

Rheological Signatures of Acrylonitrile Butadiene Rubber and Ethylene-Methyl Acrylate Copolymer Blends

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Abstract – Rheological signatures of blends of Acrylonitrile Butadiene Rubber (NBR) and Ethylene-Methyl Acrylate copolymer (EMA), having varied proportions of EMA from 0 to 100% have been studied at three different temperatures (100, 120, and 140°C) and at six different shear rates (12.26, 61.3, 122.6, 306.5, 613.0, and 919.5 S⁻¹) using a Monsanto Processability Tester (MPT). The melt viscosities of the NBR/EMA blends decrease steadily with increase in the shear rate simulating the pseudo plastic nature of the blends. The effect of temperature on the melt viscosity of the blends was examined and the shear rate-temperature superposition master curve was generated. The activation energy (E_a) of flow calculated using Arrhenius relation for NBR, EMA and their blends. Attempts have been made to correlate the flow behavior with morphology of the blends.

Key Words: Rheology, morphology, melt blending, flow behaviour

1. INTRODUCTION

Polymer blend has become materials of tremendous significance both in industrial circle as well as among the researchers because of its tremendous of interest in producing new materials with a unique combination of properties¹ not found in individual polymer constituent that too without resorting to the tedious methods of synthesizing new polymers by conventional route. Thus the commercial importance of the polymer blends has been increasing day by day.

It has become necessary to optimize the processing conditions for the blends in order to achieve a definite set of end use properties. Generally, in case of the neat polymers, the flow behavior depends on the flow geometry and processing conditions such as the temperature, shear rate, time of flow, and so on. Whereas in case of polymer blends, the flow behavior becomes more complex and it is very much influenced by additional factors like the miscibility between the blend constituent, the interaction at the interface, the morphology of the blend, interfacial adhesion, and interfacial thickness.

A large numbers of research papers have been published in the past few decades on the miscibility of polymer blends and hundreds of patents has been filled.²⁻⁴ The miscibility has been attributed to either specific interaction or chemical reaction between the blend

constituents causing an increase in density of the blend above the theoretical density obtained from the additivity rule. In most of the cases, this has been reflected in the rheological signature of the blends showing higher melt viscosity as compared to that obtained by the log-additivity rule. The complex rheological behavior of the polymer blends have been investigated by several researchers.⁵⁻⁷

The rheological properties of blends are easy to measure and relatively simple to interpret as they behave almost as a single-phase melt. Utracki and Kamal⁸ have dealt in detail the subject of melt rheology of polymer blends and have compared the rheological properties of polymer blends with those of emulsions, block polymers and homologous polymer blends.

They have been able to categorize the polymer blends into three groups, namely; (i) positively deviated blends (PDB); having higher value of experimental viscosity than that theoretically predicated by using log additivity rule ii) negatively deviated blends (NDB); a lower value of viscosity than the one predicted by the additivity rule (iii) positive-negative deviated blends (PNDB); which exhibit both positive and negative deviation from the theoretical one depending on the composition falls under this class.

Later, Utracki⁹ categorically correlated the rheological properties of these blends with their thermodynamic behavior and structure. A thorough literature survey revealed the lack of information related to the evaluation of rheological properties of NBR/EMA blends. The present research investigation concentrated on the rheological properties of NBR/EMA blends as a function of varying amounts of EMA.

2. EXPERIMENTAL

2.1 Materials

Acrylonitrile Butadiene Rubber (Perbunan 3445F), with the following specifications: Acrylo nitrile content 33%, specific gravity 0.97, Mooney Viscosity 45, ML (1+4) 1000C was supplied by M/s Lanxess Deutschland GmbH. Poly (Ethylene - co- Methyl Acrylate) copolymer (Optema TC 120) having the methyl acrylate content 21%, melting point of 810C, MFI 6 g/min and density of 0.94 g/cm³ was obtained from M/s Exxon Chemical Corporation, Belgium.

2.2 Preparation of the blend

The blends of NBR and EMA having different blend ratios were prepared in a Brabender Plasticorder (model PLE-330) at a temperature of 120 °C at a rotor speed of 60 rpm for 5 min. EMA was added first, melted for 1 min, then NBR was added and melt mixed for additional 4 min. In all the cases the total mixing time was maintained at 5 min. The blend was then taken out from the plasticorder and sheeted out on a two-roll laboratory mill (150 x300 mm) immediately at room temperature. The blends have been designated as Ex (x= 0, 30...100) where x indicates the weight percentage of EMA in the blend, for example, E30 indicates 30% EMA and 70% NBR.

3. CHARACTERIZATION OF BLENDS

3.1 Rheological Measurements

The melt flow behaviours of the NBR/EMA blends were observed at three different temperatures viz: 100, 120, and 140 °C, and at six different shear rates (12.26, 61.3, 122.6, 306.5, 613.0, and 919.5 S⁻¹) using Monsanto processability tester (MPT)-a micro-processor controlled programmable capillary rheometer fitted with a capillary having an L/D ratio of 30:1 and a barrel radius of 9.53 mm.

The test samples were charged into the barrel and preheated for 3 min for uniform temperature distribution and rheological signatures were recorded.

The variation in shear rates was achieved by automatically changing the speed of the plunger. The pressure at the entrance of the capillary was recorded automatically with the help of a pressure transducer. The entire barrel and the capillary assembly were electrically heated and controlled with a microprocessor-based temperature controller.

The entry into the capillary was conical having multiple cones of between 45° and 60° which are known to minimize the pressure drop at the entrance. Therefore, the Bagley correction was not necessary as the wall slippage at the capillary was assumed to be negligible. The apparent shear stress hence was taken to be equal to the true shear stress.

The die swell data were directly recorded by the Monsanto processability tester with the help of a laser detector at different shear rates through the microprocessor-controlled laser beam assembly according to the following equation:

$$\% \text{ of Die Swell} = \frac{d_e - d_c}{d_c} \times 100 \quad \text{----- (1)}$$

Where, d_e and d_c are the extrudate diameter and capillary diameter, respectively.

4. RESULT AND DISCUSSION

4.1 Rheological Characteristics:

The effect of blend ratio, shear rates, and temperature on the melt viscosity of neat NBR, neat EMA, and their blends are shown in Figure 1. In general, it can be observed that, at all temperatures and blend ratios, the melt viscosity decreases as a function of increasing shear rates. This is an indication of the shear thinning effect of the blends and also is the characteristic feature of pseudoplastic nature of these blends. At higher shear rate the polymer-polymer interaction leading to loosely bound structures and easy orientation of molecules along the direction of stress together with the slippage of molecules. This structural breakdown is well supported by a drastic drop in viscosity as a function of increased shear stress. At practically zero shear rate, the randomly oriented and entangled molecules may be responsible for a high viscosity. From the Figure, it can be noticed that, the viscosity of NBR is higher than that of the EMA at a given processing temperature. A reduction in the melt viscosity of NBR/EMA blends can be observed with increasing the EMA content over the entire shear stress values. On the other hand, the melt viscosity of NBR reduces steadily with an increase in shear stress. This can be attributed to high intermolecular force of interactions between the chain segments in NBR due to the presence of polar acrylic units and comparatively lesser orientation under high shear stress. The melt viscosity of all the blends and their pure components found to reduce with increase in the shear rate at all the temperatures. This may be due to shear thinning effects of the materials. A linear reduction in the melt viscosity of NBR, EMA and their blends as a function of shear rate can be observed from Figure 1.

The melt viscosity values of the blends lies in between that of pure components. The reduction in melt viscosity as a function of increased shear stress may be due to the higher wall slippage. The observed reduction in viscosity was more drastic for NBR and marginal for EMA at lower shear rates, whereas in case of the blends, the reduction is intermediate depending on the blend composition. The effect of low (12.26 S⁻¹) and high (919.5 S⁻¹) shear rate on the shear stress as a function of varying amount of EMA in NBR/EMA blends at 100, 120 and 140 °C is shown in Figure 1. A nonlinear relationship between the shear stress and EMA content in NBR/EMA blends can be noticed at both low and high shear rate. The observed higher shear stress in case of NBR may be due to the polar nature of NBR. Table 1 shows the die swells of the blends and pristine polymers at different temperatures of 100, 120 and 140 °C with varying shear rates (12.26, 61.3, 122.6, 306.5, 613.0, and 919.5 S⁻¹). It attributes to the presence of EMA in the blends as EMA higher concentration in the blends increases die swell decreases, but the decreases is rapid at lower concentration of EMA. Further increases EMA concentration lowers the die swell marginally; at all temperatures studied. Moreover, NBR

rich phases in blend shows higher die swell especially at 140 °C. This phenomenon is observed at all shear rates starting from low to high (12.26 S⁻¹ to 919.5 S⁻¹).

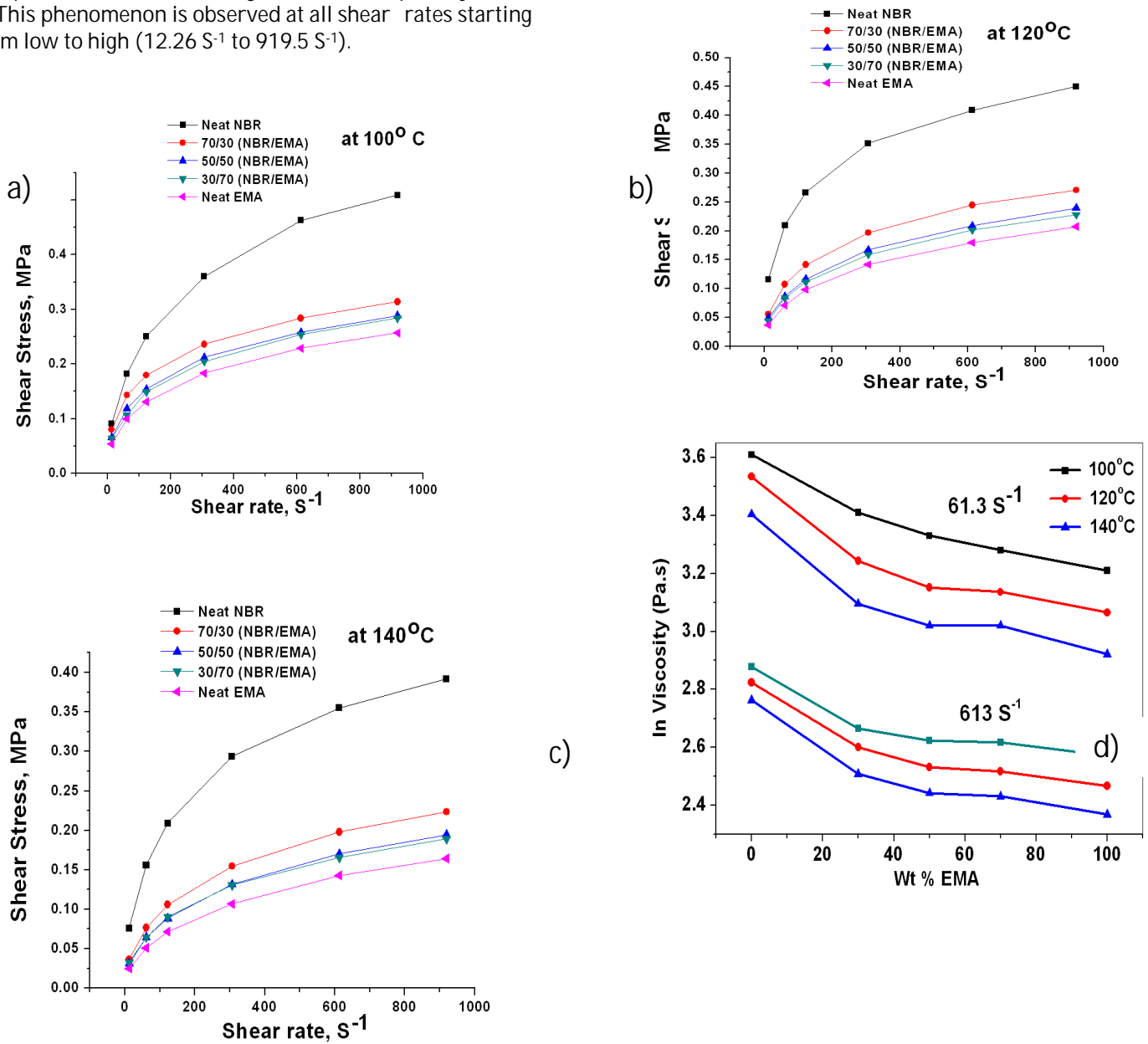


Figure 1: a) Shear Stress Vs Shear Rate graph for EMA/NBR blends at 100°C, b) Shear Stress Vs Shear Rate graph for EMA/NBR blends at 120°C, c) Shear Stress Vs Shear Rate graph for EMA/NBR blends at 140°C, d) Intrinsic Viscosity Vs Weight Percentage of EMA

Sample Code	Shear rate (S-1)	100°C	120°C	140°C
		Die Swell (%)		
E0	12.26	43.4	65.4	64.4
	61.3	48.3	69.3	69.2
	122.6	54.5	71.3	71.3
	306.5	58.3	73.6	68
	613	60.1	74.5	76.2
	919.5	65.5	77.4	79
E30	12.26	39.5	55.5	51.3
	61.3	41.6	58.3	74.4

	122.6	53.2	61.2	76.5
	306.5	55.5	64.6	68.3
	613	41.3	69.3	46.8
	919.5	43.3	71.3	44.6
	12.26	41.2	56.6	41.6
	61.3	46.6	64.4	47.2
E50	122.6	49.3	69.9	51.2
	306.5	53.3	71.4	54.4
	613	43.4	77.4	50.9
	919.5	42.9	81.3	47.4
	12.26	52.3	44.3	42.6
	61.3	54.4	45.3	57.3
E70	122.6	55.9	57.6	77.6
	306.5	59.3	62.3	63.4
	613	62.3	52.4	53.4
	919.5	52.6	50.8	51.4
	12.26	45.9	41.8	47.6
	61.3	88.4	79.9	52.2
E100	122.6	74.4	84.4	55.4
	306.5	64.3	88.3	58.6
	613	59.9	74.6	62.1
	919.5	57.4	56.6	62.6

Table 1. Die swell at different shear rates at 100°C, 120°C and at 140°C

5. CONCLUSIONS

The following conclusions have been drawn from the present investigation:

- 1) The melt rheology of the EMA/NBR blends has been investigated with reference to the effect of blend composition, shear rate, and temperature.
- 2) On increasing shear rate and temperature of shear flow, the melt viscosity decreases for all the blends and pure components concurring with the shear thinning effect of the materials.
- 3) Die swell is decreasing with increasing the concentration of EMA in the blend.
- 4) Surface finishes for the blends are better at lower shear rate as compared to those obtained at higher shear rate. Melt fracture occurs at critical shear rate.
- 5) Neat NBR and NBR rich phase extrudates are rough and have the shape of a screwed thread.

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