

Copolymerization of Vinyl Chloride with 1-Olefins. Part IV. Investigation of Rheological and Mechanical Properties of Copolymers

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Synopsis

Copolymers of vinyl chloride with propene, 1-butene, and 1-pentene having the same content of 1-olefin (4.0 ± 0.5 mol%) and various molar mass and copolymers with a comparable molar mass and the same composition were prepared. By measuring rheological and mechanical properties of this assembly of samples, which also included the reference vinyl chloride homopolymer, it was possible to estimate the effect of molar mass and of the individual comonomers. The copolymers under investigation possessed improved processing properties and did not suffer any deterioration of important mechanical properties.

INTRODUCTION

Copolymers of vinyl chloride and propene, which have been manufactured on an industrial scale for many years, are a type of internally plasticized materials, the flow properties and thermal stability of which are better than those of the usual vinyl chloride homopolymers. The possibilities of application of this copolymer are rather wide—it may be applied in any case where the processibility of hard PVC is to be improved.

The introduction of propene structural units into a poly(vinyl chloride) macromolecule renders the polymer chain more flexible.^{1,2} A similar effect can be assumed also for higher 1-olefins which so far have received only minor attention.^{3,4} The properties of these copolymers depend predominantly on the comonomer content in the copolymer and also on the degree of polymerization reached.

Both factors were studied using samples of copolymers of vinyl chloride with propene, 1-butene, and 1-pentene containing 4.0 ± 0.5 mol% olefin, with respect to their application and technological accessibility, because preparation of copolymers with a major comonomer content is greatly complicated by the low reaction rate and is connected with a pronounced drop in molar mass. The copolymerizations were carried out making use of findings obtained in our earlier work.^{5,6}

Some physical properties of the copolymers in powder form were determined, their flow and plasticization curves and dynamic thermal stability were

measured; they were subjected to tensile and notch strength tests and to tests of shape stability on heating. The respective temperature dependences of the dynamic shear modulus were also determined.

MATERIALS

Vinyl chloride (Spolana, Neratovice), content of impurities 90 ppm at most (H_2O 73 ppm, methyl chloride 9 ppm, vinylacetylene 6.5 ppm, 1,3-butadiene 5 ppm, ethyl chloride 4 ppm, iron < 0.5 ppm). Propene (Slovnaft, Bratislava), content of impurities 0.7% at most (hydrogen 1290 ppm, alkanes $\text{C}_1\text{—C}_4$ 0.5%). 1-Butene (Merck-Schuchardt), purity 99% (isobutene 0.7%, 1,3-butadiene 0.1%). 1-Pentene (Merck-Schuchardt), purity 97%. Dicylperoxydicarbonate (Kema-Nord, Stockholm), peroxide content 73.5%, active oxygen content 2.2%. Dilauroylperoxide (Peroxid-Chemie, Munich), peroxide content 96.8%, active oxygen content 3.9%. Hydroxypropylmethylcellulose (Dow Chemical Co.), viscosity of a 2% solution 4.598×10^{-2} Pa · s. Hydroxypropylcellulose (Hercules Powder Co., USA), viscosity of a 2% solution 1.933×10^{-2} Pa · s. Cyclohexanone (Lachema, Czechoslovakia), purified by boiling with K_2CO_3 and distilling. Tetrahydrofuran (VEB Laborchemie Apolda, GDR), freed from peroxides and distilled. Dioctylphthalate (Urx Works, Czechoslovakia). Stabinox VME 1057 (Henkel, FRG).

METHODS

Copolymerization

The copolymerizations and homopolymerizations of vinyl chloride were carried out in a stainless steel reactor of the duplicator type, 5 dm³ in volume (Ingenieurbureau, SFS, Zürich) with built-in stops. Revolutions of the propeller stirrer were adjusted to 500 min⁻¹, the temperature was regulated with an accuracy of $\pm 0.3^\circ\text{C}$.

The overall amount of monomers dosed into the reactor was 1237 g in all cases, the amount of distilled water was 2933 g, the total amount of suspension stabilizers was 142.5 g (3.8% solutions). Further data, including the reaction conditions of the individual experiments, are summarized in Table I.

The copolymers were decanted, filtered, and dried at 60°C to constant mass. The comonomer content was determined from the results of elemental analysis (i.e., from determination of carbon carried out with a C—H—N automatic analyzer, Perkin-Elmer, Model 240).

K value⁷ and bulk density were measured using standard procedures (Czechoslovak standard 643200 and Czechoslovak standard 640804), similar to the sieve analysis by washing with water (Czechoslovak standard 640212) and to the porosity measurement by centrifugation (cf. internal instruction).

The mass average molar mass was determined by the light scattering method. Dilute solutions of selected samples dissolved in tetrahydrofuran were measured in polarized light, wavelength 5461 nm, in an angular range 30–150° (Photo-Gonio-Diffusiometer, Fica, Model 42000, France).

TABLE I
Results of Homopolymerizations and Copolymerizations of Vinyl Chloride

Sample	DCPD ^a [g]	Temperature [°C]	Time [h]	[M ₂] ^c [mol%]	{M ₂ } ^d [mol%]	Conversion [%]	K value ^e	M _w ^f
1 ^g	0.692 ^b	68.5	6.0	0	0	78.5	46.2	37,000
2 ^g	4.448	70.0	8.5	8.5P	4.3	64.9	46.8	33,500
3	4.448	65.0	8.5	7.5P	4.0	83.0	49.1	—
4	4.448	58.0	10.0	7.5P	4.5	84.7	52.9	—
5	4.448	51.0	11.5	7.5P	4.5	78.9	57.6	—
6	8.896	58.0	12.5	9.3Bu	4.3	47.4	42.0	—
7	8.896	58.0	12.0	7.5Bu	3.7	57.2	44.2	—
8 ^g	8.896	51.0	14.0	8.5Bu	4.2	47.6	46.2	35,700
9	8.896	46.0	18.0	8.9Bu	3.8	38.4	48.5	—
10	8.896	55.0	16.0	9.0Pe	4.5	59.4	43.8	—
11 ^g	8.896	51.0	16.0	8.6Pe	4.2	59.3	46.4	36,000
12	8.896	48.0	16.0	7.5Pe	3.7	60.9	48.6	—
13	8.896	44.0	20.0	8.0Pe	3.7	54.1	51.2	—

^aAmount of dicylperoxydicarbonate.

^bDilauroylperoxide (0.829 g) and trichloroethylene (30.5 g) were also used.

^cContent of 1-olefin in the starting monomeric mixture (P = propene, Bu = 1-butene, Pe = 1-pentene).

^dContent of 1-olefin in the copolymer.

^eCf. Materials and Methods section.

^fMass average molar mass.

^gSamples used in the investigation of the effect of individual 1-olefins.

Flow Properties

The flow properties were evaluated by means of a high-pressure capillary viscometer HKV 2000 (Göttfert, FRG) at 180°C, using a 9.5 mm diameter cell and a nozzle, 1 mm in diameter and 60 mm long. The flow time of 2 cm³ of the melt was measured at various pressures, using samples with mechanical properties determined in advance.

The pseudoplastic behavior of the polymer melt was described in terms of the so-called power law, known also as the Ostwald-de Walle equation⁸:

$$\tau = K \cdot \gamma^n \quad (1)$$

in which the relation between the shear stress, τ , and the shear rate, γ , is expressed simply by means of two experimentally determined constants (i.e., by the index of flow behavior n and by the consistency index K). Using the apparent viscosity, Eq. (1) may be rewritten to

$$\eta = \frac{\tau}{\gamma} = K \cdot \gamma^{n-1} \quad (2)$$

or to its logarithmic form, which is more frequently used:

$$\ln \eta = \ln K + (n - 1) \ln \gamma \quad (3)$$

When measuring the flow properties, correction for the following factors must generally be considered: entrance effects, elastic energy absorbance, head effects, kinetic energy effects. The measurements performed in our case were comparative ones, when the uncorrected form of apparent flow curves is fully satisfying, and no corrections were therefore considered.

Plasticization Rate and Dynamic Thermal Stability

The plasticization rate and dynamic thermal stability were measured with a Plasti-Corder Brabender apparatus, type PLE 651 (FRG), provided with a kneading cell of the W 30 H type. Samples (30 g) were kneaded at 160°C for 20 min at 20 rpm. The dynamic thermal stability of a sample (36 g) was measured at 170°C and 100 rpm until the onset of its degradation, indicated by a rise in the torsional moment after plasticization of the sample.

Samples for rheological and mechanical tests were prepared with the addition of four mass parts of Stabilox, VME 1057 (combined stabilization and lubrication system) to the tested polymer of copolymer.

Mechanical Properties

The test bodies were prepared by rolling a standard blend of powder polymer, followed by pressing plates from the rolled film and mechanical processing of prethermostated plates to the normalized shapes. The tests are very demanding as regards the amount of tested material; for this reason, only some basic tests were chosen for the characterization of the assembly samples.

Conditions of preparation of test bodies: rolling proceeded 5 min at 21 rpm and friction 1:1.3; with samples 6-13 (Table I) at 120°C, samples 2-5 at

150°C, and sample 1 at 175°C. Pressing took place at 170°C and a pressure of 30 MPa with samples 2–13, and at 185°C and the same pressure with sample 1. The samples were preheated 3 min without pressure, then exposed to pressure for 5 min, and cooled with pressure for 2 min. Thermostating lasted 10 h at 70°C.

Determination of the yield stress, yield strain, tensile strength, and strain-at-break was carried out using a universal tensile tester ZWICK 1464 (FRG) at 23°C, 50% relative air moisture, and at the cross head speed 50 mm/min (Czechoslovak standard 640605).

Notch impact strength (Czechoslovak standard 640612) was tested using a CHARPY pendulum (Frank, FRG), under the same climatic conditions as in the case of the tensile test.

Thermal shape stability according to Vicat (Czechoslovak standard 640521) was determined using CEAST 6510 apparatus (Switzerland) with an oil medium.

The temperature dependence of the real component of the shear modulus G' and the mechanical loss factor $tg\delta$ were determined by the free torsional oscillations method with a ZWICK 5203 Torsiomatic apparatus (FRG) at the temperature rise rate 60°C/h and in the temperature range between -150 and +150°C. The complex shear modulus G^* is defined by

$$G^* = G' + iG'' \quad (4)$$

where G' is the real and G'' is the imaginary component of G^* . For the mechanical loss factor ($tg\delta$) we have:

$$tg\delta = G''/G' \quad (5)$$

RESULTS AND DISCUSSION

Copolymerization

The relationship between reaction conditions, composition of the reaction mixture, comonomer content in the copolymer, and the K value of the samples or their molar mass is shown in Table I. This assembly of samples was further used in rheological measurements and measurements of mechanical properties. All copolymers contained a comparable amount of the comonomer component (4.0 ± 0.5 mol%). Differences in their molecular parameters made possible an investigation of the effect of molar mass on the rheological and mechanical properties. Samples 1, 2, 8, 11, which are comparable not only with respect to their composition, but also to their molar mass, allow us to estimate the effect of the individual 1-olefins on the properties in question.

We used the K value as the criterion of molar mass of the samples, being aware that in the case of copolymers this solution is not quite correct. However, in view of the low content of 1-olefin in copolymers and of the results obtained by the light scattering method with some selected samples we assume that this procedure satisfies our purpose.

Some physical properties of the polymers are summarized in Table II. It can be seen that, compared with the vinyl chloride homopolymer, the copolymers have a much higher porosity and a lower bulk density. The higher

TABLE II
Basic Physical Properties of Samples (Powder)

Sample	Bulk density (g dm ³)	Porosity (cm ³ g ⁻¹)	Sieve analysis (%)					
			63	71	100	125	160	250 [μ m]
1 ^a	522	0.111	87.9	81.7	63.8	48.3	47.2	19.7
2 ^a	322	0.551		53.0		1.2		
3	435	0.332		80.7		1.6		
4	399	0.434	85.8	81.0	40.4	12.8	3.5	0
5	363	0.525		90.0		17.8		
6	189	0.993		88.8		23.3		
7	243	1.171	98.2	86.6	66.6	21.8	5.4	0
8 ^a	197	0.850		74.0		17.8		
9	153	0.973		51.4		43.4		
10	315	0.720		83.4		15.3		
11 ^a	324	0.795		87.2		33.0		
12	287	0.919	90.6	86.4	67.5	42.6	13.5	0.7
13	205	0.886		85.2		31.4		

^aSamples used in the investigation of the effect of individual 1-olefins.

TABLE III
Results of Measurements of Flow Properties

Sample	K value ^a	K' ^b	n ^b	γ^b (s ⁻¹)
1 ^c	46.2	1.8479	0.59	200–500
2 ^c	46.8	1.8653	0.51	300–1000
3	49.2	2.1776	0.51	150–400
4	52.9	2.9218	0.45	150–400
5	57.6	3.0801	0.49	100–250
6	42.0	0.1964	0.71	150–800
7	44.2	1.3020	0.57	70–400
8 ^c	46.2	1.8772	0.50	300–1000
9	48.4	2.4007	0.48	150–500
10	43.8	1.1575	0.56	700–2000
11 ^c	46.4	1.8045	0.51	250–1000
12	48.4	2.1943	0.49	200–600
13	51.2	2.8530	0.42	100–400

^aCf. Materials and Methods sections.

^bCf. Eq. (1), $K' = \ln K$.

^cSamples used in the investigation of the effect of individual 1-olefins.

porosity is closely connected with the relatively low final copolymerization conversions of vinyl chloride with 1-butene and 1-pentene. Similar to the case of the particle size distribution, bearing in mind the character of this study, we did not try to remove these differences by further experiments. Moreover, the preparation of copolymers of vinyl chloride with the 1-olefins investigated in this study requires a sensitive manipulation with all factors involved, such

as 1-olefin content in the starting mixture of monomers, reaction temperature, initiator concentration, copolymerization time.

Flow Properties

Constants in Eq. (1), K , K' ($K' = \ln K$) and n were obtained by the least-squares method. The values calculated for the individual regression straight lines corresponding to the measured samples are given in Table III. The range of shear rates within which the flow properties were measured are also recorded in the table. For greater clarity the effect of the molar mass of copolymers on their flow properties is illustrated using the vinyl chloride-propene copolymer (Fig. 1), that of comonomers can better be seen in Figure 2.

With increasing molar mass of the samples the flow properties deteriorate, completely in agreement with general findings. The index of flow behavior and the consistency index are very sensitive also to small differences in the K value of the samples.

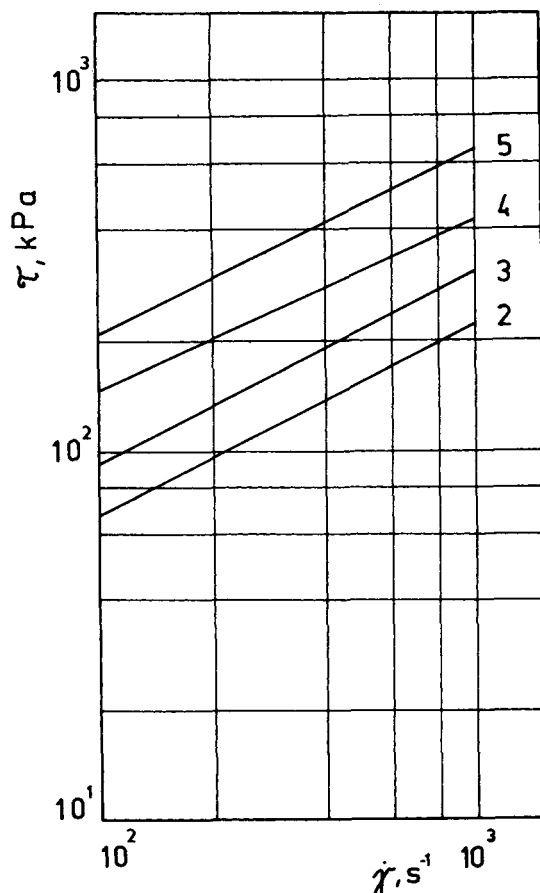


Fig. 1. Dependence of shear stress τ on shear rate $\dot{\gamma}$ for copolymers of vinyl chloride with propene having various molar mass; K values: (2) 46.8, (3) 49.1, (4) 52.9, (5) 57.6.

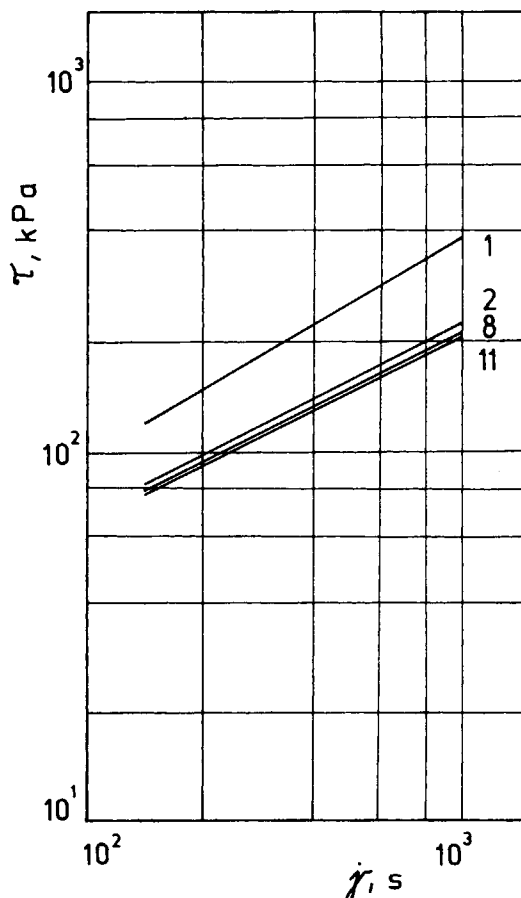


Fig. 2. Dependence of shear stress τ on shear rate $\dot{\gamma}$ for copolymers of vinyl chloride with 1-olefins and the reference homopolymer of vinyl chloride; (1) PVC, (2) VCM-P, (8) VCM-Bu, (11) VCM-Pe.

From the results presented in Figure 2 we can see that at a relatively low content of 1-olefins in the copolymer (ca. 4.0 mol%) there are no important differences between the individual comonomers with respect to their flow properties. The higher fluidity of the melt of all copolymers compared with the vinyl chloride homopolymer is due to the presence of olefinic structure units in the poly(vinyl chloride) chain and to their "softening" effect. It should be pointed out that alkyl side substituents, similar to low molecular weight plasticizers, cause an increase in the free volume and raise the mobility of chains.

Rate of Plasticization and Dynamic Thermal Stability

When measuring the plasticization curves, it was found that the time of plasticization increases with the molar mass of the samples, similar to the maximal torsional moment and to its stationary value (Table IV). With increasing molar mass it is more difficult for the polymer to pass from the heterogeneous dry blend to the homogeneous melt. Plasticization curves

TABLE IV
Results of Measurements with the Plasti-Corder Brabender

Sample	K value ^a	t^b [min]	$M_{R_{max}}^c$ [N · m]	$M_{R_{20}}^d$ [N · m]	DTS ^e [min]
1 ^f	46.2	3.7	14.0	12.0	77
2 ^f	46.8	4.0	12.5	10.3	99
3	49.2	12.0	13.3	12.5	75
4	52.9	> 20	—	—	48
5	57.6	does not plasticize	—	—	37
6	42.0	2.1	9.5	7.2	130
7	44.2	3.0	12.2	9.7	121
8 ^f	46.2	3.5	13.5	10.6	114
9	48.4	9.0	13.7	12.8	101
10	43.8	2.0	10.8	7.8	167
11 ^f	46.4	3.2	12.5	10.2	139
12	48.8	5.5	13.4	11.7	106
13	51.2	13.0	13.7	13.4	88

^a Cf. Materials and Methods sections.

^b Plasticization time.

^c Maximal torsional moment value.

^d Stationary torsional moment value.

^e Dynamic thermal stability.

^f Samples used in the investigation of the effect of individual 1-olefins.

measured for the vinyl chloride-1-pentene copolymer are summarily shown in Figure 3. Table IV also demonstrates the very small drop in the plasticization time with increasing length of 1-olefins used; the difference in the values of torsional moments between the vinyl chloride homopolymer and copolymers is more pronounced. This finding is adequately related with the better flow properties of copolymers discussed earlier.

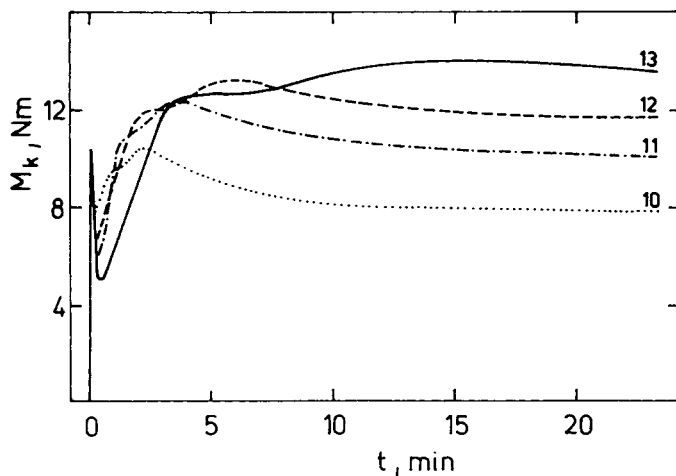


Fig. 3. Plasticization curves of copolymers of vinyl chloride with 1-pentene differing in molar mass; K values: (10) 43.8, (11) 46.4, (12) 48.6, (13) 51.2.

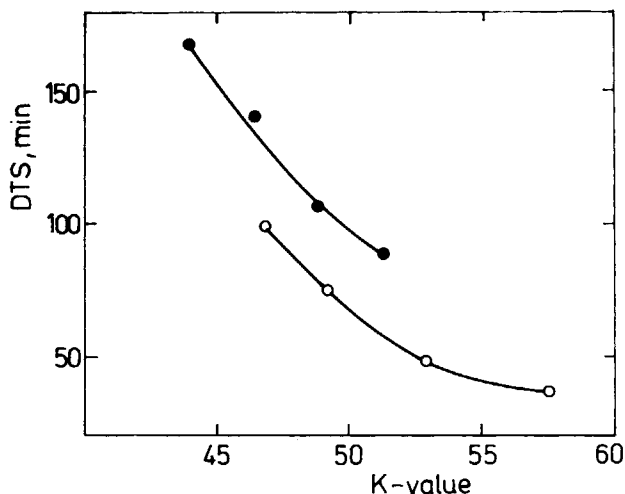


Fig. 4. Effect of molar mass on dynamic thermal stability (DTS) for copolymers of vinyl chloride with propene (○) and 1-pentene (●).

Dynamic thermal stability decreases with increasing molar mass of the polymers, because longer macromolecules raise the viscosity of polymer melt; more heat is released during kneading, and the sample is subject to greater mechanical and thermal stress. The effect of the individual 1-olefins can also be demonstrated. With increasing alkyl length on the copolymer chain plasticization of the polymer becomes more pronounced, and the dynamic heat

TABLE V
Results of Measurements of Mechanical Properties

Sample	K value ^a	σ_y^b [MPa]	ϵ_y^c [%]	σ_b^d [MPa]	ϵ_b^e [%]	a_k^f [kJ/m ²]	Vicat ^g [°C]	T_g^h [°C]
1 ⁱ	46.2	56.8	5	38.2	22	2.4	80	88
2 ⁱ	46.8	54.3	4	32.2	13	2.6	72	82
3	49.1	54.4	4	38.7	8	2.8	73	
4	52.9	64.7	5	34.9	11	2.9	74	
5	57.6	64.1	5	36.4	10	4.5	75	
6	42.0	—	—	—	—	1.0	67	
7	44.2	22.5	2	11.8	5	1.1	69	
8 ⁱ	46.2	56.3	3	35.2	12	2.7	69	80
9	48.5	56.8	5	35.9	11	2.9	71	
10	43.8	56.8	4	32.3	14	2.4	66	
11 ⁱ	46.4	56.0	5	32.6	14	3.0	68	80
12	48.6	55.8	4	35.4	14	3.5	69	
13	51.2	56.2	5	34.5	17	3.6	70	

^aCf. Materials and Methods sections.

^bYield stress.

^cYield strain.

^dTensile strength.

^eStrain at break.

^fNotch strength.

^gThermal shape stability according to Vicat.

^hGlass transition temperature.

ⁱSamples used in the investigation of the effect of individual 1-olefins.

stability values increase. These findings are documented in Figure 4, which reflects the effect of molar mass on the dynamic heat stability of the copolymer of vinyl chloride with propene and 1-pentene.

Mechanical Properties

The tensile test provided data on the strength of the copolymers at room temperature; no important effect of molar mass or of the length of the side chain on the parameters measured could be detected (Table V). With increasing molar mass there is no pronounced change in tensile strength or strain at break. Samples having the lowest K value were particularly difficult to measure, since due to their low toughness the test bodies often cracked beyond the working part. This in turn caused a higher scatter of the measured values, and thus also a greater error of measurement. With sample 6 the measurement was completely impeded.

The notch impact strength slightly increases both with molar mass and with the length of the side chain (Table V). As a rule, the K values of the samples lie below the commonly produced types of poly(vinyl chloride), for which the notch strength usually varies about 4 kJ/m². From trends known from Table V one is justified to assume that the notch strength of copolymers with the usual K values (60–70) would be somewhat higher than that of poly(vinyl chloride).

The observed effect of the comonomer length is related to the so-called "diluent" effect of side chains,⁹ the presence of which reduces the interaction

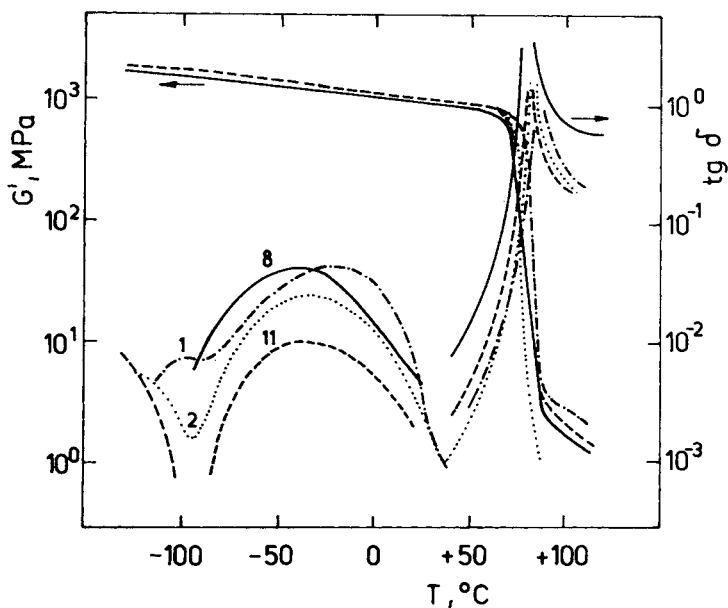


Fig. 5. Dependence of the mechanical loss factor ($tg\delta$) and of the real component of dynamic shear modulus (G') on temperature (T) for copolymers of vinyl chloride with 1-olefins and for the reference homopolymer of vinyl chloride; (1) PVC, (2) VCM-P, (8) VCM-Bu, (11) VCM-Pe.

between the main chains. This brings about a decrease in the glass transition temperature, because the motion of segments of the main chains takes place at a lower temperature. The main chains of the polymer which have become more mobile then may better absorb the impact energy, which helps to improve the toughness of the material. In the case of poly(vinyl chloride) modified with 1-olefins the side substituents, which are nonpolar and not too bulky, help to paralyze the effect of dipoles of the $-\text{C}-\text{Cl}$ bonds which otherwise also participate in producing the high softening point of poly(vinyl chloride). The same effect of the side chains on the glass transition temperature has also been observed with polyacrylates and polymethacrylates.¹⁰

Results of an investigation of the thermal shape stability (Table V) and dynamic behavior (Fig. 5) also support the preceding reasoning regarding the plasticizing effect of side chains and the effect of their length. From Table V it can be seen, however, that the thermal shape stability and the glass transition temperature are not reduced linearly with the length of 1-olefin and that the relatively strongest influence is exerted by the presence of a methyl substituent on the copolymer chain, while the transition from methyl to ethyl and then to propyl gradually becomes less and less pronounced. Measurement of the dynamic behavior is in agreement with this statement. Curves of the temperature dependence of the mechanical loss factor and of the dynamic shear modulus are correspondingly shifted towards lower temperatures (Fig. 5), thus reflecting the decrease in the glass transition temperatures (Table V). The difference in the shear modulus values can be seen only with 1-butene, but the decrease is not pronounced.

CONCLUSION

A detailed investigation of dependencies between composition of the starting reaction mixture and reaction conditions allowed us to prepare copolymers of vinyl chloride with propene, 1-butene and 1-pentene which have the same molar comonomer content and a comparable molar mass. The copolymers possess improved flow properties, their plasticization curves are shifted toward lower values of torsional moments, and they have a markedly improved dynamic thermal stability. Despite the relatively low content of 1-olefins in the polymer chain (ca. 4 mol%), one could see that in some cases the properties just mentioned become more markedly improved if higher 1-olefins are applied. The differences are not so important, however, to justify any speculations concerning the replacement of the commercially available copolymer of vinyl chloride with propene by the copolymer of vinyl chloride with 1-butene, which can be isolated from the C_4 -fraction. The low reaction rate of the vinyl chloride-1-butene⁶ system and the higher production costs involved could not be compensated for by an adequate improvement of the properties of poly(vinyl chloride) thus modified.

The mechanical properties (strength, extensibility, toughness) of the copolymers are basically on the level of those of vinyl chloride.

Hence, the investigated copolymers of vinyl chloride with 1-olefins are materials possessing improved processing properties, in which no decrease in any important mechanical property takes place. Virtually in all measurements

a pronounced dependence of the properties on the molar mass of the respective samples was recorded.

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