	2.5
Average error of ^a measurement, \bar{E}_{η} , %			3.3			8.1			4.9	
Range of error R_{η} , %			1.8-5.7			2-24			0.7-18	

^a Capillary $d = 0.077$ cm ($\pm 0.05\%$); $l/d = 33.08$, 190°C, GRM dynamometer. Designation: $\bar{\eta}$ = apparent melt viscosity, poises; \bar{P} = av. apparent shear stress, dynes/cm²; ϵ_{η} = confidence limits for viscosity $\bar{\eta}$ at $t = 0.95$ level; E_{η} = relative error, %.

^b Number of selected replications.

TABLE
Rheometric Data for Selected Replications of

Piston speed v_{hz} , cm/ min	Nominal shear rate V , sec^{-1}	Polypropylene			ASHOs 15			ASHOs 25		
		$\dot{\gamma}$	$\bar{P} \times 10^{-5}$	$\bar{\eta} \times 10^{-3}$	$\dot{\gamma}$	$\bar{P} \times 10^{-5}$	$\bar{\eta} \times 10^{-3}$	$\dot{\gamma}$	$\bar{P} \times 10^{-5}$	$\bar{\eta} \times 10^{-3}$
0.005	1.33	1.77	1.62	91.3	1.80	1.42	78.8	1.80	1.31	72.8
0.010	2.66	3.54	2.18	61.6	3.59	1.98	55.2	3.59	1.83	51.0
0.020	5.32	7.08	2.92	41.1	7.18	2.63	36.7	7.18	2.49	34.7
0.050	13.30	17.70	4.20	23.7	18.0	3.88	21.6	18.00	3.73	20.7
0.100	26.60	35.40	5.53	15.7	35.90	5.11	14.2	35.90	4.95	1.4
0.200	53.20	70.80	7.76	11.0	71.80	6.67	9.3	71.80	6.47	9.0
0.500	133.30	177.00	11.43	6.5	80.00	9.51	5.3	180.00	9.07	5.0
1.000	266	354.00	16.47	4.7	359.0	13.33	3.7	359.0	12.00	3.3
Av. flow behavior index \bar{n}^1		0.431			0.414			0.415		
Confidence interval $S_n \cdot t_{0.05}$		0.408-0.454			0.401-0.427			0.391-0.439		
Relative error $S_n/\bar{n} \times 100\%$		2.2			1.3			2.4		
Consistency index, $P^0 \times 10^{-5}$, dyne/cm ²		1.25			1.15			1.08		
Av. apparent viscosity error E_η		6.7			4.6			6.9		
Error range R_η , %		1.8-15.9			1.7-8.0			3.1-24.7		

* Standardized at $L_0 = 55$ mm; capillary: $d = 0.076$ cm ($\pm 0.5\%$); $l/d = 66$; temp. 190°C; CDM dynamometer; \bar{P} and $\bar{\eta}$ as in Table V; $\dot{\gamma}$ in sec^{-1}

^b Number of selected replications.

^c $P = P^0(V/V^0)^n$.

stress corresponding to the reference shear rate.²⁰ The sigmoidal shape of the η^0 -composition graph (Fig. 6), as well as a close similarity of η^0 -composition and η_H -composition data from the curves of Kuleznev¹¹ are worth underscoring, since these indicate that the standardization of melt flow data, an easily attainable and physically sound approach, yields results of comparable value to these obtained via tedious procedure (and not free from rough simplifications) of extrapolating low shear rate melt viscosity data η_H obtained with cone-plate shearing apparatus.

CONCLUSIONS

The blending method employed in the preparation of the polypropylene-polyethylene compositions safeguards satisfactory reproducibility of mixing and is suitable for the preparation of representative test samples. The polypropylene-polyethylene blends obtained in this way are microheterogeneous systems. Melt flow behavior studies indicate that the fluidity of the blends containing up to 25 wt-% polypropylene is markedly higher than that of the components and of the blends of other composition. This find-

VI
 Blends—Second Series of Measurements^a

ASHos 50			ASHos 75			HDPE		
$\dot{\gamma}$	12 ^b		$\dot{\gamma}$	4 ^b		$\dot{\gamma}$	—	
	$\bar{P} \times 10^{-5}$	$\bar{\eta} \times 10^{-3}$		$\bar{P} \times 10^{-5}$	$\bar{\eta} \times 10^{-3}$		$\bar{P} \times 10^{-5}$	$\bar{\eta} \times 10^{-3}$
1.77	1.67	94.4	1.7	1.18	69.4	1.69	2.08	123.0
3.54	2.30	65.0	3.4	1.72	50.6	3.38	2.96	87.6
7.08	3.20	45.2	6.81	2.42	35.5	6.76	4.22	62.4
17.70	4.76	26.9	17.00	3.79	22.3	16.90	6.70	39.6
35.40	6.37	18.0	34.00	5.20	15.3	33.80	9.36	27.7
70.80	8.41	11.9	68.10	7.04	10.3	67.60	13.05	19.3
177.0	12.27	6.9	170.00	10.73	6.3	169.0	19.65	11.6
354.00	16.30	4.6	340.00	14.60	4.3	338.00	25.80	7.6
	0.430			0.471			0.479	
	0.414–0.498			0.959–0.483			0.451–0.507	
	1.6			1.0			2.3	
	1.33			0.966			1.68	
	2.1			4.7			—	
	0.5–6.4			1.6–9.2			—	

ing is significant both for processing applications of the blends as well as in that it extends the melt "viscosity depression" range for the blends beyond 9% polypropylene content.¹¹ The limit of increased fluidity reported in this work is compatible with the mutual solubility criterion of Horino et al.⁴⁸ based on his blend model as well as with the findings of Atarashi³⁶ and Uemura-Takayanagi¹⁸ for polyethylene-polybutene-1 blends. The extent of the melt fluidity increase phenomenon depends on the range of shear rates considered.

It was shown that for the investigation into the composition correlation of blend melt viscosity and of flow curves, analysis of variance is a basic prerequisite. It was also suggested that the assessment of the state of aggregation and of the reproducibility of the mixing process for blends of crystalline polymers should be performed on melt rheometry data, since the viscoelastic behavior of the crystalline polymer blends at temperatures below T_m depends, in an involved way, upon the thermal history of the test samples.

As indicated previously,⁵⁷ the blends of polyethylene containing up to 25% polypropylene exhibit both satisfactory performance characteristics

TABLE VII
Rheometric Data for Selected Replications of Blends—Third Series of Measurements: Data for Least-Squares Melt Flow Curves and for Estimation of Flow Activation Energy^a

Rate of piston travel $\dot{\eta}$, cm/min	Apparent shear rate \dot{V} , sec ⁻¹	Polypropylene			ASHos 25			ASHos 50			HDPE		
		$\dot{\gamma}$	$\bar{P} \times 10^{-3}$	$\dot{\eta} \times 10^{-3}$	$\dot{\gamma}$	$\bar{P} \times 10^{-3}$	$\dot{\eta} \times 10^{-3}$	$\dot{\gamma}$	$\bar{P} \times 10^{-3}$	$\dot{\eta} \times 10^{-3}$	$\dot{\gamma}$	$\bar{P} \times 10^{-3}$	$\dot{\eta} \times 10^{-3}$
0.005	1.32	1.85	1.32	70.80	1.78	0.98	55.1	1.74	0.94	53.4	1.68	1.26	75.00
0.010	2.64	3.70	1.78	48.10	3.56	1.37	38.5	3.48	1.34	38.5	3.35	1.82	54.80
0.020	5.28	7.39	2.36	31.90	7.13	1.90	26.6	6.97	1.88	23.6	6.70	2.54	37.90
0.050	13.20	18.50	3.43	18.50	17.80	2.88	16.2	17.40	2.90	16.7	16.80	4.05	24.10
0.100	26.40	37.00	4.46	12.00	36.60	3.85	10.8	34.80	3.91	11.2	33.50	5.74	17.10
0.200	52.80	73.90	5.77	7.80	71.30	5.04	7.07	69.70	5.24	6.57	67.00	7.93	11.80
0.500	132.00	185.00	7.90	4.25	178.00	7.07	3.97	174.00	7.52	4.32	168.00	11.90	7.09
1.000	264.00	370.00	9.86	2.70	356.00	8.92	2.81	348.00	9.39	2.70	335.00	15.60	4.86
Statistics of rheometric data													
-Av. flow behavior index \bar{n}			0.381			0.418			0.438			0.478	
-Confidence interval, $S_{\bar{n}} \cdot t_{0.05}$			0.369-0.393			0.396-0.440			0.416-0.460			0.461-0.495	
-Rel. error $E_{\bar{n}}$, %			1.3			2.2			2.0			1.4	
-Consistency index $P^0 \times 10^{-3}$, dynes/cm ²			1.09			0.82			0.77			1.02	
-Av. app. viscosity error E_{η} , %			6.5			5.7			4.3			7.6	
-Error range, %			5.4-7.7			4.2-9.5			3.0-7.2			3.0-15.1	

^a Capillary $l/d = 33.08$; temp., 210°C; CDM dynamometer; \bar{P} , $\bar{\eta}$, and $\dot{\gamma}$ as in Table VI.

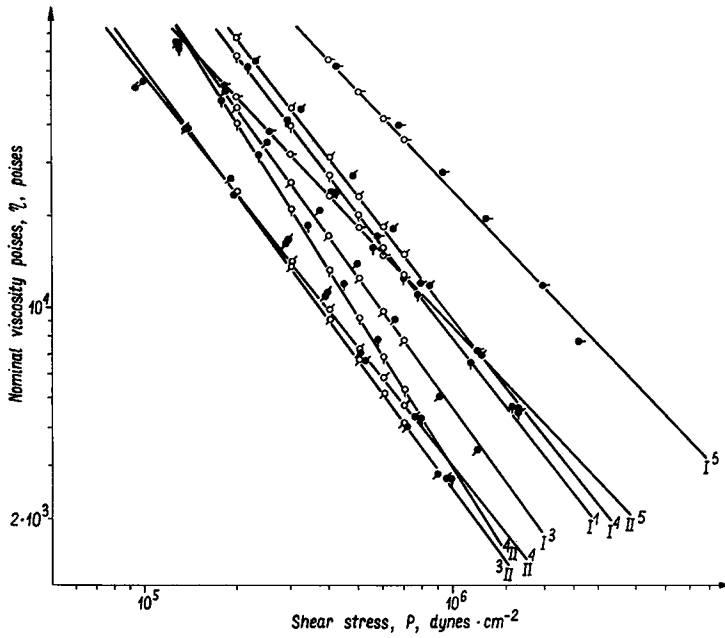


Fig. 3. Shear stress dependence of the apparent melt viscosity η for blends and the blend components at 190°C (I) and 210°C (II). Comparison of least-squares calculated (open circles) and experimental (filled circles) data for (1) polypropylene; (2), (4) blends ASHos 25 and 50, resp.; (5) linear polyethylene.

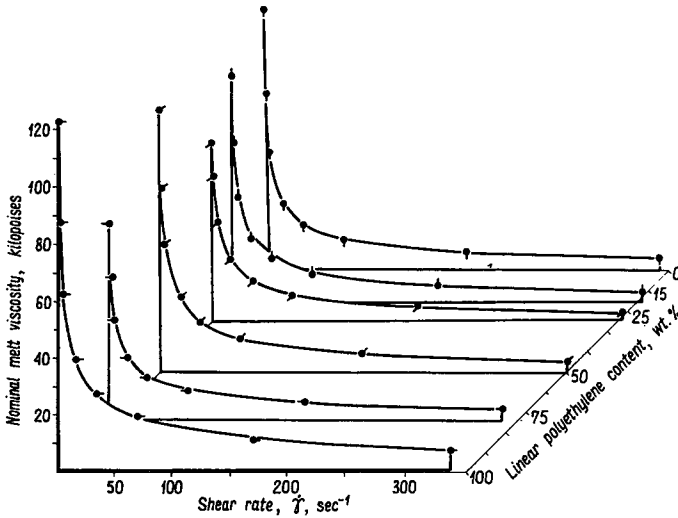


Fig. 4. Composition and shear rate dependence of the apparent viscosity for molten polypropylene-polyethylene blends.

(low brittleness temperatures, high stiffness, high softening point) as well as a good processability (40-70% higher than that of linear polyethylene as estimated from melt fluidities at 190°C).

TABLE VIII
 Statistics of Rheometric Characteristics of Blends and Their Components from Least-Squares Treatment of Data

HDPE-in-the-blend content, wt-%	Average flow behavior index \bar{n} at*		Standard deviation of n , S_n (at 190°C)	Consistency coefficient $P^0 \times 10^{-5}$, dynes/cm ² (at 190°C)	Apparent flow activation energy E_P , kcal/mole
	190°C	210°C			
0 (polypropylene)	0.431	0.381	+0.0096	1.250	11.2-19.5
15 (ASHos 15)	0.414	—	± 0.0055	1.150	—
25 (ASHos 25)	0.415	0.448	± 0.0100	1.080	13.9
50 (ASHos 50)	0.431	0.438	± 0.0068	1.330	25.6
75 (ASHos 75)	0.471	—	± 0.0049	0.966	—
100 (HDPE)	0.479	0.478	± 0.0113	0.680	22.8

* Valid for shear stress (P) range $(2-5) \times 10^6$ dynes/cm².

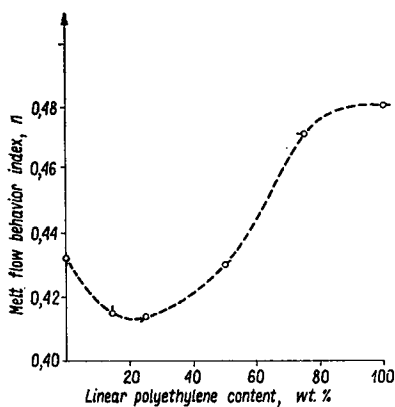


Fig. 5. Composition dependence of the power law exponent for polypropylene-linear polyethylene blends.

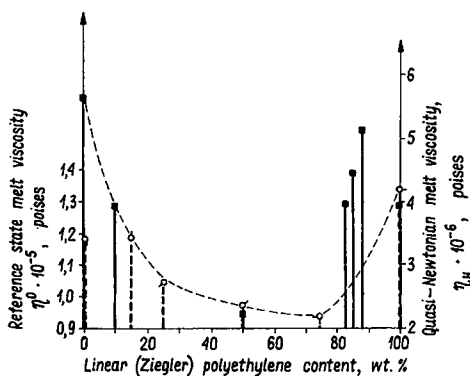


Fig. 6. Composition dependence of standardized apparent viscosity η° (open circles) for Poiseuille's flow and zero shear melt viscosity, η_H (filled squares) for Couette's flow¹¹ for molten blends of polypropylene and linear polyethylene.

List of Symbols

- B* = index referring to the reservoir of the rheometer
C = index referring to the capillary
d = diameter ($2r$) of capillary, cm
D = reservoir I.D. ($2r$), cm
E = relative error (e.g., E_η , Table IV)
E_P = melt flow activation energy, kcal/mole
f = frequency, cps
F = parameter of the analysis of variance
F_e = force for the piston-in-reservoir displacement, kg
*G** = complex shear modulus ($G^* = G' + iG''$), dynes/cm²
GTR = glass temperature relaxation process
HTR = high-temperature (i.e., above T_g) relaxation process
l = length of capillary, cm
L = elevation of the piston above the capillary entrance, or the height of melt in the reservoir, cm
LVN = limiting viscosity number, dl/g
n = flow behavior index exponent in $\tau = \tau^0 (\dot{\gamma}/\dot{\gamma}^0)^n$
N = number of measurements
0 = index for a reference state, e.g., η^0 , L_0
p_T = total pressure drop ($p_T = p_B + p_C$) kg/cm²
Q = volume melt flow rate, cm³/sec
P = nominal, i.e. uncorrected, shear stress, ($P = r \cdot p_T (2l)^{-1}$) dynes/cm²
P_{0.05} = fiducial limits at 0.95 probability level
R = range, e.g., R_η
S = standard deviation, e.g., S_n
S_r = standard deviation of an average
t_{0.05} = Student's parameter at 0.95 level
T = temperature, °C
v_{nz} = speed of piston displacement, cm/min
V = nominal shear rate ($= 4Q/\pi r^3$), sec⁻¹
α_c = compare HTR
α_m = HTR at temperatures in vicinity of melting point
β = compare GTR
 $\dot{\gamma}$ = shear rate ($= V(3n + 1)/4n$), sec⁻¹
ε = confidence interval ($= t_{0.05} S$)
η = nominal melt viscosity ($= P/V$), poises
η⁰ = reference state (here at $\dot{\gamma}^0 = 1 \text{ sec}^{-1}$) melt viscosity, poises
η_H = Newtonian range melt viscosity, poises

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References

1. G. Illing, *Kunstst. Gummi*, **7**, 275 (1968).
2. T. Boianiu, *Mater. Plast.*, **3**, 140 (1966).
3. A. Płochocki, *Plaste. Kautschuk*, **13**, 71 (1966).
4. A. Płochocki, *Polimery* (Warsaw), **10**, 23 (1965).
5. P. F. Corish, *Rubb. Chem.*, **40**, 324 (1967).
6. J. Dasch, *Kunststoffe*, **57**, 328 (1967).
7. Z. Rigbi, *Rheol. Acta*, **5**, 134 (1966).
8. S. L. Rosen and Z. Rodriguez, *J. Appl. Polym. Sci.*, **9**, 1601 (1965).
9. S. L. Rosen, *J. Appl. Polym. Sci.*, **9**, 1615 (1965).
10. S. L. Rosen, *Polym. Eng.*, **7**, 115 (1967).
11. V. N. Kuleznev, et al., *Kolloid Zh.*, **27**, 540 (1965).
12. K. Kunert, Institute for Basic Technical Problems (Warsaw) Report No. 2, 1969.
13. S. Uemura and M. Takayanagi, *J. Appl. Polym. Sci.*, **10**, 113 (1969).
14. F. M. Jaeger, 2nd Rept. on Viscosity and Plasticity, North Holland Publishing Co., Amsterdam, 1938.
15. J. M. Deutch and R. Zwanzig, *J. Chem. Phys.*, **46**, 1612 (1967).
16. R. M. Bowen, *Arch. Rat. Mech. Anal.*, **24**, 370 (1967).
17. Gul V. Ye. et al., *Kolloid. Zh.*, **27**, 341 (1965).
18. P. J. Flory, B. E. Eichinger and B. A. Orwall, *Macromolecules*, **1**, 39, 287 (1968).
19. J. T. Bergen, in *Rheology*, R. F. Eirich, Ed., Academic Press, 1967, Vol. 4, p. 285 ff.
20. J. M. McKelvey, *Polymer Processing*, Wiley, New York, 1962, p. 229.
21. W. D. Mohr, in *Processing of Thermoplastic Materials*, Reinhold, New York, 1959, p. 117, 409; *Ind. Eng. Chem.*, **49**, 1855 (1957).
22. R. E. Lee, et al., *Ind. Eng. Chem.*, **49**, 1949 (1957).
23. A. Kennaway, *Proc. Congr. Problems of Choice*, London, 1963.
24. R. S. Spencer and R. M. Wiley, *J. Colloid Sci.*, **6**, 133 (1951).
25. G. Döring and G. Leugering, *Kunststoffe*, **53**, 11 (1963).
26. R. F. Heitmiller, R. Z. Naar, and H. H. Zabuski, *J. Polym. Sci. A*, **8**, 2977 (1964).
27. R. Longworth and W. F. Busse, *Trans. Soc. Rheol.*, **6**, 179 (1962).
28. R. Ye. Smielkov, V. V. Petrayev, and Y. Y. Sem'chkina, *Plast. Massy*, No. 1 (1966).
29. R. Ye. Smielkov, *Zh. Prikl. Khimii*, **37**, 1310 (1964).
30. P. Dubois, *Ind. Plast. Mod.*, **17**, 101 (1965).
31. M. V. Natov and E. Dzhagarova, *Makromol. Chem.*, **117**, 231 (1968).
32. J. L. Zakin, R. Simha, and H. C. Hershey, *J. Appl. Polym. Sci.*, **10**, 1455 (1966).
33. K. Friese, *Plast. Kautschuk*, **12**, 90 (1965); **13**, 65 (1966).
34. W. R. Krigbaum and F. T. Well, *J. Polym. Sci.*, **5**, 505 (1950).
35. G. R. Williamson and B. Wright, *J. Polym. Sci.* **3A**, 3885 (1965).
36. Y. Atarashi, *Kobunshi Kagaku*, **21**, 210 (1964).
37. E. M. Barral, R. S. Porter, and J. F. Johnson, *J. Appl. Polym. Sci.*, **9**, 3061 (1965); *J. Polym. Sci. 5A*, **2**, 113 (1967).
38. G. A. Clegg, D. R. Gee, and T. P. Melia, *Makromol. Chem.*, **119**, 184 (1968).
39. D. W. Filbert, *Karbotsepynye Volokna, Khimia*, Moscow, 1966, pp. 82-89.
40. G. N. Foster, III, N. Waldman, and R. G. Griskey, *Mod. Plast.*, **43**, 245 (1966).
41. M. Hiram, *Polymer*, **8**, 482 (1967).
42. M. Inoue, *J. Polym. Sci.*, **1A**, 3427 (1963).
43. A. Płochocki, *Kolloid-Z.*, **208**, 168 (1964).
44. M. Wajnryb, *Polimery* (Warsaw), **12**, 117 (1967).
45. T. Yoshimoto and A. Miyagi, *Kogyo Kagaku Zasshi*, **69**, 1771 (1966).
46. T. Asada and S. Onogi, *Zairyo-shiken*, **17**, 59 (1969).
47. H. A. Flocke, *Kolloid-Z.*, **180**, 11 (1962).
48. T. Horino, I. Ogawa, T. Soen, and H. Kawai, *Zairyo-shiken*, **16**, 494 (1967).

49. L. J. Hughes and G. L. Brown, *J. Appl. Polym. Sci.*, **5**, 580 (1961).
50. A. D. McIntyre, *J. Appl. Polym. Sci.*, **5**, 195 (1961).
51. S. P. Kabin and O. G. Usyarow, *Vysokomol. Soedin.*, **2**, 46 (1960).
52. S. Krozer and M. Wajnryb, *Polimery* (Warsaw), **7**, 367 (1962).
53. K. Nakamura, et al., *Rept. Progr. Polym. Phys.*, **11**, (1968).
54. K. Ninomiya, *J. Colloid Sci.*, **17**, 759 (1962).
55. K. Ninomiya and E. Maekawa, *Zairyo-shiken*, **39**, 595 (1966); **40**, 463 (1967).
56. S. Onogi, et al., *Zairyo-shiken*, **15**, 371 (1966).
57. A. Płochocki and Z. Kohman, *Polimery* (Warsaw), **11**, 403 (1966).
58. K. Schmieder, in *Kunststoffe*, R. Nitsche, Ed., Springer-Verlag, Berlin, 1963, Vol. 1, p. 791.
59. C. A. F. Tuijman, *J. Polym. Sci.*, **16C**, 2379 (1967).
60. T. Ueno, Preprints Int. Congr. Macromol. IUPAC, Tokyo, 1966, p. VIII-29.
61. G. V. Vinogradov, et al., *Kolloid Zh.*, **28**, 809 (1966).
62. E. I. Frenkin, Yu. G. Yanovskii, and G. V. Vinogradov, *Mekhanika Polimerow*, **895**, (1966).
63. D. Heinze, *Makromol. Chem.*, **101**, 166 (1967).
64. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1961.
65. V. N. Kuleznev and B. A. Dogadkin, *Kolloid Zh.*, **24**, 652 (1962).
66. V. N. Kuleznev and L. S. Krokhnina, *Kolloid Zh.*, **27**, 211 (1965).
67. G. L. Slonimski, I. N. Musayelan, and V. V. Kazanceva, *Vysokomol. Soedin.*, **6**, 219 (1964).
68. S. Fujiwara and H. Narasaki, *J. Polym. Sci.*, **B1**, 139 (1963).
69. J. Barton and J. Rak, *J. Appl. Polym. Sci.*, **11**, 499 (1967).
70. V. N. Kuleznev and K. M. Igosheva, *Vysokomol. Soedin.*, **4**, 1858 (1962).
71. R. Longworth and D. L. Funck, *J. Appl. Polym. Sci.*, **10**, 1612 (1966).
72. K. Fujino et al., *J. Appl. Polym. Sci.*, **8**, 2147 (1964).
73. M. Horio, et al., *J. Phys. Chem.*, **68**, 778 (1964).
74. T. Kataoka, and S. Ueda, *J. Polym. Sci.*, **5A1**, 3071 (1967).
75. S. Manabe, M. Takayanagi, and S. Uemura, *Kogyo Kagaku Zasshi*, **70**, 525,529 (1967).
76. T. Okamoto and M. Takayanagi, *J. Polym. Sci.*, **C23**, 597 (1969).
77. M. Takayanagi, et al., *Zairyo-shiken*, **12**, 389 (1963); *Mem. Faculty Eng., Kyushu Univ.*, **23**, 1 (1963).
78. K. Thinius, *Plast. Kautschuk*, **15**, 164 (1968).
79. G. V. Vinogradov, et al., *Kolloid Zh.*, **28**, 640 (1966).
80. A. Płochocki and J. Baranówna, *Proc. IVth Symposium on Rheology*, Vroclav, **1**, 129 (1969); see also ref. 88.
81. G. V. Vinogradov, et al., *DAN USSR Seria Khim.*, **179**, 1366 (1968).
82. G. Schuur, *Kolloid-Z.*, **108**, 123 (1966).
83. A. K. Vegt, and P. P. A. van den Smit, *S.C.I. Monographs*, **26**, 313 (1966).
84. G. V. Vinogradov, et al., *Vysokomol. Soedin.*, **10**, 726 (1968).
85. A. Ya. Malkin, private communication, 1966.
86. R. F. Westover and B. Maxwell, *SPE J.*, **13**, 27 (1957).
87. S. J. Skinner, *J. Appl. Polym. Sci.*, **5**, 55 (1960).
88. A. Płochocki, *Polimery* (Warsaw), **16**, 223 (1971).
89. J. W. Tukey, *The Problem of Multiple Comparisons*, Princeton, N. J., 1953; unpublished: cited after W. Volk in *Applied Statistics for Engineers*, New York, McGraw-Hill, 1958, ch. 7.
90. M. B. Duncan, *Biometrics*, **11**, 1 (1955).
91. Z. Hashin, *Appl. Mechanics Rev.*, **17**, 1 (1964).
92. M. V. Natov and E. Ch. Dzhagarowa, *Vysokomol. Soedin.*, **8**, 1835 (1966).
93. N. W. Michailov and E. Z. Fainburg, *Vysokomol. Soedin.*, **4**, 237 (1962).
94. V. Semjonow, *Advan. Polym. Sci.*, **5**, 387 (1968).

95. H. Ohyo and T. Miyauchi, *Kagaku Kogaku*, **5**, 118 (1967).
96. E. V. Minkin, H. K. Baramboim, and A. G. Akudimov, *Plast. Massy*, No. 4, 8 (1967).

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