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BLEND CONTAINING CORE-SHELL IMPACT MODIFIERS PART 2. MELT RHEOLOGY OF RUBBER-TOUGHENED PLASTICS

(IUPAC Technical Report)

Prepared for publication by
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Blends containing core-shell impact modifiers

Part 2. Melt rheology of rubber-toughened plastics

(IUPAC Technical Report)

Abstract: The influence of impact modifiers composed of an elastomer-based core and a poly(methyl methacrylate) (PMMA) shell on the melt flow properties of different thermoplastics has been studied, using both steady-state and dynamic viscosity measurements. The melt viscosities of the rubber-toughened blends were similar to those of the matrix polymers, over the range of shear rates commonly applied during melt processing. In the case of the matrix polymers, viscosity curves obtained under dynamic conditions coincided with those obtained under steady-state conditions. However, for blends the two curves show a slight divergence at low strain rates, where yielding is observed.

1. INTRODUCTION

IUPAC Working Party 4.2.1 (Structure and Properties of Commercial Polymers) has been involved for some years in a series of studies on the mechanical properties, morphology, and melt rheology of polymer blends and composites. This program, entitled "Blends Containing Core-Shell Impact Modifiers" (project 421/29/91), has been aimed at understanding the effects of matrix composition and type of rubber modifier on the properties of rubber-toughened plastics. The impact properties of such materials depend predominantly on their morphology [1–3], but are also affected by the viscoelastic characteristics of the matrix and dispersed phases, and by the properties of the matrix–rubber interface [4–8].

This report addresses the rheological behavior of two-component polymers composed of commodity thermoplastics blended with impact modifiers. The melt rheology of this class of toughened plastics is of importance to processors, who have to know how the heterogeneous blends behave in the melt state in order to obtain high impact levels in molded products. The melt flow behavior of multi-phase polymeric systems is controlled mainly by their structure, and in particular the size and shape of the dispersed phase domains, and the interfacial tension between the phases.

The following six laboratories participated in this study:

- Solvay SA, Brussels, Belgium (C. Dehennau)
- Huls AG, Marl, Germany (S. Röber)
- ECP - Enichem Polymères France SA, Mazingarbe, France (D. Constantin)
- BASF AG, Ludwigshafen, Germany (H. M. Laun)
- Technical University of Denmark, Lyngby, Denmark (J. Lyngäae-Jørgensen)
- Technical University of Wrocław, Wrocław, Poland (M. Kozłowski)

2. EXPERIMENTAL

2.1 Materials

Four thermoplastics were selected as matrix materials for this program:

PC polycarbonate: a general-purpose injection molding grade

PMMA	poly(methyl methacrylate): a medium-molecular-weight injection molding grade
PSAN	poly(styrene- <i>co</i> -acrylonitrile): a medium-molecular-weight injection molding grade
PVC	poly(vinyl chloride): a medium-molecular-weight, tin-stabilized, dry blend, with $K = 53.5$

Two core-shell modifiers were chosen, one based on polybutadiene and the other on poly(butyl acrylate-*co*-styrene). In the first modifier, coded PB, a 200-nm-diameter spherical core of polybutadiene is grafted to a 10-nm-thick PMMA shell. In the second, coded PBA, a 240-nm core of lightly cross-linked PMMA is grafted to a 20-nm-thick inner shell of PBA, over which is grafted a 10-nm outer shell of PMMA.

Blends were designed to have a volume fraction of 20% of rubber particles. Calculations of the amounts to be blended were based on rubber particles occupying 70% of the PB modifier, and 60% (including the PMMA core) of the PBA modifier, the remaining material being PMMA shell, which was not counted as part of the rubber particle. Blends were made in a compounding extruder with co-rotating twin screws at temperatures of: 300 °C (PC); 280 °C (PMMA and PSAN/PB); 260 °C (PSAN/PBA); and 175 °C (PVC).

2.2 Measurements

Two types of flow were evaluated: steady-state shearing (capillary flow) and oscillatory shearing (cone-plate and plate-plate geometries). The rheological measurements were performed according to specific rules, which allowed application of general rheological relationships, even if the basic principles of continuum mechanics (continuity, homogeneity, and isotropy) are not necessarily valid for multiphase materials. According to Brenner [9], to obtain valid data within a 1% error, the size of dispersion should be at least 10 times smaller than the characteristic dimension of the measuring device. Therefore, minimum radii of capillaries in viscometers were set at 1 mm, plate-to-plate distances at 1 mm, and cone angles at 4°. Details of the equipment used by particular participants are provided in Table 1.

Table 1 List of participants and details of their rheological equipment.

Participant	Acronym	Rheometer type	Capillary, cone, and plate data
C. Dehennau	SV	Instron capillary	$L/d = 0.5, 5, 15, 30$
S. Röber	HU	Göttfert 2001 capillary Rheometrics RMS800	$L/d = 10, 20, 30$; $d = 1.0, 1.5$ mm Cone angle 4°
M. Kozłowski	WR	Instron capillary	$L/d = 40$; $d = 1.27$ mm
D. Constantin	EN	Carri-Med CSL 500	Cone angle 4°
J. Lyngåae-Jørgensen	TD	Rheometrics RDS II plate-plate	Plates 1 mm apart
H. M. Laun	BA	Rheometrics DSR plate-plate	Plates 1 mm apart

The predrying and test conditions were as follows: PC - vacuum drying for 8 h at 80 °C, tests at 250 °C; PMMA and PSAN - vacuum drying for 8 h at 80 °C, tests at 220 °C; PVC - no predrying, tests at 190 °C.

3. RESULTS AND DISCUSSION

Melt viscosities were obtained using capillary rheometers over the range of shear rates 2 to 40 000 s⁻¹. Measurements of oscillatory shear flow extended this range to 10⁻⁶ s⁻¹. The data are presented in Figs. 1–6. All three neat thermoplastics and their rubber-toughened blends exhibited non-Newtonian (shear thinning) behavior. The variation between results from different laboratories was in general sat-

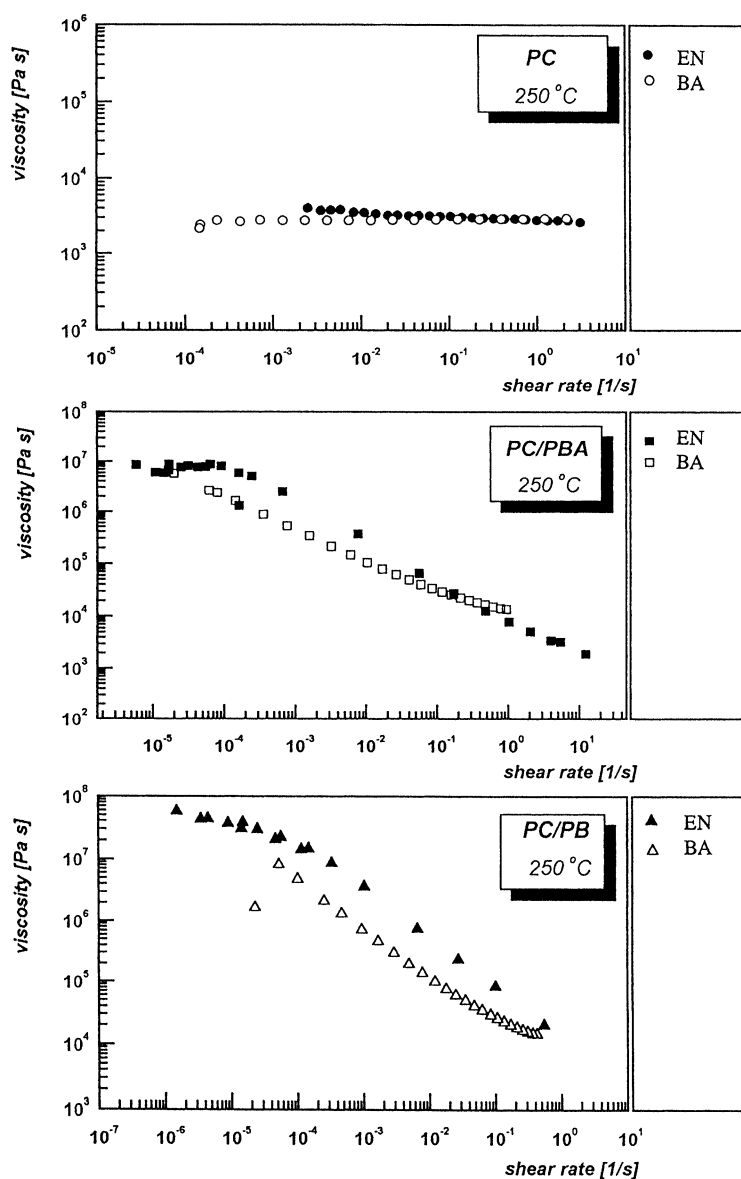


Fig. 1 Viscosity behavior of PC and its blends at 250 °C at low shear rates.

isfactorily low, probably because of the participants' adherence to the predetermined rules (high L/d ratio, Bagley-corrected viscosity) and their experience in rheological measurements. Steady-state viscosities for the neat polymers (PMMA, PSAN, and PC) coincided with the corresponding dynamic viscosities, as has frequently been observed in other polymers.

The data show that the Cox–Merz rule is valid for the matrix polymers, but not for blends containing impact modifiers, where melt viscosities measured at low frequencies and low strain rates

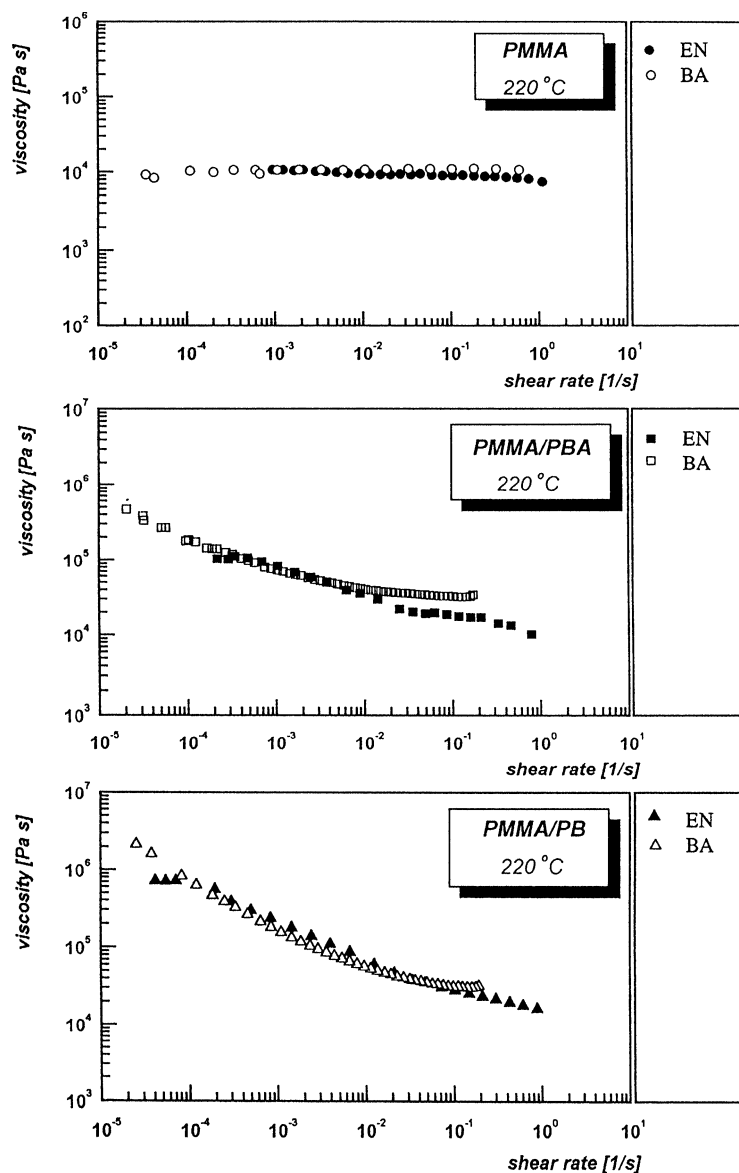


Fig. 2 Viscosity behavior of PMMA and its blends at 220 °C at low shear rates.

(dashed lines in Figs. 4–6) are slightly higher than steady state viscosities (points). This may imply that steady-state shearing is more effective than dynamic shearing in dispersing aggregated particles.

The influence of impact modifiers on the melt viscosities of the matrix polymers is shown in Table 2, which compares apparent viscosities at shear rates of 10 , 10^2 , and 10^3 s^{-1} . The blends have higher viscosities than the parent polymers at the lowest shear rate, but differences decrease with increasing shear rate. In general, the melt viscosities of blends toughened with PB and PBA are com-

Table 2 Melt viscosity in kPa.s determined by capillary rheometry.

Shear rate / s ⁻¹	10	10 ²	10 ³
PSAN	2.04	0.79	0.15
PSAN/PB	2.63	0.99	0.26
PSAN/PBA	3.22	0.99	0.26
PMMA	4.22	1.95	0.39
PMMA/PB	5.81	1.95	0.39
PMMA/PBA	9.24	1.95	0.38
PC	3.53	2.62	0.79
PC/PB	4.21	2.33	0.62
PC/PBA	5.24	2.60	0.66
PVC	3.79	1.31	0.35
PVC/PB	6.37	2.01	0.46
PVC/PBA	6.94	2.09	0.46

parable at the higher shear rates, which might be due to their similar particle sizes and the presence of a thin PMMA shell on both types of particle.

The Newtonian plateau viscosity η_0 at low shear rates has been estimated for PMMA, PSAN, and PC, but not for PVC, nor for any of the blends. Over the same range of shear rates, the blends, especially those with a PC matrix, show an upturn in melt viscosity as the shear rate decreases, as illustrated in Figs. 7–9, which compare the apparent viscosity functions of the neat thermoplastics with those of their blends over a wide range of shear rates.

Extension of the experimental range to very low rates revealed yield phenomena in the blends, whereas a simple relationship between shear stress and shear rate was observed in the matrix polymers under the same conditions. The phenomenon of yielding in melts has frequently been reported for heterogeneous polymer blends and polymer composites [10–12]. It is associated with the existence in the blend of a three-dimensional structure, caused by aggregation of dispersed particles, or by interparticle interactions, or by steric-elastic effects in the matrix. The yield stress σ_y , which is the stress required to break down the three-dimensional structure, increases with the aspect ratio of the particles, their rigidity, and concentration.

The yield phenomena reported in this study mean that, in order to initiate flow in the melt, substantially higher stresses have to be applied to rubber-modified blends than to the matrix polymer. Higher σ_y values are observed for PB blends than for PBA blends, although both types of modifier have the same outer PMMA shell, and similar interfacial phenomena are therefore to be expected. The differences in σ_y are probably due to differences in diameter (and hence inter-particle spacing) or in the elastic properties of the particles. Both types of particles are cross-linked to prevent breakdown during processing, but the degree of cross-linking is known to be higher in the PB than in the PBA particles [13]. Also, the PB-particles are monodisperse, homogeneous polybutadiene spheres, with diameters of 0.2 μm , whereas the PBA particles are larger (0.3 μm), have a wider distribution of diameters, and have central cores of cross-linked PMMA, with the PBA elastomer forming a thin shell around the core. These differences in spacing, association–dissociation behavior, and elastic response to stress, combine to produce different σ_y values. Similar behavior has been reported in polymer composites containing solid particles [14].

The melt viscosities of the blends become closer to those of the corresponding matrix as the shear rate increases. At the high shear rates that are typically used for processing (10^2 to 10^3 s⁻¹), the melt flow behavior is almost identical for the modified and neat polymers. Slight differences are observed in the case of PSAN, where the blends are of higher viscosity than the matrix polymer over the full range of shear rates.

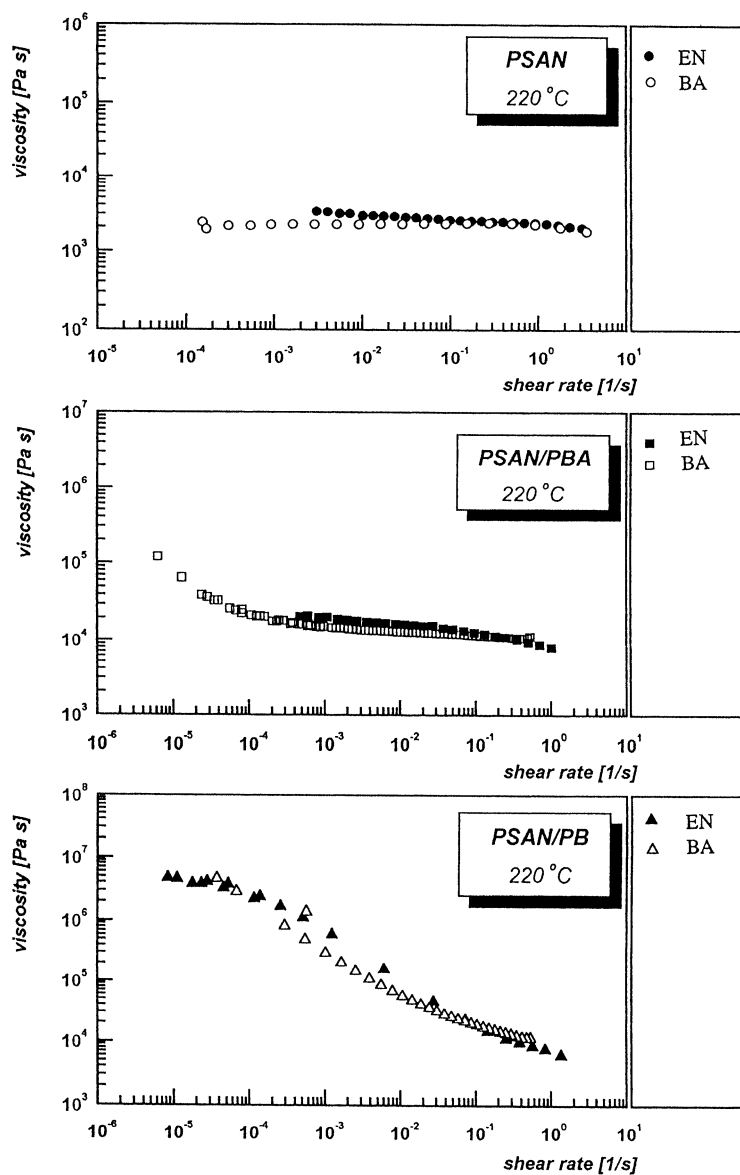


Fig. 3 Viscosity behavior of PSAN and its blends at 220 °C at low shear rates.

In order to obtain an analytical description of the relationship between melt viscosity η and shear rate several semi-empirical equations describing pseudoplastic behavior have been examined. The expression of Utracki [15] was found to fit the data best:

$$\eta = \eta_0 \left[1 + (\tau \dot{\gamma})^{m_1} \right]^{-m_2} + \sigma_y \frac{[1 - \exp(-a \dot{\gamma})]}{\dot{\gamma}} \quad (1)$$

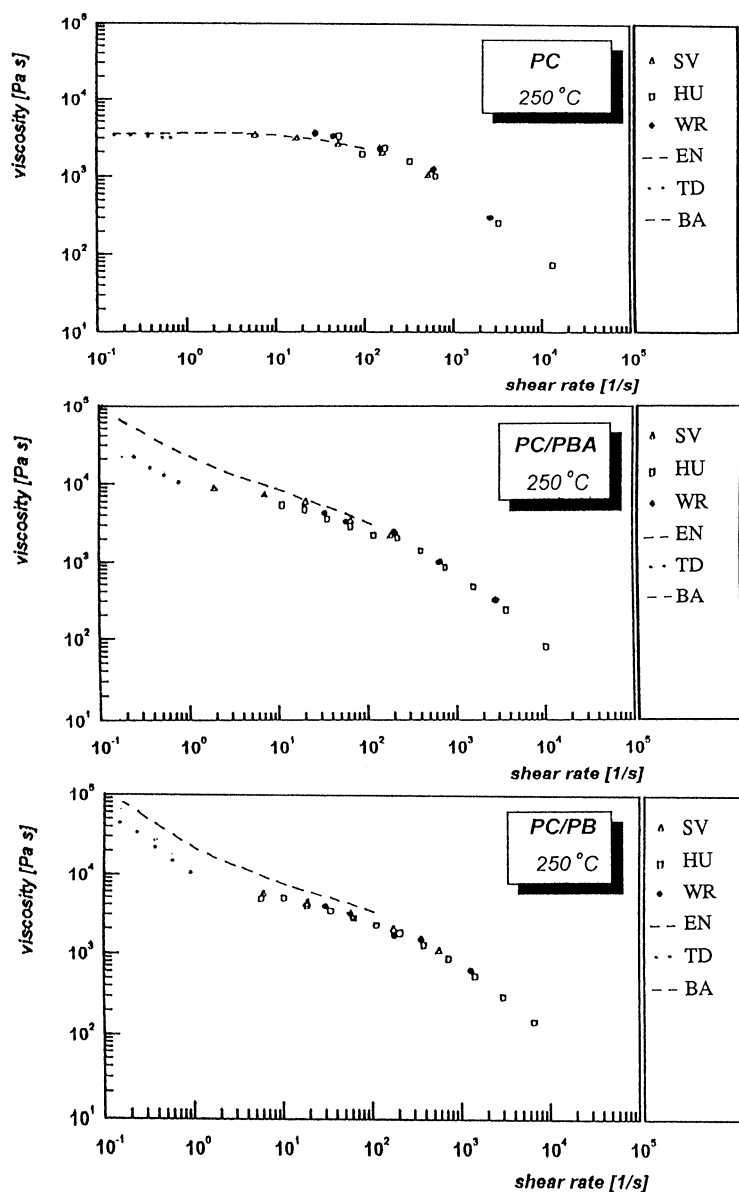


Fig. 4 Viscosity behavior of PC and its blends at 250 °C at high shear rates.

where τ is the relaxation time, and the parameters η_0 and σ_y are constants. The magnitudes of these two parameters for particular systems are listed in Table 3.

Within the range of shear rates covered in these experiments, the extrudates obtained from capillary viscometry were smooth. The die swell (B) decreased in the order: PMMA > PSAN > PC. Die swell

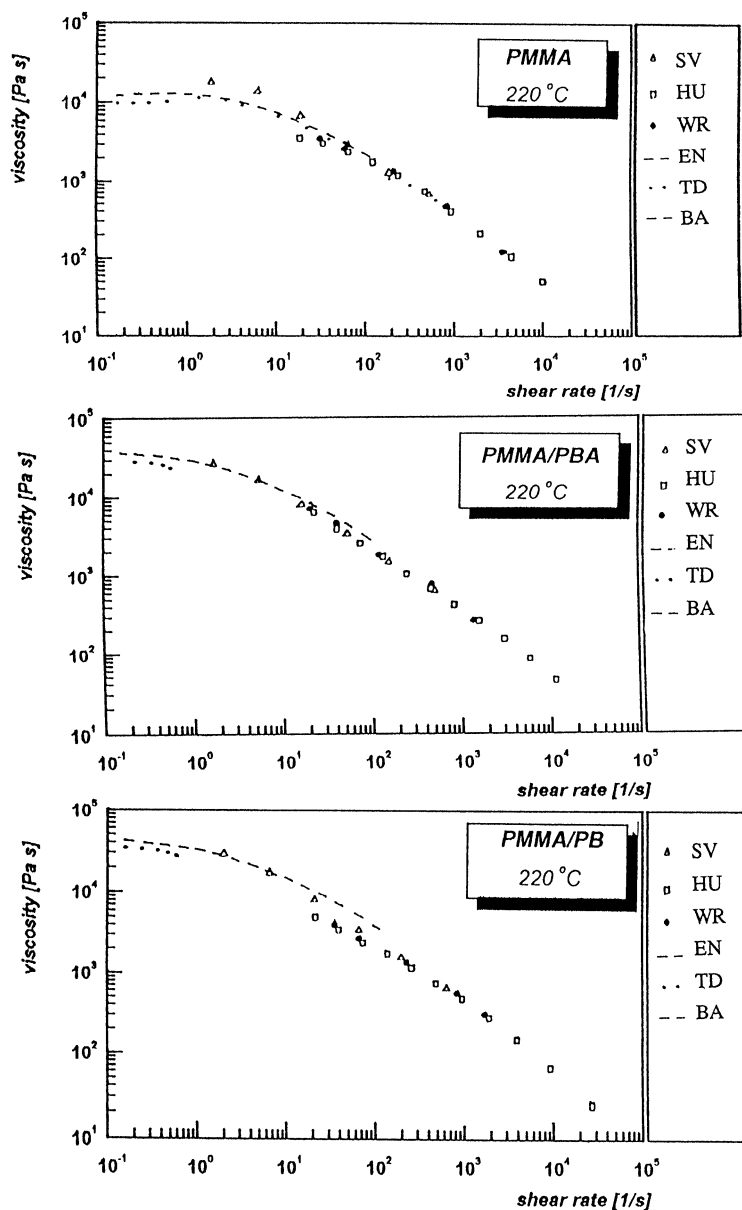


Fig. 5 Viscosity behavior of PMMA and its blends at 220 °C at high shear rates.

was strongly reduced in blends containing PB, and still further in blends containing PBA. A decrease in die swell is frequently reported on addition of solids to polymer melts. The main cause of swelling in blends is the elastic recovery of domains that were extended during convergent flow in the capillary entrance. Therefore, one can expect the less cross-linked PBA modifier, which has a smaller capacity to store elastic energy, to give lower values of B .

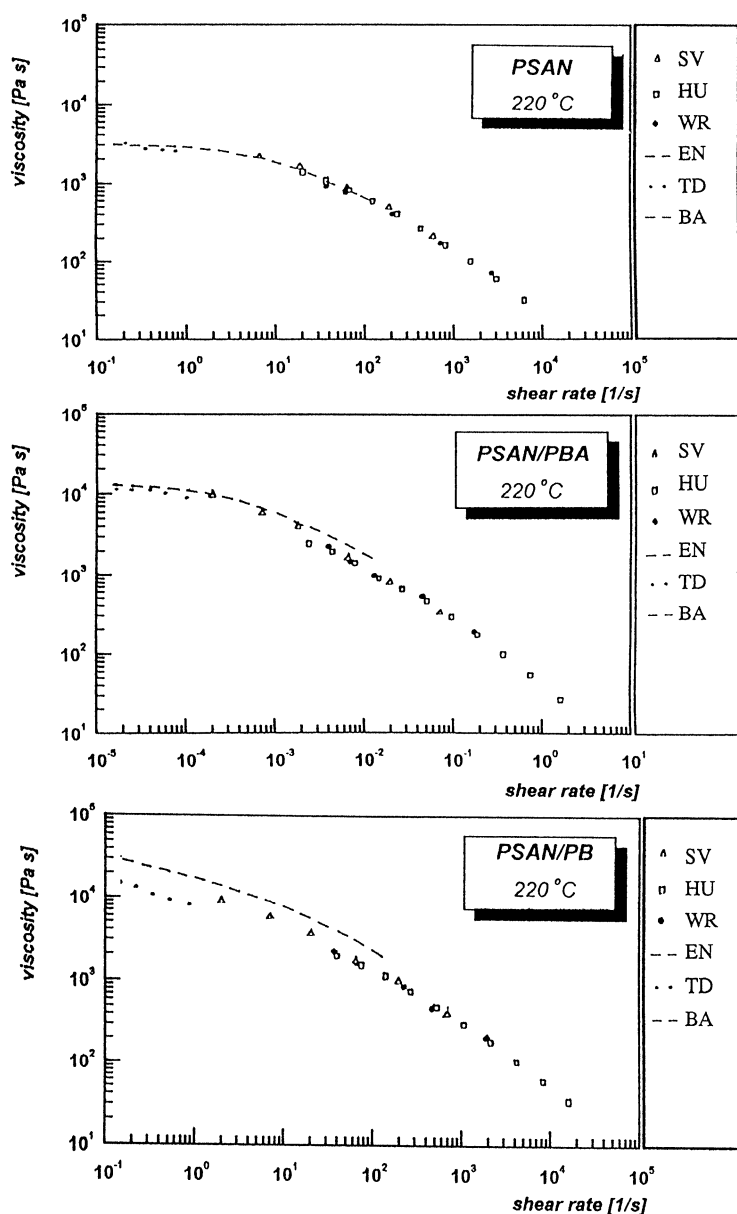


Fig. 6 Viscosity behavior of PSAN and its blends at 220 °C at high shear rates.

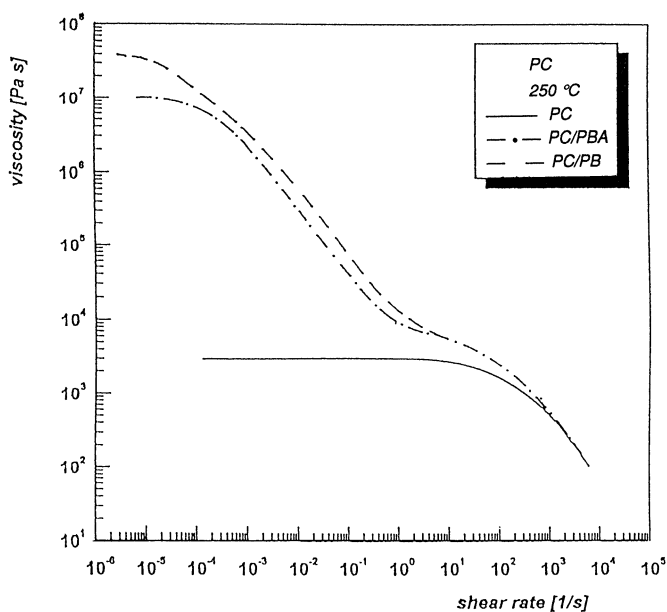
Melt viscosity curves for PVC-based polymers differ significantly from those of the other polymers. Over the entire range of shear rates studied, a “power law” dependency was observed for both PVC and its blends (Fig. 10). The rubber-modified materials reached higher viscosity levels than PVC alone. Again, at high shear rates there was no difference in viscosity between blends based on different

Table 3 Characteristic parameters of eq. 1.

Polymer system	η_0 / (kPa.s)	σ_y / Pa
PSAN	2.20	-
PSAN/PB	-	38
PSAN/PBA	-	0.7
PMMA	10.0	-
PMMA/PB	-	29
PMMA/PBA	-	9
PC	2.28	-
PC/PB	-	85
PC/PBA	-	50

Table 4 Die swell of PVC melts.

Shear rate	10 s^{-1}			10^2 s^{-1}			10^3 s^{-1}			
	L/d ratio	0.5	5	30	0.5	5	30	0.5	5	30
PVC		1.48	1.35	1.19	1.71	1.37	1.28	2.07	1.64	1.36
PVC/PB		1.27	1.17	1.05	1.32	1.17	1.05	1.45	1.15	1.02
PVC/PBA		1.31	1.11	1.07	1.41	1.13	1.10	1.58	1.27	1.11

**Fig. 7** Viscosity behavior of PC and its blends at 250 °C over a wide range of shear rates.

modifiers. The results suggest that the particulate flow of PVC is dominant, and that the rubber particles act like a filler in the PVC melt.

Data on die swell are presented in Table 4. The elastic recovery decreases on addition of impact modifiers to PVC and with increasing L/d ratio.

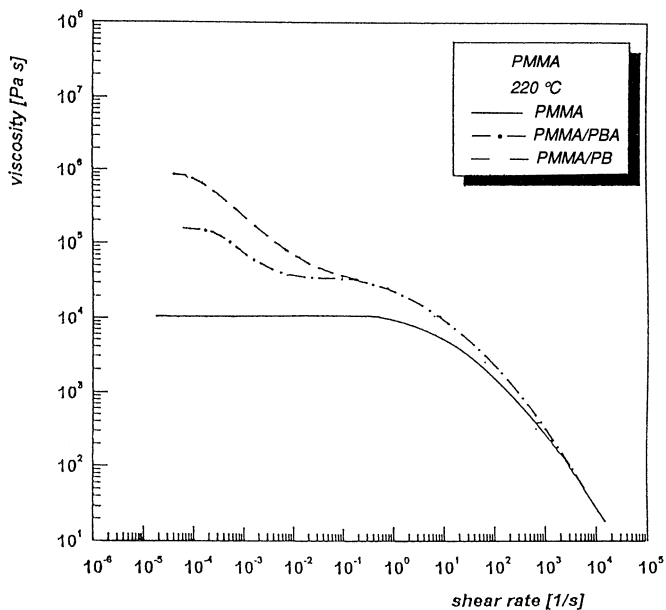


Fig. 8 Viscosity behavior of PMMA and its blends at 220 °C over a wide range of shear rates.

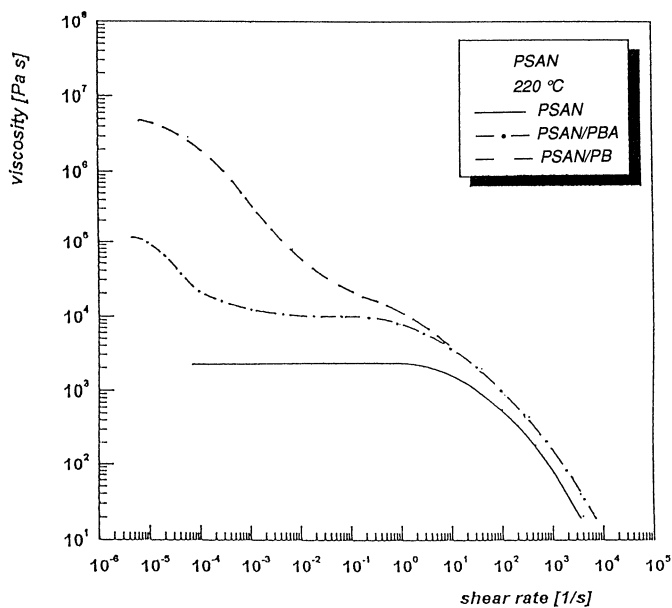


Fig. 9 Viscosity behavior of PSAN and its blends at 220 °C over a wide range of shear rates.

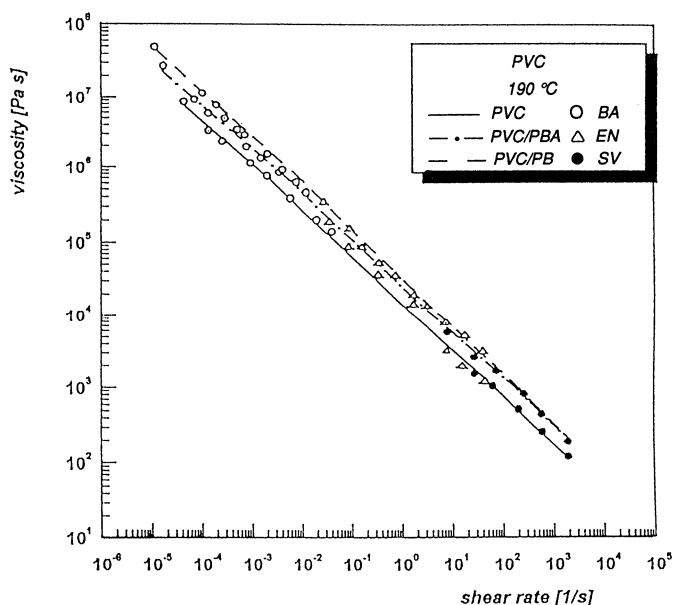


Fig. 10 Viscosity behavior of PVC and its blends at 190 °C over a wide range of shear rates.

4. CONCLUSIONS

This work has shown that:

- The Cox–Merz rule, which is valid for the matrix polymers, does not apply to heterogeneous blends of these polymers with small rubber particles.
- The melt viscosity of rubber-toughened plastics does not differ significantly from that of the corresponding matrix polymers in the range of shear rates commonly used in processing.
- Rubber-toughened blends based on PMMA, PSAN, and PC exhibit yield behavior in the melt. Low strain rate dynamic methods of viscometry provide valuable information concerning the entanglement networks formed in these heterogeneous blends.
- The size and internal structure of a modifier have pronounced effects on the flow of polymer blends at low shear rates, whereas the properties of the matrix polymer are predominant at high shear rates.

ACRONYMS AND ABBREVIATIONS

PB	polybutadiene: The letters are used to denote both the elastomer itself and the modifier in which the elastomer is the main constituent.
PBA	poly(butadiene- <i>co</i> -styrene): The letters are used to denote both the elastomer itself and the modifier in which the elastomer is the main constituent.
PC	polycarbonate (of Bisphenol A)
PMMA	poly(methyl methacrylate)
PSAN	poly(styrene- <i>co</i> -acrylonitrile)
PVC	poly(vinyl chloride): the rigid form, without plasticizer
TEM	transmission electron microscope/microscopy

The following two-letter acronyms are used to identify active participants: BA, EN, HU, SV, TD, and WR. See Section 1 (Introduction) and Table 1 for details.

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