J.Sci.Soc.Thailand,18(1992) 195-215

THE INFLUENCE OF VISCOSITY RATIO ON THE MORPHOLOGY AND MECHANICAL PROPERTIES OF POLYAMIDE 6/NATURAL RUBBER BLENDS

F.H. AXTELL, P. PHINYOCHEEP, AND P. MONTHACHITRA

Department of Chemistry, Faculty of Science, Mahidol University, Rama VI Road, Bangkok 10400, Thailand.

(Received November 29, 1992)

ABSTRACT

Natural rubber samples were prepared having a wide range of molecular weights using two techniques: mastication, and reaction with phenylhydrazine. The rheological properties of polyamide 6 and the natural rubbers were determined. Blends of polyamide 6 and the natural rubbers were prepared by melt blending. The blends were tested for their impact strength and other properties. The molecular weight of the natural rubber controlled the viscosity ratio of the blend components during mixing. The dispersion of the natural rubber in the polyamide 6 was found to be dependent on the viscosity ratio of the blends. The dispersion of the masticated natural rubbers were better than the liquid natural rubbers. The blend impact strength was found to be dependent on the degree of dispersion, with the best impact strength at a mean rubber particle size of 0.33 microns and a particle size range of 0.20-3.00 microns. The dependence on the rubber molecular weight of the rubber was significant, with low blend impact strength at molecular weights below 10,600. At higher rubber molecular weights the natural rubber toughened the polyamide significantly, reaching a peak Charpy impact strength of 18 kJ/m² at a rubber molecular weight of 290,000. This blend was prepared having a viscosity ratio of 0.65 during mixing. The effect of molecular orientation and crystallisation behaviour were studied and found to be minor. The uncrosslinked natural rubber toughened the polyamide 6 without loss of hardness but with a drop in the heat distortion temperature.

INTRODUCTION

Polyamides have been toughened by elastomeric impact modifiers and studied widely.[1-8] The dependence of toughness on dispersed phase droplet size has been established.[4] The dispersion of the elastomer can be controlled by matching the rheology of the elastomer with the polyamide in the mixer, if the viscosity ratio can be controlled at unity, a fine dispersion can be obtained.[2,9] Good impact strength should be obtained in blends having a fine dispersion, i.e. mixed at a viscosity ratio of unity.

Interest in developing new applications for natural rubber (NR) is intense in natural rubber producing countries. This study investigates the possibility of replacing ethylene-propylene elastomers by natural rubber in toughened polyamide applications. Keskkula and Turley have worked with polyisoprene toughened polystyrene but their tough blends became brittle on shearing.[10]

In this work the viscosity of natural rubber has been varied by producing a range of

different molecular weight rubbers by cold mastication of block rubber and by reaction of latex with phenylhydrazine to produce liquid natural rubber (LNR). By varying the molecular weight of the minor phase in the blend, we have controlled the viscosity ratio during mixing. The resultant blends were a range of polyamides with different levels of NR dispersion and different impact strengths.

The major obstacle to using NR in polyamides is the high temperature used in the melt processing. At the high processing temperature thermal degradation of the natural rubber takes place. To reduce the extent of this degradation a suitable antioxidant had to be found for the polyamide 6/natural rubber blends.

EXPERIMENTAL

Materials

The polyamide 6 (PA6) used for preparing the blends was a low viscosity, rapid processing grade polymer (Akulon M223D, Akzo Plastics b.v.). The PA6 was dried at 80°C for 16 hours prior to processing. A high impact polyamide 6 (HI-PA6) (Akulon K223 B2P1, Akzo Plastics b.v.) was used for comparison with the blends. Technical grade natural rubber (Thai Technical Rubber TTR5L) was used in the polyamide blends containing unmasticated and masticated rubbers. Mastication was used to prepare rubbers having different molecular weights. The masticated NR polymers were prepared by cold two roll milling for different durations, maintaining a mill temperature of 30°C. The range of rubber molecular weights obtained and used in blends with PA6 are shown in Table 1.

Liquid natural rubbers The liquid natural rubbers were prepared by an oxidative degradation reaction using phenylhydrazine and oxygen. The reaction procedure was carried out as follows: 300ml of concentrated NR latex, dry rubber content (d.r.c.) 60 w/w% was diluted to a d.r.c. of 30% with distilled water and stabilised with a non-ionic stabiliser (3phr Vulcastab LW, Vulnax International). The latex was stirred overnight at ambient temperature.

The stabilised latex was transferred to a well stirred glass reactor fitted with a condenser, dropping funnel, and an inlet tube. After heating the latex to 60°C and adjusting the air flow rate to about 2-3 litre/minute, the desired amount of phenylhydrazine (5-40ml) was dropped into the latex. The reaction was stirred and maintained at 60°C for 24 hours. At the end of the reaction, the water was distilled off and a viscous brown liquid natural rubber was obtained. The liquid natural rubbers produced are listed in Table 1. Two liquid isoprene rubbers were used for comparison, having molecular weights of 39,500 and 71,100 (LIR 30 and LIR 50 respectively, Japanese Synthetic Rubber).

Antioxidant It was essential to use a suitable antioxidant to prevent excessive oxidation of the natural rubber during blending with the polyamide melt at 235°C. A screening program to test commercial antioxidants was conducted using eleven commercial high temperature antioxidants.

The antioxidants were cold milled into the natural rubber to prepare a masterbatch which was then let-down into the molten polyamide on a two roll mill at 235°C. Compression moulded sheets of blends containing the different stabilisers were compared

for their mechanical properties and discoloration. Due to the relatively long moulding time used, degradation was observed in all cases. Parallel experiments were undertaken involving the stabilised rubber masterbatch being moulded alone (without blending into the PA6). The sheets were moulded for 2 and 12 minutes. The sheets were analysed by infra-red spectrophotometry (I.R.). In these experiments the natural rubber degradation taking place during the long moulding period was compared. From the results of drop in tensile strength, change in I.R. spectra, and degree of discoloration, a bis(2,4-di-t-butylphenyl) pentaerythritol diphosphite stabiliser (Ultranox 626, GE Speciality Chemicals) was selected for use in all the blends.

Melt blending

Melt blending of the PA6 with the masterbatch of antioxidant in rubber was carried out at 235°C, on a temperature controlled two roll mill. The melt blending was completed within 20 minutes and the 90/10 PA6/NR blends (containing 1% antioxidant, by weight of total polymer) were cooled, granulated the dried prior to injection moulding.

Injection moulding

The impact bars conforming to ASTM D256 (i.e. 128mm x 12.8mm x 6.5mm) were prepared by injection moulding (Dr.Boy 22S) with a barrel temperature profile of 240-250°C and an injection pressure of 3 MPa. The overall cycle time was 4.8 minutes. The two cavity mould was side gated with relatively large rectangular gates (W=5.2mm x H=3mm x L=2.4mm). The bars were notched with a broach type tool (Daventest) prior to testing.

Characterisation

NR molecular weight determination

The viscosity average molecular weight ($\bar{M}_v$) of the polymers was determined at 25°C using an automatic solution viscosity apparatus (Schott) and a Ubbelhode capillary viscometer. The solvent used for the NR was toluene. The viscosity average molecular weights are shown in Table 1.

Rheological characterisation

The rheological properties of the polymers studied were characterised using a concentric cylinder rheometer (Haake Rotoviscometer) for the liquid rubbers; and a capillary rheometer (Monsanto Melt Processability Tester) for the natural rubber and polyamide polymers. A double superposition method for temperature and molecular weight[11] was applied to the liquid rubber data to enable us to produce a mastercurve for the LNR polymers at 40°C. The mastercurve is shown as Figure 1, and the shift factors are listed in Table 2. The mastercurve was then used to extrapolate the rheological properties of the LNR polymers up to the melt blending temperature of the polyamide 6 (235°C, see Figure 3). A molecular weight superposition mastercurve was also prepared for the natural rubber and masticated natural rubbers at 235°C (shown as Figure 2). The shift factors are listed in Table 3. The flow curves for the polyamide 6 and all the natural rubber polymers at 235°C are shown as Figure 3.

TABLE 1. Molecular weight of NR.

NR Code	Mastication Time (minutes)	$\bar{M}_v$	Amount of Phenylhydrazine (ml.)
M0	0	1,200,000	
M1	5	608,000	
M2	15	290,000	
M3	120	92,400	
M4	180	67,500	
M5	300	43,000	
L1		35,100	5.0
L2		10,600	10.0
L3		8,100	15.0
L4		6,800	27.8
L5		4,000	35.0
L6		3,400	40.0

TABLE 2. Shift factors for LNR polymers.

NR Code	$\bar{M}_v$	Temperature Shift Factors at 1000Pa a_T				Mv Shift Factors b_M at 40oC & 1000 Pa
		30°C	40°C	50°C	60°C	
L1	35,100	-	1.00	0.52	0.30	100
L2	10,600	1.79	1.00	0.51	0.28	2.94
L3	8,100	1.82	1.00	0.38	0.17	1.44
L4	6,800	1.91	1.00	0.48	0.31	1.00
L5	4,000	2.22	1.00	0.53	0.29	0.48
L6	3,400	2.11	1.00	0.58	0.35	0.24

TABLE 3. Molecular weight shift factors of NR polymers.

NR Code	$\bar{M}_v$	Molecular weight shift factors b_{Mv} at 235°C and 10,000 Pa
M0	1,200,000	1.85
M1	608,000	5.01
M2	290,000	1.29
ref	180,000	1.00
M3	92,400	0.74
M4	67,500	0.20
M5	43,000	0.082

TABLE 4. Dispersion of NR in PA6

BLEND	NR Molecular Weight (Mv)	Blend Viscosity Ratio	Mean NR Droplet Size (micron)	Range of NR Droplet Sizes (micron)
PA6/M0	1,200,000	18.71	0.45	0.20-2.80
PA6/M1	608,0001.10	0.43	0.20-2.50	
PA6/M2	290,000	0.65	0.33	0.20-3.00
PA6/M3	92,400	0.55	0.26	0.12-2.07
PA6/M4	67,500	0.40	0.21	0.12-1.15
PA6/M5	43,000	0.0832	0.55	0.20-6.50
PA6/L1	35,100	0.1524	0.77	0.20-6.90
PA6/L2	10,600	0.0049	0.66	0.20-5.00
PA6/L3	8,100	0.00468	0.58	0.20-5.00
PA6/L4	6,800	0.00186	0.46	0.20-5.00
PA6/L5	4,000	0.00015	0.52	0.20-5.00
PA6/L6	3,400	0.00058	0.57	0.20-5.00
PA6/LIR30	39,500	0.01	0.23	0.12-1.85
PA6/LIR50	71,100	1.78	0.42	0.20-7.30

TABLE 5. Crystallisation characteristics

BLEND	mean NR Droplet Size (microns)	DSC Peak Area (J/g_{PA6})	DSC Peak Onset (°C)	DSC Peak Half-height Width (°C)	Blend Shrinkage (%)
_PA6	-	64.88	184.0	10.8	0.1
HI-PA6	-	72.41	184.2	5.6	0.2
PA6/M0	0.45	72.22	200.1	6.8	0
PA6/M1	0.41	79.20	195.9	4.7	0
PA6/M2	0.33	76.16	182.8	5.2	0
PA6/M3	0.26	61.20	204.4	6.6	0
PA6/M4	0.21	76.61	200.1	4.7	0.2
PA6/M5	0.55	70.56	177.3	6.1	-
PA6/L1	0.77	70.52	176.6	5.9	-
PA6/L2	0.66	63.41	197.9	4.2	0
PA6/L3	0.58	66.23	199.0	4.8	0
PA6/L4	0.46	65.24	203.0	4.0	0
PA6/L5	0.52	71.43	200.4	4.7	0
PA6/L6	0.57	84.83	200.9	3.8	0
PA6/LIR30	0.23	72.19	201.4	5.9	0.2
PA6/LIR50	0.42	74.47	200.0	5.4	0.2

TABLE 6. Physical properties of the blends

BLEND	Charpy Impact Strength (kJ/m^2)	Izod Impact Strength (kJ/m^2)	H.D.T. (°C)	Hardness (Shore D)
PA6	6.8	6.2	89.8	68.1
HI-PA6	20.0	15.2	95.0	71.0
PA6/M0	14.5	10.4	84.8	71.0
PA6/M1	13.1	8.7	86.5	71.4
PA6/M2	17.9	12.0	74.5	71.9
PA6/M3	14.4	9.2	85.5	73.8
PA6/M4	14.8	9.1	94.0	70.4
PA6/M5	10.9	7.0	-	72.9
PA6/L1	9.9	7.3	-	72.5
PA6/L2	5.8	8.5	88.5	69.8
PA6/L3	5.7	7.4	81.0	70.0
PA6/L4	8.3	8.5	82.1	70.0
PA6/L5	5.8	8.2	84.0	70.3
PA6/L6	6.3	7.9	71.4	69.7
PA6/LIR30	15.7	9.3	82.5	74.1
PA6/LIR50	6.7	6.6	65.5	73.0

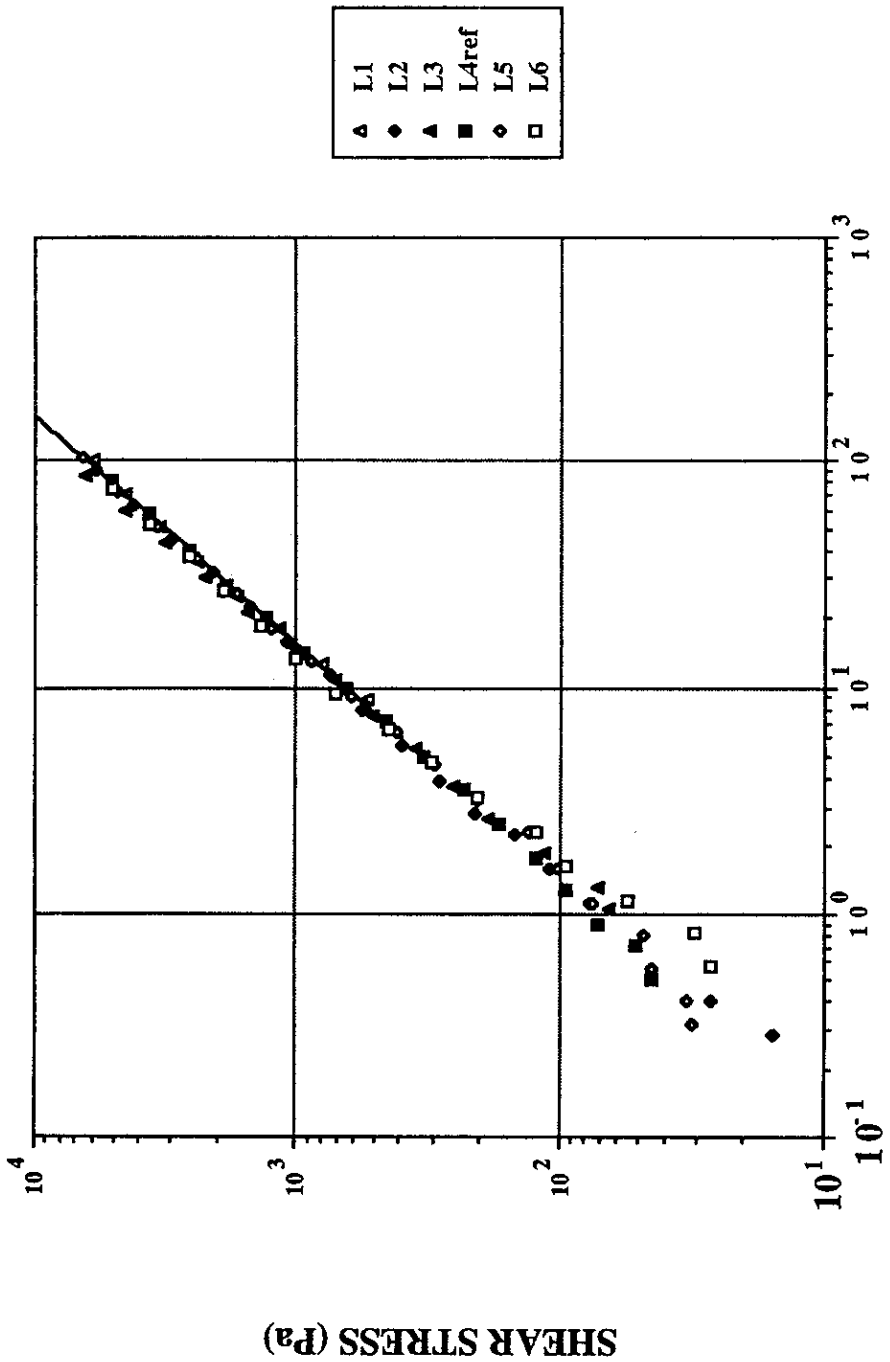

Fig. 1. Mastercurve of LNR polymers.

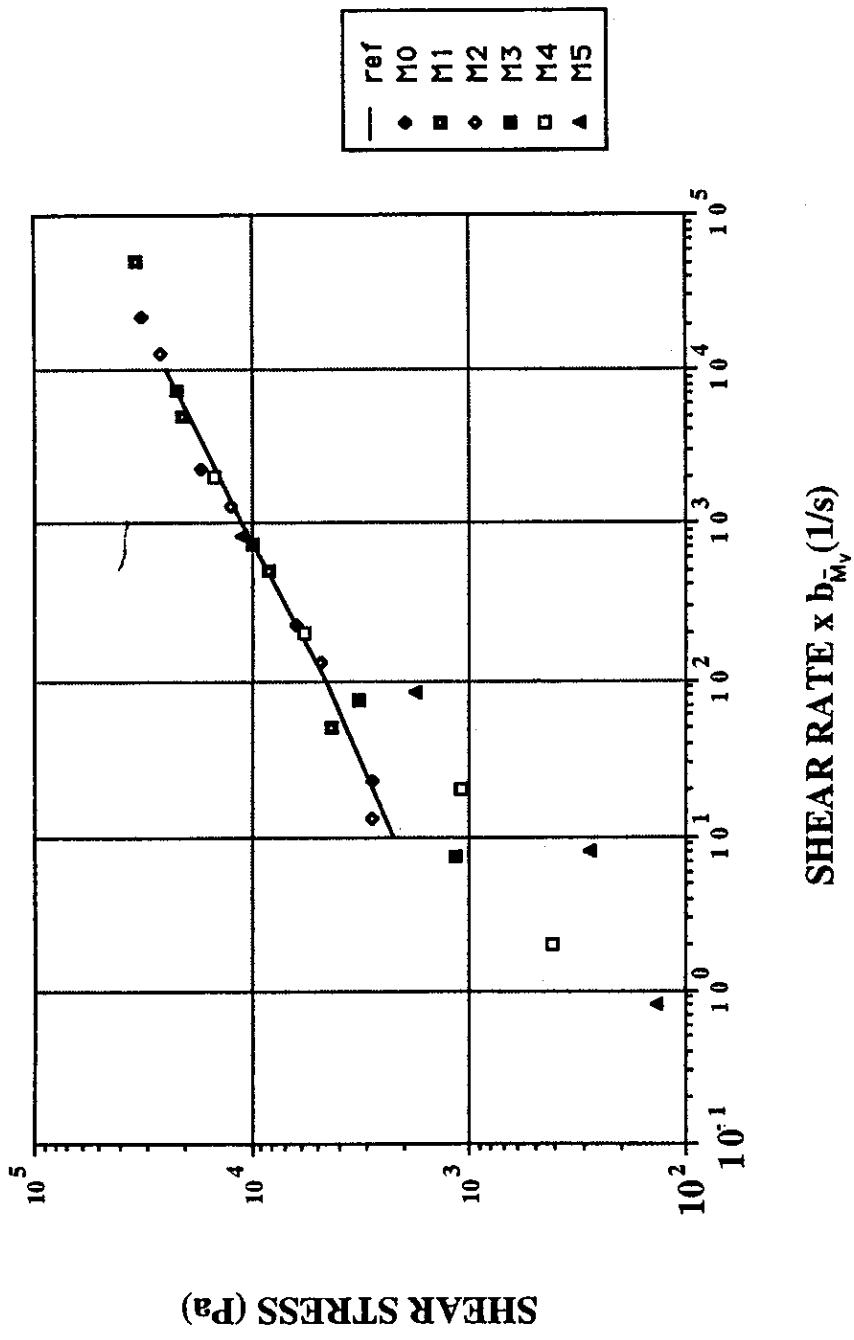

Fig. 2. Mastercurve of masticated NR polymers at 235°C.

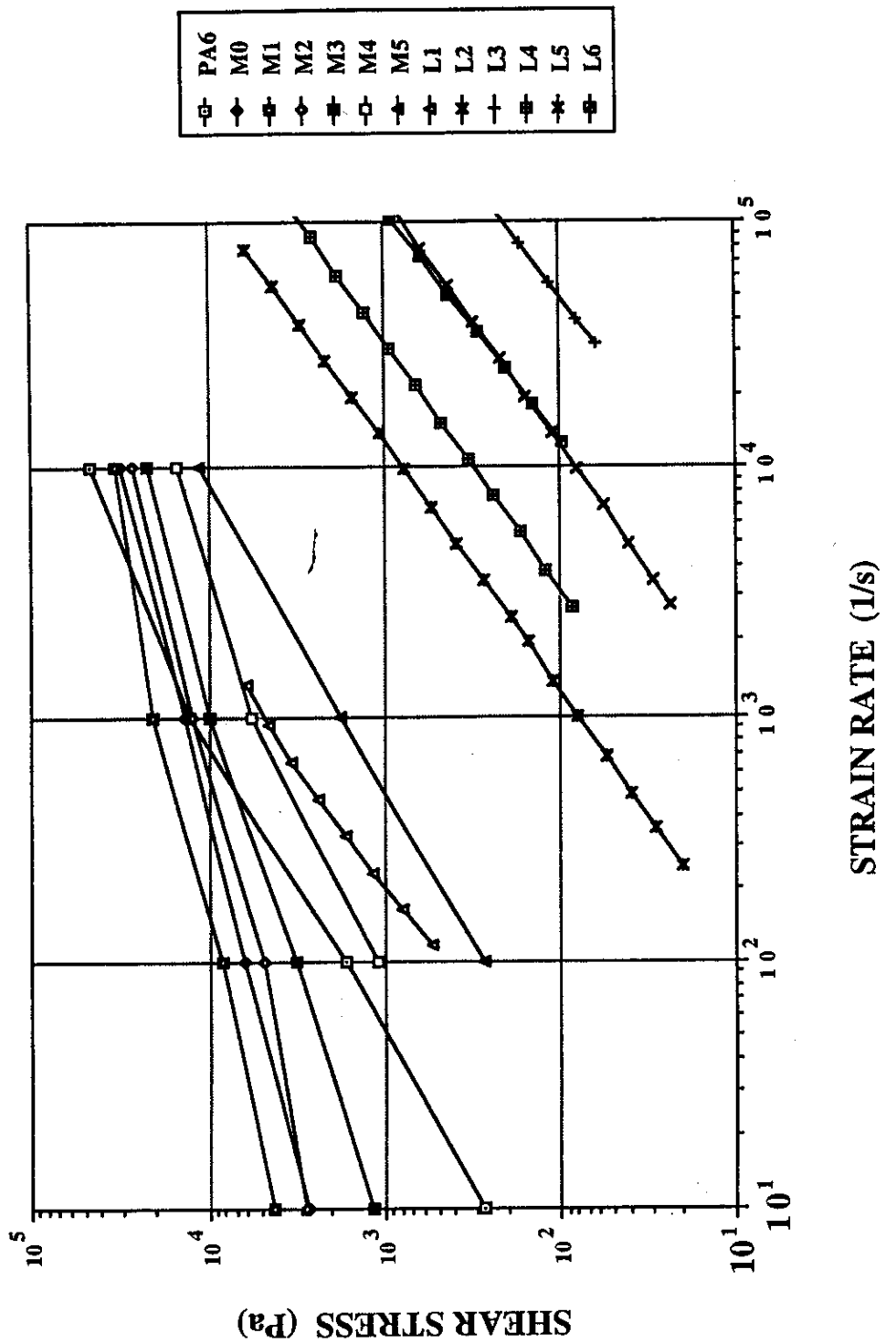

Fig. 3. Rheology of PA6 snd NR polymers at 235°C.

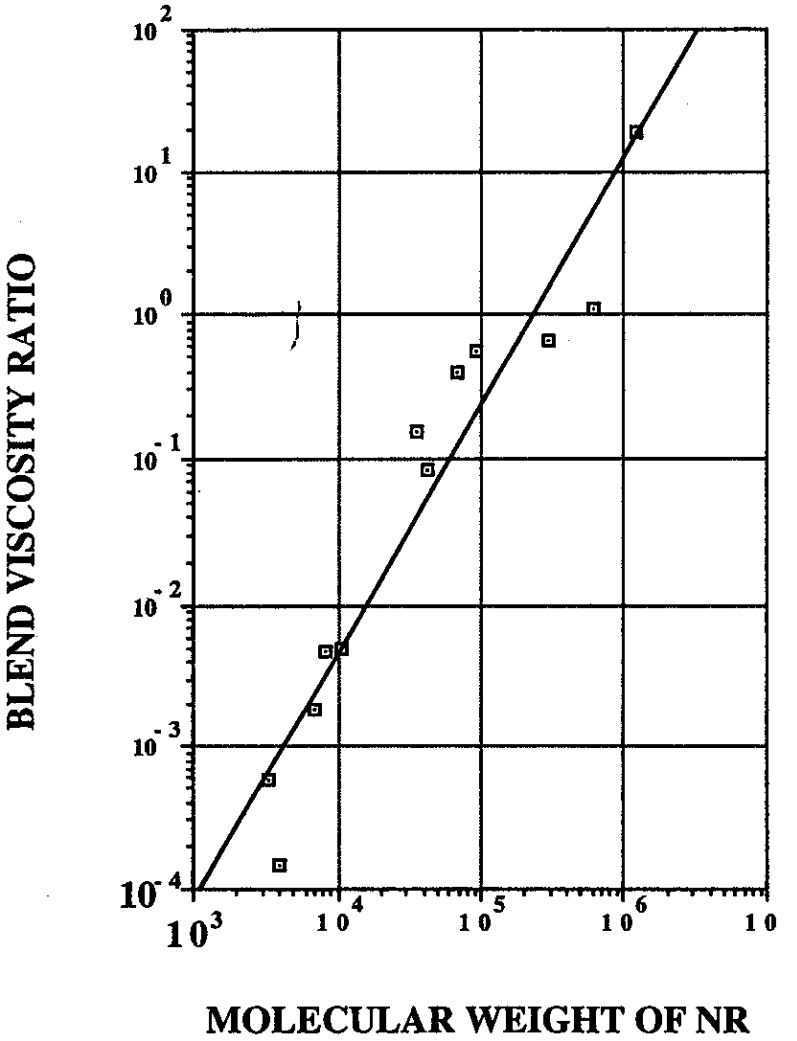

Fig. 4. Effect of NR molecular weight on viscosity ratio.

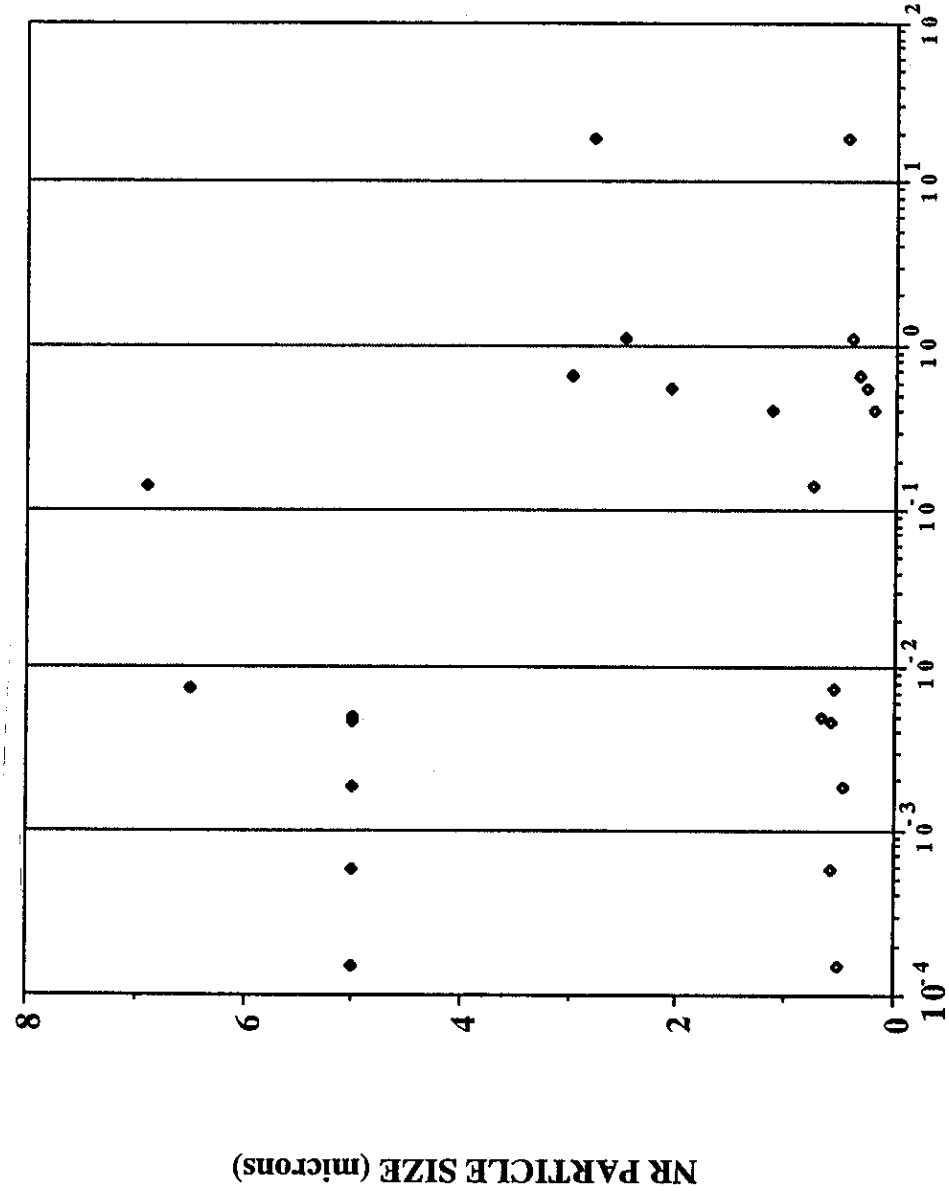

Fig. 5. Effect of blend viscosity ratio on NR dispersion.

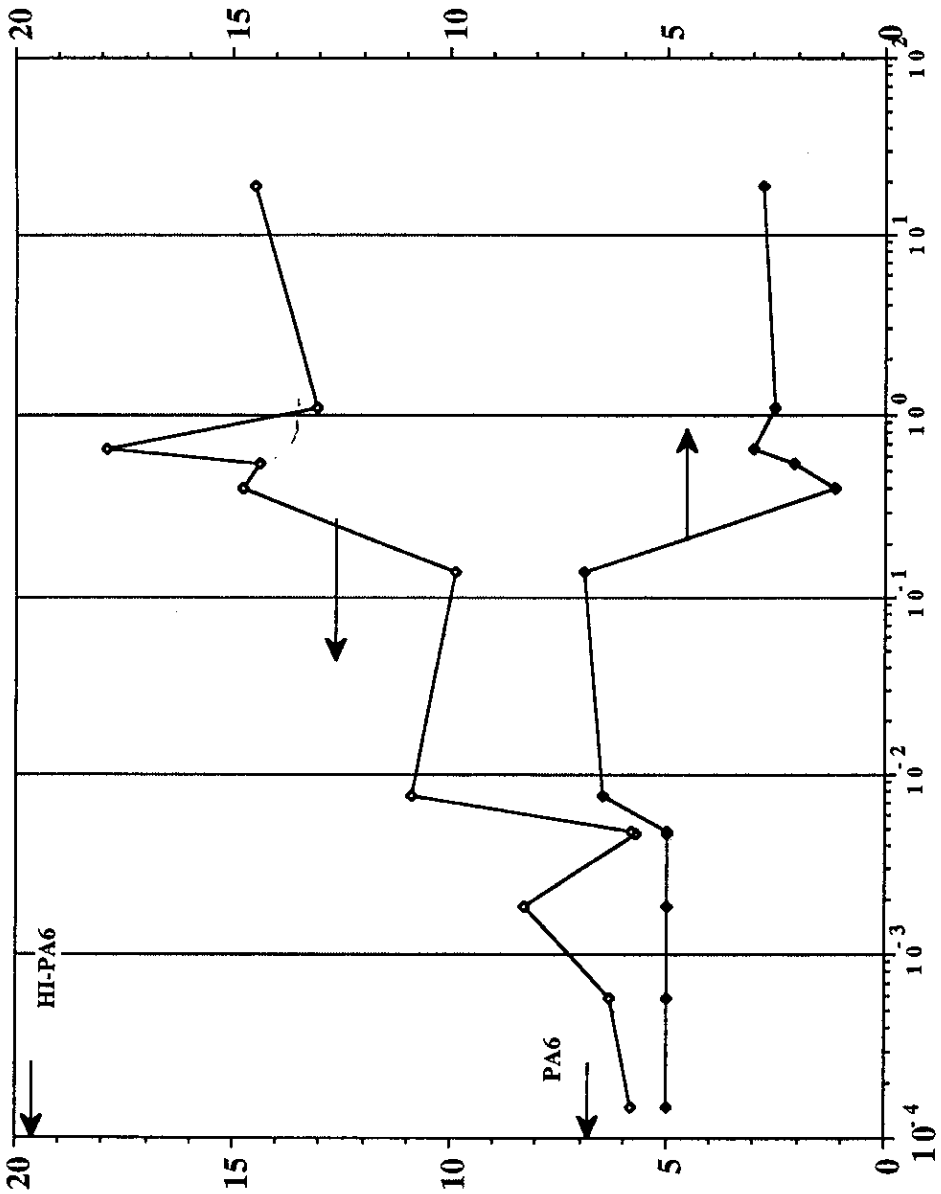

Fig. 6. Viscosity ratio effect on dispersion and toughness.

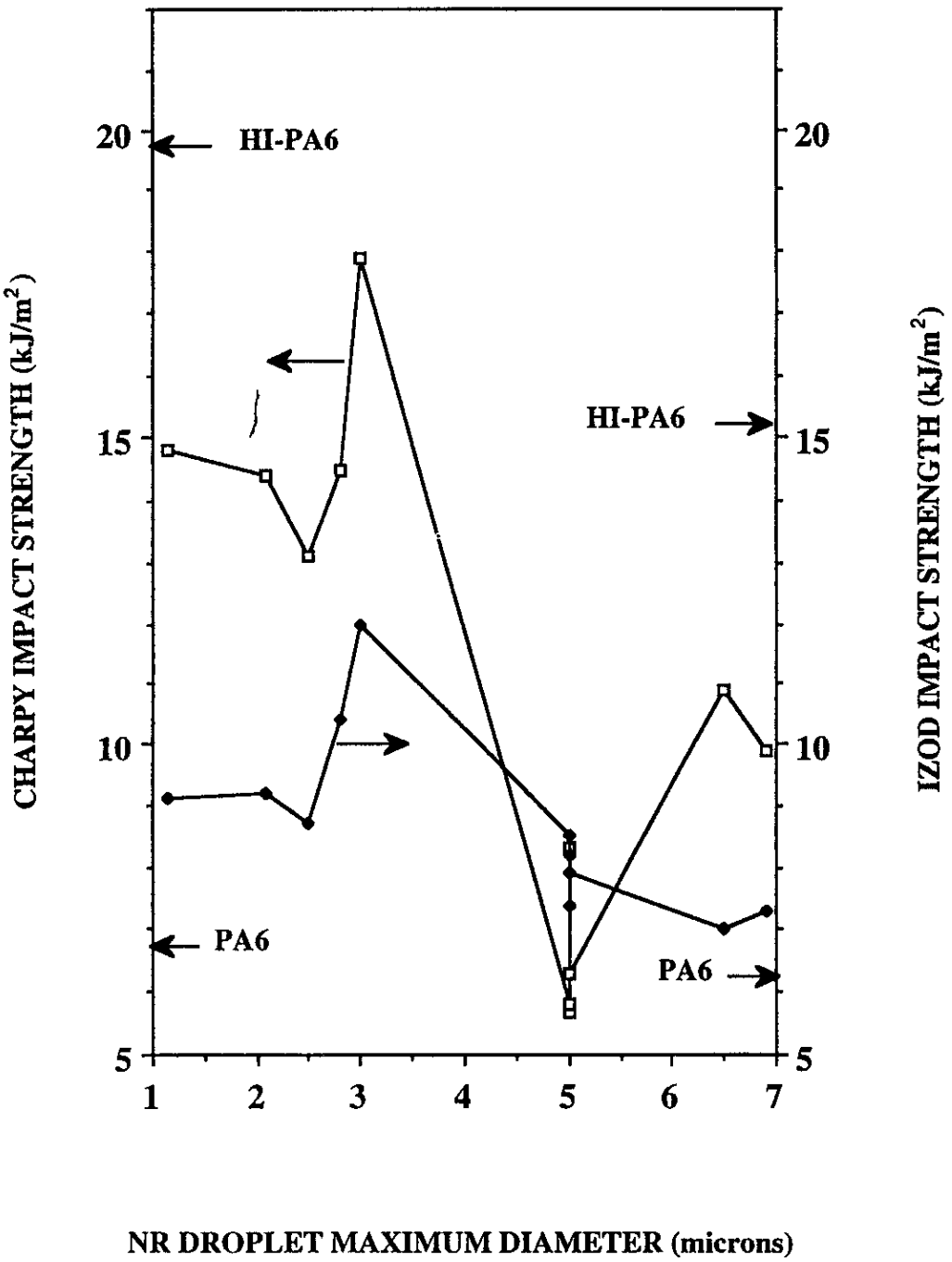

Fig. 7. Effect of NR dispersion on blend toughness.

Calculation of shear stress during mixing

A theoretical model of the two roll mill [12] was used to calculate the maximum shear stress occurring during blending of the polyamide 6 and the natural rubber. The equation for maximum shear stress (τ_{max}) is shown as equation (1)

$$\tau_{max} = \frac{3\mu U}{H_o} \cdot \frac{1}{4(1+X^2)} \qquad (1)$$

where μ is the polymer viscosity, U is the mill velocity, H_o is the nip gap, and X is the distance from nip to where the band detaches from the second roll.

Viscosity ratio of PA6/NR blends on the 2 roll mill

From the flow curves shown as Figure 3, the shear strain rates at the maximum shear stress (calculated from equation (1)) were determined, and the viscosity values calculated. The viscosity of the natural rubber divided by the viscosity of the polyamide at these shear rates gave the viscosity ratio of the blend during milling (listed in Table 4). It has been reported that a viscosity ratio of unity should give the optimum blend dispersion.[9]

Characterisation of degree of NR dispersion in the blend

Scanning electron microscopy (SEM) (Jeol JSM T100) was used to determine the size distributions of the rubber droplets dispersed in the polyamide matrix. Freeze fractured surfaces were etched with toluene overnight then sputter coated with gold. Specimens prepared both across and along the samples showed the dispersed phase to be present as spherical droplets. Measurements of dispersed phase droplet diameter were taken from electron photomicrographs which showed holes where the NR was dissolved during etching of the blend. The NR droplet size distribution data (mean and range values of NR droplet diameters) for the PA6/NR blends are shown in Table 4.

Characterisation of frozen-in molecular orientation

Shrinkage tests showed that the moulded impact bars had almost zero shrinkage on reheating at 90°C for up to 360 minutes, (see Table 5). The low shrinkage indicates that not much molecular relaxation took place during the test. These results imply that there was no significant large scale molecular orientation frozen into the bars.[13] This was a consequence of using the large gates in the mould and gentle processing conditions.

Characterisation of polyamide crystallisation behaviour.

Differential scanning calorimetry (DSC) (Perkin Elmer PC system 7) was used to study the crystallisation behaviour of the polyamide in the blends. Cooling from 260°C to 50°C at a scan rate of 20°C/minute the endothermic peak for the polyamide crystallisation was recorded. From analysis of the peak area, onset position and half-height width it was possible to compare the degree of crystallisation, onset temperature of nucleation, and spherulite size distribution.[14] Table 5 summarises the DSC results for the blends.

Physical properties testing

The physical properties of the PA6/NR blends were tested using the following test methods: Charpy impact strength (2J pendulum, Ceast), Izod impact strength (2J pendulum, Kao Tieh), heat distortion temperature (0.45Pa stress, Wallace), and hardness (Shore D, Zwick). Table 6 summarises the physical properties of the blends.

DISCUSSION OF RESULTS

Rheology

Effect of rubber structure on rheology

The rheology of natural rubber depends on the molecular weight, molecular weight distribution (MWD), branching, gel, the presence of abnormal groups, and strain induced crystallisation.[15] Long chain branching has been confirmed [16] and can affect the relaxation behaviour of uncured rubber.[15] The presence of long chain branching also leads to the formation of gel. The presence of abnormal groups on the isoprene molecules, such as epoxide, esters and long chain fatty acid esters, has been established and they are reported to be the cause of storage hardening and low temperature crystallisation.[16]

The technology of mastication has been known since Hancock introduced his "pickler" in 1820.[17] However, the diversity of reactions occurring during the mechanochemical free radical process have still not been fully characterised.[18] The variability in the raw unmasticated NR ensures that the reactions taking place during mastication are unpredictable. This results in variations in the molecular structure of the NR after mastication. The MWD for TTR5L NR changes from a bimodal distribution to a unimodal distribution as mastication proceeds.[19] Chain scission can occur in the branch chains as well as in the molecule backbone and as the molecular weight of the main chain decreases the length of the branch chains become more significant. When the branch chain length exceeds the entanglement spacing of the main chains then a significant change in the melt rheology will be observed.[15] The mastercurve shown in Figure 2 illustrates the change in rheological characteristics due to structural rearrangements that occur on mastication. The deviations from the mastercurve at lower shear rates for the NR masticated for very long times (M4 and M5) are clearly seen. These rubbers differ structurally from the NR masticated for shorter times. The deviations represent the dependence of the flow behaviour on the molecular weight distribution of the NR. This may be due to differences in the degree of branching, or length of the branch chains [19] in a similar manner as that reported previously for PBT [20] and PET [21], or to changes in the degree of free radical crosslinking in the NR.

The mechanical properties of the rubbers will also be affected by the molecular weight and the structural changes and this may affect their performance as impact modifiers.[5]

LNR was developed to find a method to reduce the molecular weight of NR with a reduction in the diversity of the side reactions that occur with mastication. The structural changes that take place in the NR when reacting the latex with phenylhydrazine to prepare LNR have been characterised by Pautrat.[22] Some of the polyisoprene molecular chains become terminated with hydroxyl, carbonyl and epoxy groups.[22] The MWD polydispersity and degree

of branching are much less affected during LNR preparation than in the mastication process. This observation can be verified by the good fit of the data to the mastercurve shown in Figure 1.

Effect of natural rubber molecular weight on viscosity ratio

The viscosity ratio for the different blends covered a very wide range from 0.00015 to 18.71, the ratio decreasing with decreasing molecular weight of NR, (see Figure 4). The blends containing the masticated rubbers had a viscosity ratio range of 1.1 to 0.0832 for a wide NR average molecular weight range of 608,000 to 43,000. The blends containing LNRs had lower viscosity ratio values covering a range of 0.1524 to 0.00015 over a NR molecular weight range of 35,100 to 3,400.

The difference in magnitude of the viscosity values for LNR compared to the masticated NR, (see Figure 3), was due to the degree of molecular entanglement being dependent on molecular weight. Brydson reported that viscosity is linearly dependent on molecular weight up to a critical molecular weight of about 15,000 for most linear polymers. Above that critical molecular weight the viscosity dependence is much greater.[23] This phenomena agrees with our observation of the big step in viscosity ratio from 0.0049 up to 0.1524, as the molecular weight of the LNR increased from 10,600 (LNR2) up to 35,100 (LNR1), (see Figure 4). It may also be partly due to structural differences in their molecules, e.g. degree of branching, length of branch chains, level of crosslinking. These differences result from the reaction route to obtain the desired molecular weights. The masticated rubbers are mechanochemically degraded and can undergo a wide variety of side reactions during molecular weight reduction, such as long chain branching and crosslinking.[19] Whereas in the preparation of liquid natural rubber less active radicals are formed which are less likely to form long chain branching or crosslinking.[22] The presence of more long chain branching in the rubber melt would lead to higher viscosity and elasticity, as exhibited by the masticated rubber compared to the LNR, (see Figure 3).

In plastic/liquid crystal polymer blends a low viscosity ratio of the order of 0.005 has been found to lead to fibrillar morphologies which are advantagous, giving high modulus.[24] However, from our SEM analysis of specimens prepared from different planes within the blend samples the rubber was always observed as having a morphology of spherical NR droplets in a PA6 matrix, even in the PA6/LNR blends of very low viscosity ratio.

The blends containing LIR also had lower viscosity ratio with decreased LIR molecular weight. The viscosity ratio for PA6/LIR50 was four times greater than the PA6/M4 blend that had a similar rubber molecular weight. This maybe due to the better uniformity of the LIR molecular structure, where the molecular weight has been controlled by the polymerisation reaction, compared to the inconsistent structure resulting from the NR mastication mechanochemical reaction.

Effect of viscosity ratio on dispersed phase droplet size

The NR molecular weight controlled the dispersed phase viscosity and hence should control the degree of dispersion achieved during mixing.[4,9] However the average particle size of the rubber droplets, observed from SEM (see Table 4), were small for all the blends and were relatively unaffected by the blend viscosity ratio over the wide range of NR

viscosities used, (see Figure 5). The values obtained for mean particle size of the NR droplets (see Table 4) are similar to those reported by Wu (0.35-2.42 microns) for well dispersed hydrocarbon rubber in polyamide 6,6.[2] Favis reported a similar insensitivity of particle size to the viscosity ratio for polypropylene/polycarbonate blends.[25]

The mean NR droplet diameter of the PA6/masticated NR blends decreased (from 0.55 to 0.26 microns) with decreasing viscosity ratio. The mean diameter of the LNR droplets were slightly larger (between 0.41 and 0.77 microns) than the masticated NR (0.45 microns) and LIR droplets (from 0.23 to 0.42 microns). However all the mean diameter values are within a narrow range of 0.21 to 0.77 microns, compared to the very wide range of viscosity ratio values (0.00015 to 18.1).

The lack of sensitivity of mean particle size with viscosity ratio maybe due to the complexity of the mixing process. Two-roll milling is not an isothermal process of constant shear stress, a range of conditions will exist at different places in the material being processed and consequently a range of real viscosity ratios will occur at different locations, some of which could be equal to unity.

The ranges of NR particle sizes in the blends are shown in Table 4. The particle size range of the masticated rubbers in PA6 were narrower than those of the LNR polymers in PA6, with smaller maximum particle sizes, indicating better uniformity of the rubber dispersion, (see Figure 5). The step increase in viscosity ratio between the blends PA6/M4 and PA6/M5 corresponds with an increase in the maximum particle size and a drop in impact strength, (see Figure 6). Agreeing with the observation by Borrgreve *et al.* that a poorer dispersion will give a lower impact strength.[4]

The dispersion of the LIR polymers in the PA6 were different as shown by the maximum particle size values. This may explain the difference in impact strength values for the two blends, as a larger diameter droplet will have less surface area per unit mass, and therefore be less effective at toughening the PA6.

Effect of viscosity ratio on impact strength

Figure 7 shows how the impact strengths varied with blend viscosity ratio. Better impact strength values were obtained when the viscosity ratio was close to one and an optimum impact behaviour occurred at a blend viscosity ratio of 0.65, close to the theoretical optimum of unity.

Blend morphology

Effect of dispersed phase characteristics on blend impact strength

From the very low shrinkage results obtained it could be concluded that molecular orientation was low and did not significantly affect the impact strength results.[13]

The Izod notched impact strengths, (shown in Table 6 and Figure 7), were higher for all the blends than for PA6, but were lower than for the HI-PA6 material. Figure 7 shows the notched impact strengths increased with the molecular weight of the NR with the Charpy values being more sensitive than the Izod results. The blends containing masticated rubbers had higher Charpy impact strengths than PA6 but lower than HI-PA6. The PA6/LNR blends had impact strengths similar to PA6.

Table 6 shows that the blend containing LIR30 had high impact strength, between the values of PA6 and HI-PA6. But the PA6/LIR50 blend had similar impact strength to PA6.

Effect of natural rubber on polyamide crystallisation

The low shrinkage values of the moulded blends, (listed in Table 5), indicate an absence of high levels of molecular orientation from injection moulding.[13] Therefore the observed increases in crystallisation (larger DSC peak areas) are not due to any significant increase in PA6 molecular orientation in the blends but are caused by the heterogeneous nature of the blends. The surface of the natural rubber droplets nucleated the PA6, giving the blends a DSC crystallisation peak at a higher onset temperature and with a narrower half-height width (indicating a more uniform spherulite size) than for the unblended PA6, (see Table 5). The peak areas of the blends were greater (indicating a greater amount of crystallinity) than that for PA6 except in some cases, i.e. PA6/L2, PA6/L3, PA6/L4, and PA6/M3. In these blends a similar amount of crystallisation occurred as with PA6. The surface area of the rubber droplets is a function of their particle size, but in these blends it did not affect the crystallisation behaviour of the PA6, in any discernable trend. The onset temperature and half-height width values were within a narrow range for all the blends and so were independent of the NR droplet particle size. However, the mean NR particle sizes measured for the blends were within a limited range.

Effect of natural rubber characteristics on physical properties

The inclusion of NR in PA6 led to a drop in H.D.T. compared to unblended PA6, (see Table 6), except for blends PA6/M4, PA6/M5, PA6/L1 and PA6/L2. The PA6/LIR blends also showed a drop in H.D.T. compared to PA6, particularly the PA6/LIR50 blend.

The Shore D hardness was slightly higher than PA6 for all the blends due to the increase in PA6 crystallinity.

SUMMARY

To allow blends of various viscosity ratios to be prepared, natural rubber was masticated for various times to give a series of natural rubbers with different molecular weights. Together with the liquid natural rubbers prepared, (listed in Table 1), a series of rubbers with a range of molecular weights from 1,200,000 to 3,400 were blended with the PA6 and then were injection moulded into impact bars. The results of the impact strength tests are shown in Figures 6 and 7.

A problem of using natural rubber is the inconsistent molecular structure, even after mastication, as opposed to polymers synthesised to a controlled MWD and degree of branching. This leads to difficulties in the optimisation of NR molecular weight for use as an impact modifier in polyamide 6. It can be seen that the highest impact strength (18 kJ/m^2) was obtained for a PA6/NR blend with a mean NR particle size of 0.33 microns and a maximum NR particle size of 3.00 microns, mixed at a viscosity ratio of 0.65, (close to unity). This contained NR masticated for 15 minutes, having a viscosity average molecular weight of 290,000.

The difference in performance as an impact modifier in PA6 of LNR compared to masticated NR is attributed to different levels of molecular entanglement and different molecular structures existing in the rubbers prepared by the two methods. For rubbers of similar molecular weight prepared by each method (M5 and L1) the impact performance of the blends was similar.

ACKNOWLEDGEMENTS

This work was supported by a research grant from the Ministry of Science, Technology and Environment. One of the authors (P.M.) wishes to express her gratitude to the King Prajadhipok and Queen Rambhai Barni Memorial Foundation for the bursary she received whilst doing this research work for her M.Sc. thesis. The authors are grateful to King Mongkut Institute of Technology Thon Buri, King Mongkut Institute of Technology Ladkrabang, and Samut Prakarn Technical College for their co-operation in providing access to their facilities used to conduct some parts of this work.

REFERENCES

1. Wu, S. (1985). Phase structure and adhesion in polymer blends: A criteria for rubber toughening. *Polymer* **26**, 1855-1863.
2. Wu, S. (1987). Formation of dispersed phase in incompatible polymer blends: Interfacial and rheological effects. *Polym. Eng. Sci.*, **27**, 335-343.
3. Martuscelli, E., Riva, F., Sellitti, C., and Silvestre, C. (1985). Crystallization, morphology, structure and thermal behaviour of nylon 6/rubber blends. *Polymer*, **26**, 270-282.
4. Borggreve, R.J.M., Gaymans, R.J., Schuijer, J., and Ingen Housz, J.F. (1987). Brittle-tough transition in nylon-rubber blends: effect of rubber concentration and particle size. *Polymer*, **28**, 1489-1496.
5. Borggreve, R.J.M., Gaymans, R.J., and Schuijer, J. (1989). Impact behaviour of nylon-rubber blends: 5. Influence of the mechanical properties of the elastomer, *Polymer*, **30**, 71-77.
6. Borggreve, R.J.M., Gaymans, R.J., and Luttmer, A.R. (1988). Influence of structure on the impact behaviour of nylon-rubber blends. *Makromol. Chem. Macromol. Symp.* **16**, 195-207.
7. Borggreve, R.J.M., Gaymans, R.J., and Eichenwald, H.M. (1989).Impact behaviour of nylon-rubber blends: 6. Influence of structure on voiding processes; toughening mechanism. *Polymer*, **30**, 78-83.
8. Crespy, A., Caze, C., Coupe, D., Dupont, P., and Cavrot, J.P. (1992). Impact resistance performances of polyamide 6 blended with different rubber phases. *Polym. Engng. Sci.*, **32**, 273-279.
9. Karger-Kocsis, J., Kallo, A., and Kuleznev, V.N. (1984). Phase structure of impact-modified polypropylene blends. *Polymer*, **25**, 279-286.
10. Keskkula, H., and Turley, S.G. (1978). Polyisoprene modified polystyrene. *Polymer*, **19**, 797-800.
11. Gregory, D.R., and Watson, M.T. (1970). Steady-state flow properties of PET melts. *J. Polym. Sci., Part C*, **30**, 399-406.
12. Tadmor, Z., and Gogos, C.G. (1979). Mixing chapter 11 in "*Principles of polymer processing*" publ. Wiley-Interscience, New York, pp.442-447.
13. Fritch, L.W. (1989). The Izod-orientation concept for impact characterisation. *Plastics Engineering*, September, 43-45.
14. Gupta, A.K., and Ratnam, B.K. (1991). Crystallisation, tensile and impact behaviour of polypropylene/ polybutadiene blend. *J. Appl. Polym. Sci.*, **42**, 297-315.
15. Fuller, K.N.G., and Fulton, W.S. (1990). Influence of molecular weight distribution and branching on the relaxation of uncrosslinked natural rubber. *Polymer*, ***31***, 609-615.

16. Tanaka, Y. (1989). Structure and biosynthesis of natural polyisoprene. *Prog. Polym. Sci.* **14**, 339-371.

17. Stern, H.J. (1971). History, chapter 1 in "*Rubber Technology and Manufacture*", ed. C.M.Blow, publ. Newnes-Butterworth, London, pp.2.

18. Fries, H., and Pandit, R.R. (1982). Mastication of rubber. *Rubb. Chem. Technol.*, **55**, 309-317.

19. Wiriyasathit, S. (1990). A study of structural factors affecting rheological properties of natural rubber. *M.Sc. thesis, Mahidol University,* , p.114.

20. Buchneva, T.M., Kulichikhin, S.G., Gabrielyan, G.A., Artemova, M.N., AnanûEva, L.A., Malkin, A.Ya., and Rogovin, Z.A. (1983). Viscometric syudy of some structural features of modified polyethylene terephthalate. *Polymer Science USSR*, **25**, 931-936.

21. Axtell, F.H. (1987). A study of the flow properties and processability of thermoplastic polyesters. *Ph.D. thesis, Loughborough University*, pp.67-89.

22. Pautrat, R. (1980). Cauotchoucs liquides de polyisoprene naturel preparation et proprietes. *Caoutchoucs et plastiques*, no.600, April, 91-97.

23. Brydson, J.A. (1981). *Flow properties of polymer melts.* 2nd ed. Godwin, London, , p.69.

24. He, J.S., Bu, W.S., and Xu, X.Q. (1992). The effect of viscosity ratio on the LCP fibril formation in blends containing a liquid crystalline polymerû, Paper OB1, *Proceedings of International Symposium on Polymer Alloys and Composites (ISPAC)*, 9-11 December 1992, Hong Kong Polytechnic.

25. Favis, B.D. (1990). The effect of processing parameters on the morphology of an immiscible binary blend. *J. Appl. Polym. Sci.*, **39**, 285-300.