

RHEOLOGICAL CHARACTERIZATION OF PROCESSABILITY OF UNVULCANIZED POLYBUTADIENE

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ABSTRACT

Rheological investigation on a series of unvulcanized polybutadiene elastomers of different processability has been carried out by means of a capillary extrusion rheometer. It is found that the processability of unvulcanized polybutadiene can be correlated with the occurrence of unsteady flow and the wall stress, dependence of the dimensionless number e characterizing the entrance elongational elasticity which has been found to be sensitive to the branching structure and the molecular weight distribution of the samples. Interpretations based on the structural data of unvulcanized polybutadiene were discussed.

INTRODUCTION

The processability of *cis*-1, 4-polybutadiene (PB) is found to be severely dependent on the polymerization conditions. Using the traditional methods, such as molecular weight determination in dilute solution, Mooney viscosity, are less sensitive for the characterization of the processability of PB products obtained in different polymerization conditions. The method of maximum relaxation time of stress relaxation^[1,2] and capillary extrusion^[3-5] were developed. The relationship among the processability, rheological behavior and molecular structure of rubber have been investigated^[6]. Various structural factors were emphasized by different authors: such as molecular weight, molecular weight distribution, long chain branching, gelling, the content of *trans*-1, 4- and 1,2-polybutadiene elements and crystallization. It has been found that the milling behavior of PB can be correlated with the uncontinuity of the flow curves^[4,5]. More attention is currently being paid to the shear viscoelasticity for this system^[8,9]. However the elasticity behavior in large deformation and the relation between elasticity and the microstructure of the system are less understood. This paper presents the results of structurally well characterized unvulcanized PB samples with quite different milling processability. The dynamic properties of polybutadiene were measured with the Rheometrics Mechanical Spectrometer. Interpretation based on structural data of polymers were discussed. The flow curves, elastic turbulence in shear flow and the elongational elastic responses in the entrance convergent flow were carried out by means of an Instron Capillary Rheometer with diameters of capillary of 0.05" and 0.03", $L/D = 40.0$, entrance angle 90° in temperature range of 80–140°C. Where-in the systems were proved to be stable during testing. A series of Ni-catalytic polymerized PB with very different milling behavior (produced by Yan Shan Petroleum Chemical Company, Beijing) and a rare-earth metal-catalytic polymerized PB sample were chosen. The structural data of the samples are listed in Table 1.

Generally the unsteady flow of polymer melt owing to the high elasticity during extrusion can be divided into three types: (1) Entrance unsteady flow. It can be flow line rotation or swing which causes the extrudate distortion and, even more, the flow lines may be broken, or the elastic turbulence or melt fracture happens. (2) So-called "shark-skin" of the extrudate surface, which is caused by the regulation of the velocity profile at the exit. (3) In the capillary, wall slip may occur

when the shear stress increases to a critical value. These phenomena have been observed in unvulcanized elastomer^[4,7,8]. In our experiment the steady laminar flow appeared at the lower shear rate only for the sample 1[#] and BR-01, which show excellent processability. As the shear rate increase, the shark-skin emerged next then the shear stress increases to a critical value τ_c , the slip on the wall arises. The period of the extrudate of slip (see Fig.1) corresponds the stress-oscillations (as shown in Fig. 2). Shark-skin appears in the region of shear stress increasing, smooth surface of extrudate corresponds to shear stress decreasing sharply and irregular extrudate begins at the minimum of shear stress. It should be pointed out that the irregular extrudate exist even in the case of the short die $L/D=0$, which implies that melt fracture occurs in entrance region.

Table 1 Characterization of unvulcanized PB*

Sample	1 [#]	PR-01	2 [#]	3 [#]	4 [#]	5 [#]
$\bar{M}_n \times 10^{-4}$	14.8	7.1	16.7	13.5	10.7	10.9
$\bar{M}_w \times 10^{-4}$	53.9	32.9	83.9	127	85.2	121
Branching factor $\langle g \rangle$	0.982	0.983	0.950	0.702	0.819	0.429
Content of gel $W/W\%$	1.1	1.7	3.5	2.6	3.8	14.0
cis-1,4 %	96.6	96.1	95.5	95.1	95.4	93.2
trans-1,4 %	1.6	2.4	3.2	3.6	3.4	5.7
1,2 %	1.1	1.1	1.8	1.3	1.3	1.2
Mooney viscosity	44	43	50	49	51	52
Processability behavior	excellent	excellent	not so good	bad	bad	non-processable

* Structure data were measured by Changchun Institute of Appl. Chem., Acad. Sinica.

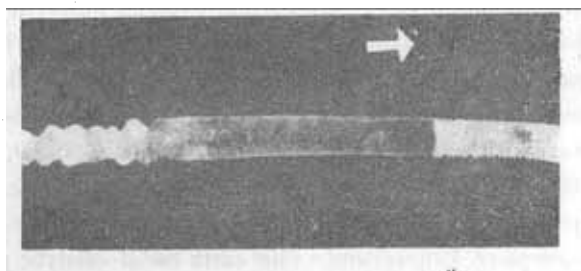


Fig. 1 The shape of the extrudate during one period on extrudate of sample 1[#] at 140°C Capillary $L/D=40$, $0.05'' \times 2''$, arrow indicates the direction of extrusion

The shear stress oscillation was observed for the sample 2[#], too. However, for sample 2[#]—5[#] the entrance unsteady flow emerged at whole range of shear rate of the capillary extrusion. No obvious differences in the surface were observed. Of course it is also possible to measure the pressure loss as a function of the rate of extrusion as some authors did, but the curve does not mean the true flow curve. Fig. 2 shows the typical curves of extrusion for PB samples, Where the

recorded curve of shear stress oscillation is shown in inset. These curves do not reflect the wide different processability of the samples.

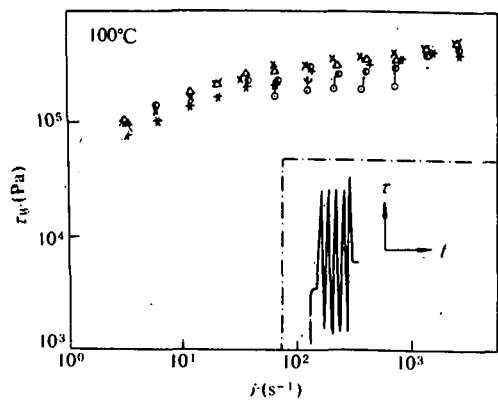


Fig. 2 Pressure loss as a function of shear rate of PB at 140°C, Capillary $L/D = 40, 0.05'' \times 2''$, ■ 1[#], ● 2[#], × 3[#], △ 4[#], • 5[#]. The recorded shear stress oscillation is shown in inset

The entrance unsteady flow exists even for the melt of linear polymer^[9]. Critical shear rate where the unsteady flow occurs will move to the lower rate as the molecular weight increases or especially as the high molecular weight part exists. As shown in Table 2 the range of steady flow for the samples of excellent processability are broader while for the samples with poor processability the entrance unsteady flow is dominant.

The dynamic viscoelastic properties of the samples were measured in Rheometrics RMS-605 as shown in Fig. 3. The difference between G' and G'' indicates the extent of elasticity of the samples. For sample 2[#] and 5[#] the difference is much larger than that of BR-01 and 1[#]. The

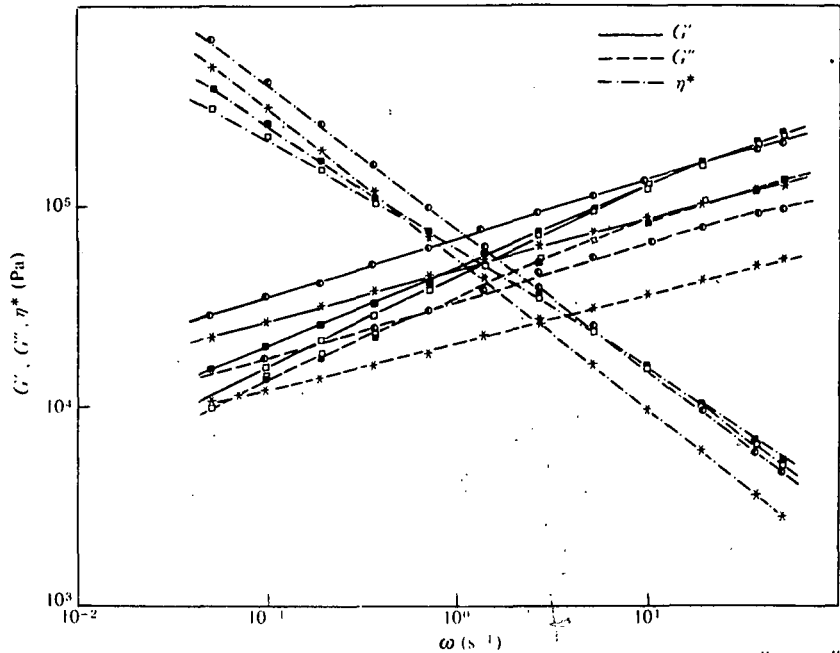


Fig.3 Small amplitude dynamic shear data of PB samples at 140°C. □ BR-01; ■ 1[#]; ● 2[#]; * 5[#]

absolute values of modulus and viscosity have no correlation with processability of rubbers, but the slopes of curves of η^* and G' as a function of frequency shows some differences. The influences of long chain branching on the dynamic responses present similar tendency. Therefore from linear viscoelastic properties it is difficult to judge if the bad processability of PB is caused by long chain branching or by broad MWD.

Table 2 Extrusion property of PB samples

Sample	Smooth laminar flow	Shark skin	Slip at the wall	Start point of the slip		The shape of entrance unsteady flow	
				critical stress (Pa)	critical shear rate (s^{-1})	spiral	elastic turbulence
1 [#]	Y	Y	Y	3.0×10^5	3.0×10^1 (100°C)	Y	Y
				3.3×10^5	8.1×10^1 (140°C)		
BR-01	Y	Y	Y	3.25×10^5	2.7×10^1 (140°C)	Y	Y
2 [#]	N	N	Y	2.3×10^5	3.0×10^1 (100°C)	Y	Y
				3.0×10^5	2.7×10^1 (140°C)		
2A	N	N	Y	3.0×10^5	2.7×10^1 (140°C)	Y	Y
3 [#]	N	N	N			N	Y
4 [#]	N	N	N			N	Y
5 [#]	N	N	N			N	Y

Here we use a useful dimensionless number $e = \Delta P / 2\tau_w$ to reflect the elongational elastic properties of fluid in convergent flow field at the entrance region^[10, 11], where ΔP is the pressure loss of a short die ($L/D \approx 0$) and τ_w is the shear stress at the wall of a long die at the same shear rate. We noted that e is very effective for the characterization of high molecular weight of linear polypropylene^[12] and of the long chain branch PVA^[13], LDPE. Fig. 4 shows the dimensionless number e as a function of shear stress at 140°C for PB samples (2A is the sample with similar behavior to 2[#]). The value e of steady flow increases with increasing shear stress. However in the unsteady flow e may increase or decrease with increasing shear stress. Figure 4 shows clearly that the e - τ curves for samples with excellent process behavior goes up and those with bad processability go down. The arising curves are mostly in the laminar flow region, while all the dropping curves are completely in the unsteady flow region. For several branching polymers it has

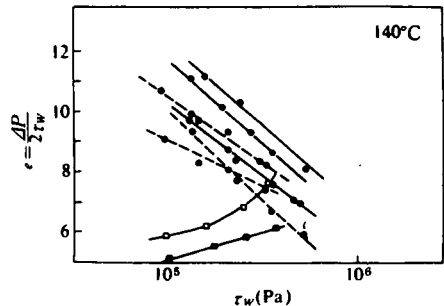


Fig.4 e as a function of shear stress for PB samples at 140°C Dotted line are the data after degraded.

□ BR-01, ■ 1[#], ● 2[#], ○ 2A, ● 3[#]

been reported^[13] that the value of e is high at low shear stress and may even decrease at high shear stress of unsteady flow. It is noted that some samples in Fig.4 were previously degraded by extrusion through capillary several times at 140°C. So their e value are lower compared with original samples (see the dotted line in Fig.4) but the curves keep the same shape as before. In Table 1 the branching level of sample 2[#] seems near that of sample 1[#], the influence of different trans-1,4 and 1,2 contents between the relationship of these short range interaction with processability should be considered.

Generally linear polymers have low e value, which is not sensitive to the average molecular weight but controlled by the high molecular weight part of the molecular weight distribution [13]. For the sake of comparison we studied a sample of rare-earth element catalytic polymerized polybutadiene B37 which has been proved to be linear chain structure [14]. The measured value of e are plotted as a function of shear stress in Figure 5. The value e increases with increasing shear stress, but its value is much higher than that of sample 1[#] and BR-01. Melt fracture occurs in the whole measured shear rate range.

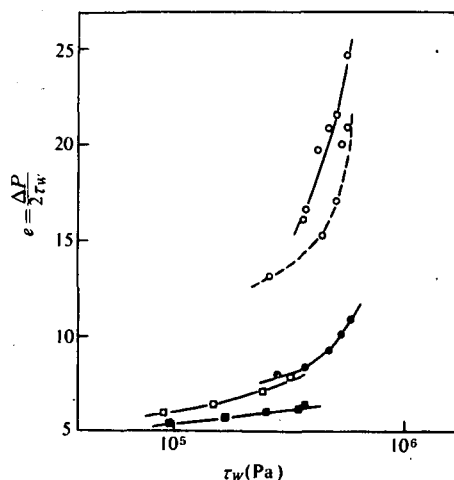


Fig. 5 e as a function of shear stress at 140°C for a few samples with the same shape of curves. □ BR-01, ■ 1[#], ○ B37, dotted line shown the data after repeated milling-passes. ●—B37 the data after milling-passes at 80°C

The milling property was obviously improved after repeated milling-passes at 100°C about 1hr., Also the value of e became lower (see Fig.5). At the same time it was found that the shear rate of the laminar flow scheme was observed, the distortion of the extrudate was reduced and showed less oscillation of the shear stress. All of these phenomena indicate the long chain molecular sample B37 were degraded during milling and therefore its behaviors approached the sample BR-01 and 1[#]. Tests were carried out at 80°C for B37. The value of e was lower than 140°C. It may be due to the entropy elasticity. In Table 3 typical data were collected at 80°C and 140°C for sample B37. The value of ΔP dropped to about half the value of 140°C. As a result the value of e reduced as well.

One of existing problems in polymer rheology is to separate the effect of long chain branching from that of high molecular weight of the molecular weight distribution rheologically. In this work, it suggested that e as a function of shear stress can be used as a critical quantity characterizing polymer long chain structure. Linear polymer melts show low e value which increases with increasing shear stress (rate) monotonically. However, long branching chain polymers have high e

Table 3 The data of B37 after repeated milling passes at different temperatures

Sample	Shear rate (s ⁻¹)	140°C		80°C	
		$\Delta P \times 10^{-7}$ (Pa)	$\tau_w \times 10^{-5}$ (Pa)	$\Delta P \times 10^{-7}$ (Pa)	$\tau_w \times 10^{-5}$ (Pa)
B37	1.01×10^3	2.31	4.0	1.21	5.6
	3.02×10^2	2.09	3.9	1.06	5.3
	1.01×10^2	1.65	3.85	0.845	4.0
	3.02×10^1	1.32	3.70	0.613	3.7
	1.01×10^1	1.10	3.40	0.441	2.8
	3.02×10^0	0.638	3.02	0.303	1.7

value even in low shear rate and e may decrease with shear stress (rate) in unsteady flow region. In fact, e value reflect the large elastic deformation in elongational superior flow. The low value of e at low shear stress (rate) corresponds to the excellent processability. In the case of PB rubber processing, the long chain branching caused large elastic deformation which is harmful for the processing behavior in mixing, milling and forming equipments.

Keywords:

Rheology; Polybutadiene; Processability; Elongational elasticity

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