Rheological studies of NRL-PAA blends and Impact of Concentration, Temperature and speed range on their properties

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Abstract

Blends of Natural Rubber Latex (NRL) and Poly Acryl Amide (PAA) have been prepared by varying PAA concentration. Rheological properties of the blends at different temperatures and variable speed ranges have been compared with those of NRL and PAA under similar conditions. Both PAA and the NRL-PAA blends show non-Newtonian Bingham nature, the blends have been showed more shear thickening effect with increased PAA contents.

The yield stress enhances with increasing PAA concentration in the blends. It is also observed that the shear stress and yield stress increase and viscosity decreases with increasing speed ranges. The change of nature of NRL rheogram on addition of PAA indicates the interaction between NR and polymer segments. With increasing speed range, the decreasing trend of viscosity indicates the orderliness of molecular segments in the blends. The temperature effect on the rheology of NRL-PAA blends shows enhanced shear thinning effect with increasing temperature. The activation energy of the blends decreases with increasing temperature.

Introduction

Blends of polymers have been developed to meet several industrial requirements such as the need for easier processing and broadening of the properties range either by varying the type, relative amount of each compound. The macromolecular chemistry and technology of water soluble polymers have been actively pursued area due to their ever increasing demand in many industries. Their usage in a variety of processes involving blend systems containing different chemical species characterzation and basic information regarding their interactions with other molecules in the systems are important for optimizing their behavior as well as to enhance durability with minimized the cost. These systems are of great interest as viscosity modifiers in various applications such as coatings.

The shear thinning properties were reported by Seethamrajul et al[1] for starch-synthetic polymer blends. Effect of salt content on the rheological properties of hydrogel based on oligomeric electrolysis was reported by Kundu et al[2]. Ratnam and Ahmad[3] reported

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on the rheological properties of radiated PVC-ENR blend and showed that the blend remains pseudo plastic in nature. Arayaprance and Rempul[4] showed that the addition of compatibilizer as methyl methacrylate-Butadien-Styrene (MBS) improved the compatibility of the blends. Rheological behavior and compatibility of NR/BR blends were studied by Hsien et al [5]. Tiu et al[6] studied the yield stress with variation of shear properties for the viscoelastic materials. The physicochemical properties of NR/PVA blend was studied by our research group [7]. Rheological studies of NRL-PVP blends were also reported by the authors [8].

In the present study, we interested to make NRL-PAA blends and investigate their rheological properties and studied the impact of concentration of PAA in the blends, temperature variation and speed ranges on the properties of blends.

Experimentals

Materials

Polycrylamide (PAA) MW 72000 was used from BDH (AnalaR) England.

Collection of Latex

NRL was collected from Satgaon Rubber Estate, Sylhet, Bangladesh. To prevent coagulation, the freshly collected latex was immediately diluted with 20-25 ml/L of 25% aqueous ammonia solution (GPR,BDH England). The preserved field latex was then concentrated by centrifuge method using laboratory scale centrifuge machine, SPL-100, Saito Separator Ltd., Japan. The required amount of 1.5% aqueous ammonia was added to centrifuge NR latex to adjusted 50% total solid content (TSC).

Preparation of blends

The 25g of solid PAA polymer was poured into a beaker containing 250 ml hot water and stirred continuously to give a homogeneous solution.

NRL of 50% total solid content (TSC) was mixed with definite proportions of 10% polymer solution of Polyacrylamide (PAA) for different NRL- PAA blends. PAA solution was added to NRL dropwise and stirred with a mechanical stirrer for one hour to yield the blends.

Measurement of rheological properties

Rheological properties of the blends were determined with a Rheo-stress HAAKE Viscometer Model MV_1 using coaxial cylinder sensor system. Dice shaped with inner cylinder radius 20.04 mm, height 60 mm and outer cylinder cup radius 21 mm was used. The shear stress and viscosity of the samples at different shear rate were measured with variation of speed ranges such as 1%, 10% and 100%.

Rheological properties of blends were also determined at different temperatures such as

25^0, 30^0, 35^0 and 40^0

Results and Discussion

Flow curve and viscosity curve of PAA

Figures1a(i-iii) and 1b(i-iii) show the flow and viscosity curves of PAA at 25^0 C at different speeds (1%, 10% & 100%) for MV_1 system respectively. The yield stresses of PAA were also calculated and found that the shear stress as well as yield stress increases with increased shear rate as well as speed range. It is found that the viscosity decreases with increasing shear rate showing shear-thinning. The yield stress and viscosity (at zero shear) of the PAA solutions at 25^0 C and at different speeds are shown in Table 1. From the flow and viscosity curves PAA could be categorized as Bingham plastic[8]. The rheological properties of NRL has also been reported by us[9].

Flow curve and viscosity curve for NRL- PAA blends

Flow curve and viscosity curve for NRL-PAA blends at 25^0 C and 1% speed are shown in Figures 2a and 2b respectively. Figure 2a shows that the shear stress increases with increasing shear rate and the yield stress also increases with shear rate. The effect of PAA content in the blend was investigated and it is observed that the shear stress and yield stress increase with PAA content in the blends. Figure 2b shows that the viscosity decreases with shear rate and trend of decrease in viscosity is found higher at higher PAA content in the blends compared to those at lower ones. From the flow and viscosity curves it is assumed that the increasing content of PAA in the blend enhances the shear thickening.

Above results show that in NRL-PAA blend, the strong interaction takes place between the two compounds. The interaction probably arises from the rearrangement of the amide groups of PAA in the formation of a hydroxyl group which is capable of interaction with the π-electrons of NR. It may be noted that similar interaction has been proposed by Sovilj et al [10] for the interaction between hydroxypropyl methylcellulose and sodiumdodecylsulfate blends. The results are consistence with the NRL-PVP blends [8].

Effect of speed range on the NRL-PAA blend

It is observed that the shear stress as well as yield stress of the blends increases with increasing speed. Comparing the results, it is observed that the viscosity decreases with increasing speed. Such decrease may arise from the orientation of polymer molecules at high speed. The polymer segments in solution are present in disorderly but at increasing speed with consequent high force cause the molecular segments to arise ordered orientation and the viscosity decreases.

Table 1: *Yield stress and viscosity (at zero shear) for NR, NRL-PAA blend and PAA at 25^{0}C and different speeds.*

Yield stress [Nm^{-2}]				
Sp	NR	NRL-1.0PAA	NRL-2.0PAA	PAA
1%	0.044	4.154	2.949	83.598
10%	0.099	6.858	5.152	101.11
100%	0.682	12.075	8.823	92.092
Viscosity (at zero shear) [Pa.s]				
1%	0.633	35.50	25.20	712.8
10%	0.085	5.86	4.40	86.42
100%	0.058	1.032	0.754	8.745

Effect of temperature on the rheology of NRL, PAA and NRL-PAA blends

The temperature effect on the flow curve and viscosity curve for NRL, NRL-2.0PAA and PAA at 1% speed are shown in Figures 3a-b, 4a-b and 5a-b respectively. Figures 3a, 4a and 5a show that the shear stress increases with shear rate but the shear stress decreases with temperature for NRL, NRL-2.0PAA blend as well as PAA. The yield stresses are determined from the plots and observed that the yield stress decreases with temperature (Table 2).

Figure 3b, 4b and 5b show that the viscosity decreases with shear rate as well as temperature for NRL, NRL-2.0PAA blend and PAA. It can be suggested that at high temperature, the kinetic energy of the polymer segments increases and the interaction between the polymer segments decreases. Hence the energy required to flow is less at higher temperature than that at lower ones. Compared to NRL and PVA, NRL-PVA blend shows smaller temperature effect on flow. That is the variation of viscosity with temperature decreases for NRL-2.0PVA blend. At lower temperature, the viscosity decreases rapidly and it has a tendency to recover from large deformation. Table 2 shows the viscosities obtained from the plots.

Table 2: *Yield stress and viscosity (zero shear) forNRL, NRL-1.0PAA, NRL-2.0PVA and PAA blend at different temperatures and different speeds.*

Yield stress [Nm^{-2}]												
Speed	NRL-1.0PAA				NRL-2.0PVA				PVA			
	25^0 C	30^0 C	35^0 C	40^0 C	25^0 C	30^0 C	35^0 C	40^0 C	25^0 C	30^0 C	35^0 C	40^0 C
1%	4.15	2.57	3.38	3.16	2.95	1.86	1.41	1.09	83.53	18.99	6.12	-
10%	6.86	7.21	7.89	7.66	5.15	4.15	3.57	3.67	101.11	9.98	9.38	-
100%	12.07	15.36	14.75	14.91	8.82	7.98	6.73	7.66	92.09	13.52	-7.08	

Speed	Viscosity (zero shears) [Pa.s]											
	NRL-1.0PAA				NRL-2.0PVA				PVA			
	25^0 C	30^0 C	35^0 C	40^0 C	25^0 C	30^0 C	35^0 C	40^0 C	25^0 C	30^0 C	35^0 C	40^0 C
1%	35.50	22.01	28.62	26.97	25.20	15.90	12.11	9.36	712.8	162.3	52.29	-
10%	5.86	6.16	6.74	6.55	4.40	3.55	3.05	3.14	86.41	8.53	7.98	-
100%	1.032	1.31	1.26	1.25	0.754	0.68	0.57	0.655	8.746	1.16	0.61	-

Activation energy for NRL-PAA blends

The activation energy of the NRL-PAA blends and PAA was calculated from the following Arrhenius type plots of viscosity verses reciprocal of Kelvin temperature at different shear rates.

$$\eta = A\exp\left(\frac{E}{RT}\right) \quad \text{.......... (1)}$$

and the logarithmic form is

$$\log\eta = \log A + \frac{E_n}{2.303R}.\frac{1}{T} \quad \text{........ (2)}$$

where, A is a constant and E_n is the energy of activation of viscous flow both depending on the system. Plot of log η vs 1/T, yields straight lines and the slope of the lines give activation energy.

Results show that activation energy decreases with increased shear rate for 1% and 10% speeds. For 100% speed activation energy initially increases and then decreases with shear rate. Effects of shear rate on the activation energy for NRL-PAA blends are shown in Figures 5a-5c. The effect of speed on the activation energy for NRL-2.0PAA and PAA is shown in Figure 5d. It is observed that activation energy increases with speed for PAA at lower speed and at higher speed activation energy decreases. But for NRL-2.0PAA blend activation energy decreases at all the speed and the decreasing trend is sharp at lower speed compared to those at higher speed.

The activation energy for NRL-2.0PAA blend and PAA system at different speeds are given in Table 3.

Activation energy [kJ]					
	NRL-2.0PAA		PAA		
1%	10%	100%	1%	10%	100%
68.24	31.92	14.78	219.24	343.17	299.93
61.77	32.5	16.25	216.23	334.78	245.76
63.84	27.84	15.39	215.98	319.92	230.31
55.73	27.75	14.59	218.88	309.8	217.25
52.86	29.2	17.05	218.3	298.27	213.16
46.93	28.06	15.64	238.85	334.56	218.93
38.21	28.34	19.35	273.47	308.2	259.62
34.62	27.88	17.43	301.43	261.59	354.98
33.35	23.83	13.74	295.3	262.69	442.05
26.47	21.03	14.88	290.79	196.42	513.21

Effects of speed e on the log viscosity vs 1/T plot and activation energy for NRL-PAA blends are shown in Figures 5e-g and 5h respectively. Activation energy decreases with increase in speed for all the NRL-PAA blends as well as PAA. Activation energy increases with increased PAA content in the blend.

Table 3a: *Effects of speed on activation energy for NRL-PAA blends*

Sample types	Activation energy [kJ]		
Speed range	1%	10%	100%
NRL	-1.03	-0.22	-0.09
NRL-1.0PAA	6.22	-19.60	-3.72
NRL-2.0PAA	337.32	22.49	3.74
PAA	25650	2396.3	187.02

The increases of activation energy indicate the reduction of fluidity of samples. Therefore, it is shown that the presence of PAA in the NRL, the fluidity reduces and increasing of speed the flowing capability of the blend becomes easier.

Conclusion

NRL and PAA polymer are blended with varying concentrations and their rheological properties were investigated at different temperatures and different speeds such as 1%, 10% & 100% respectively. The behavior of the rheogram of PAA is categorized to be pseudoplastic Bingham nature and the behavior of the rheogram of NRL changes significantly with increasing concentrations of PAA in the blends. The yield stress of the blends are also calculated and found that the yield stress increases with content of PAA in the blend. The increasing trend of stress increases with PAA content in the blend. The speed increases the shear stress. The yield stress of the blend also increases with increased speed. The increased of PAA in NRL shows the more shear thickening. The change of the nature of rheogram of NR in presence of PAA indicates the interaction between the NR particle and polymer matrix. With increasing speed, the decreasing trend of viscosity indicates the orderliness of molecular segments in the blends. The shear stress, yield stress increase and viscosity decreases with increased temperature for NRL, NRL-PAA blends and PAA samples. Thus with increased temperature all the samples show shear thinning effect. Activation energy decreases with increasing the speed for all the NRL-PAA blends as well as PAA. Activation energy increases with increased PAA content in the blend.

Aknowledgement

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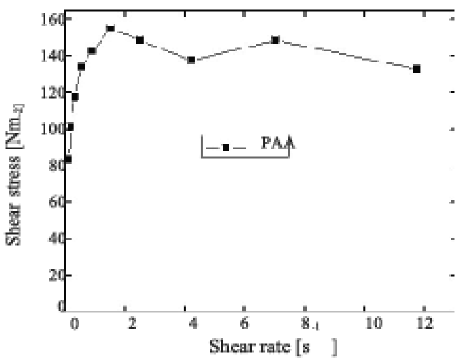

Fig. 1a (i): Shear stress vs shear rate curve of PAA curve at 25^0 C 1% speed .

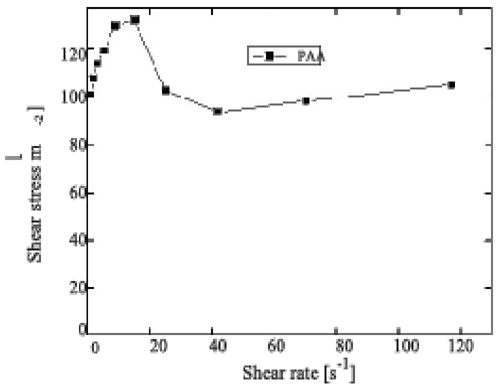

Fig 1a (ii): Shear stress vs shear rate of PAA at 25^0 C 10% speed.

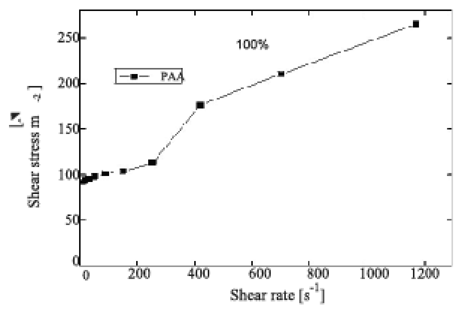

Fig. 1a (iii): Shear stress vs shear rate curve of PAA at 25^0 C 100% speed .

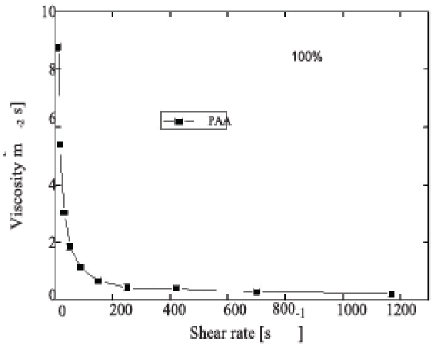

Fig. 1b(i): Viscosity curve of PAA at 25^0 C 100% speed

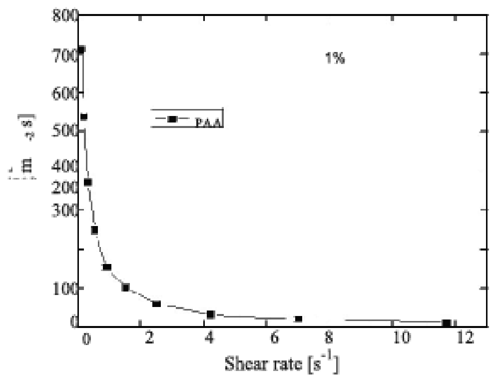

Fig. 1b(ii): Viscosity curve of PAA at 25^0 C 1% speed.

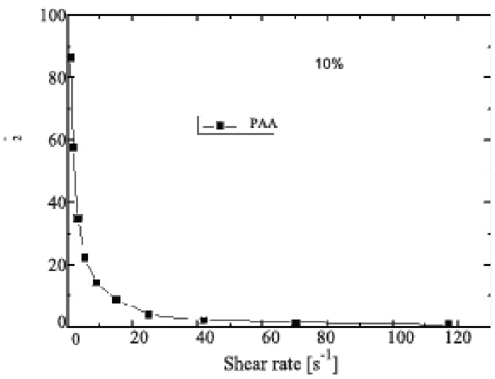

Fig. 1b(iii): Viscosity curve of PAA at 25^0 C 10% speed.

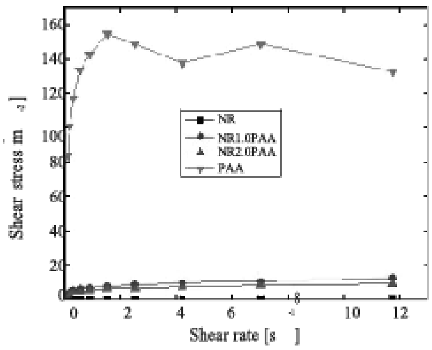

Fig. 2a: Shear stress vs shear rate curve of NRL-PAA blends at 25^{0} C 1% speed.

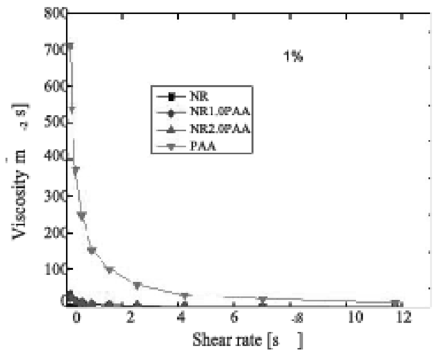

Fig. 2b: Viscosity curve of NRL-PAA blends at 25^{0} C 1% speed.

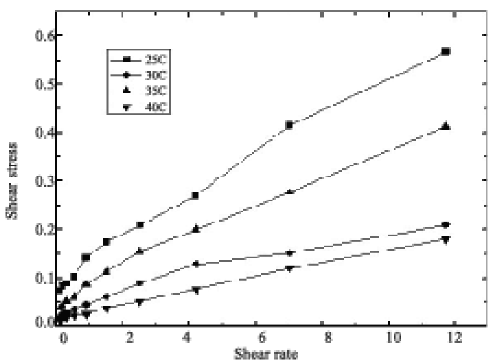

Fig. 3a: Effect of temperature on stress vs rate plot for NRL at 25^{0} C.

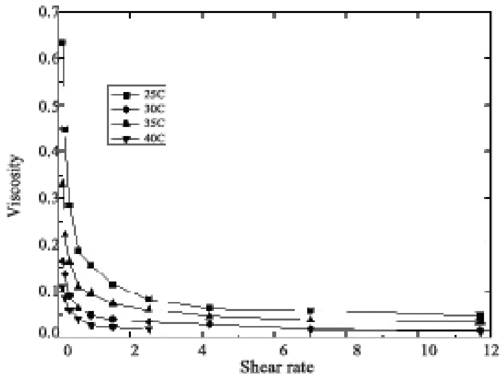

Fig. 3b: Effect of temperature on viscosity curve for NRL at 25^{0} C.

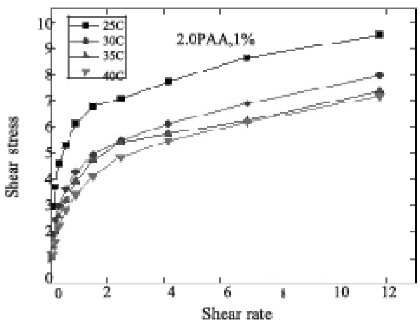

Fig. 4a: Effect of temperature on stress vs rate plot for NRL-2.0PAA blend at 25^{0} C.

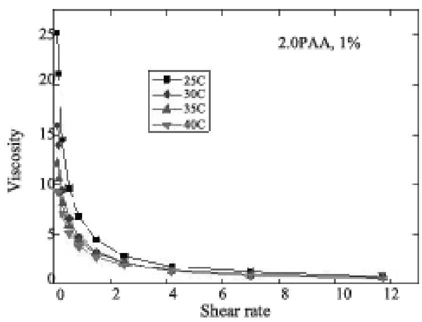

Fig. 4b: Effect of temperature on viscosity curve for NRL-2.0PAA blend at 25^{0} C.

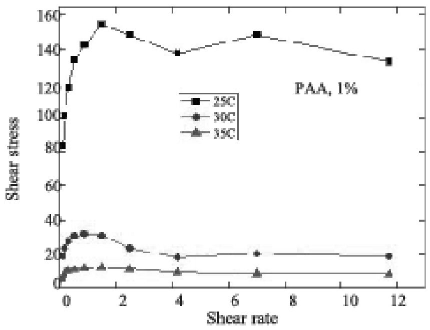

Fig. 5a: Effect of temperature on stress vs rate plot for PAA blend at 25^0 C.

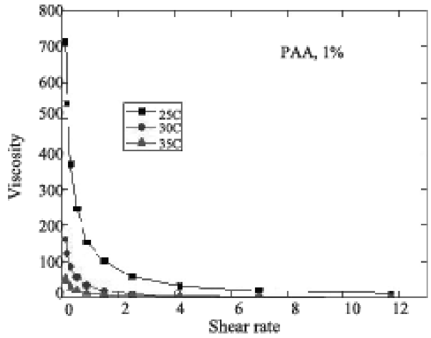

Fig. 5b: Effect of temperature on viscosity curve for PAA blend at 25^0 C.

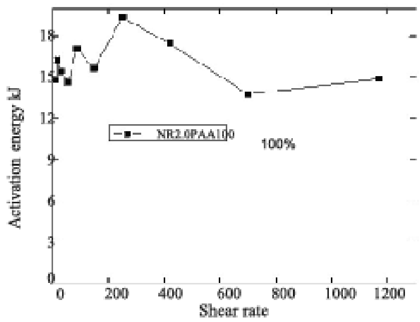

Fig. 5c: Effect of shear rate on activation energy for NRL-2.0PAA blend at 100% speed.

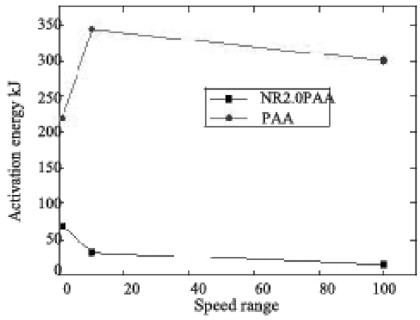

Fig.5d: Effect of speed range on activation energy for NRL-2.0PAA blend and PAA.

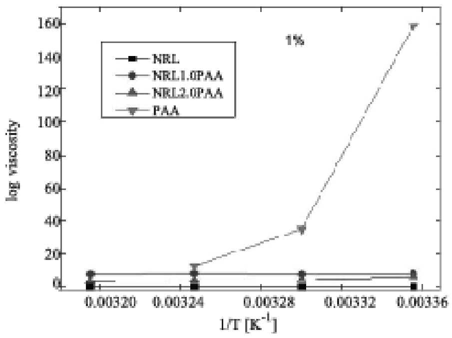

Fig. 5e: Effect of temperature on viscosity for NRL-PAA system at 1% speed

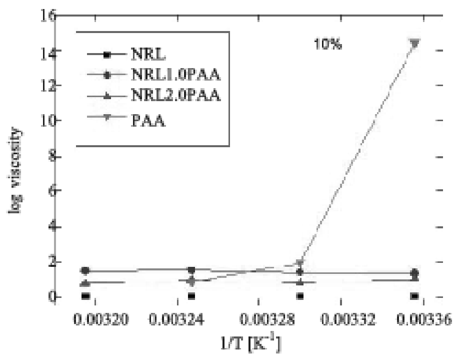

Fig. 5f: Effect of temperature on viscosity for NRL-PAAsystem at 10% speed

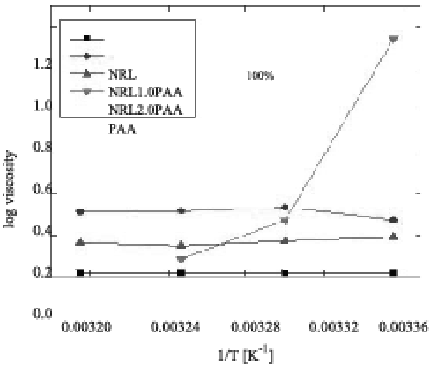

Fig. 5g: Effect of temperature on viscosity for NRL-PAA system at 100% speed

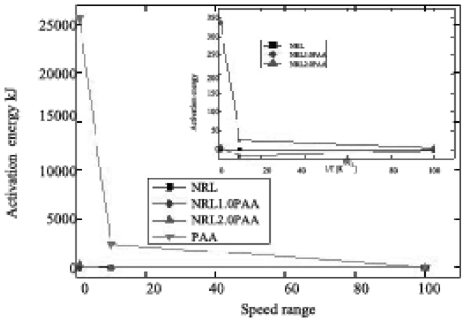

Fig. 5h: Effect of speed range on activation energy for NRL- PAA system