

# Studies on Rheological Behaviour of Thermoplastic Elastomer Derived from PVC and NBR Using Torque Rheometry

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## ABSTRACT

Plasticized poly(vinyl chloride)/nitrile butadiene rubber thermoplastic elastomers (PVC/NBR TPEs) were melt mixed using a Brabender Plasticorder. Rheological behaviour of PVC/NBR TPEs was evaluated using a Brabender torque rheometer. The plastogram of the PVC/NBR blend revealed that the mixing process was completed after 4 min, the blend was left to homogenize for another 4 min. The effect of rubber (NBR in this case) content on the rheological behaviour was evaluated, using the power law index (shear dependence of viscosity) and activation energy for viscous flow (temperature dependence of viscosity). The overall viscosity was found to decrease with the increase in NBR concentration. This might be related to plasticization role of NBR on PVC due to the dilution of the PVC viscosity phase. Furthermore, it has been found that the increase in rubber loading decreases the activation energy of the PVC/NBR formulation.

### Key Words:

rheology;  
melt flow index;  
plasticizer;  
NBR;  
PVC.

## INTRODUCTION

Thermoplastic elastomers from the blends of rubber and thermoplastics for property enhancement continue to represent a field of intensive research activity. One of the most common blends in the modern sense is PVC with NBR. Miscibility stud-

ies of PVC/NBR blends revealed that the two polymers are miscible as evidenced from a single  $T_g$  [1-4]. Hence, PVC/NBR blends can be classified as thermoplastic elastomers that look, feel and perform like vulcanized rubber [3-6]. The

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rheological parameters of the blend control its processibility under operating conditions. Several rheological studies on the uncured and cured blends have been carried out [7-11]. According to Coran [12,13], in the plastic/rubber blends such as polyolefin-EPDM thermoplastic vulcanizate the shear modulus depends on the shear modulus and the viscosity of the rubber phase and crystallization of the plastic phase. Various factors affecting the die swell, melt fracture and deformation of the extrudates have been reported [14]. Flot and Smith [15] had already stated that the flow behaviour of the blend depends on the heat history and the morphology. In this regard the rheological and viscoelastic behaviour of dynamically cured PVC/ENR TPEs as well as the effect of the processing variables on the flow properties have been reported by us [16-18]. Recently, the rheological and mechanical properties of the dynamically cured PVC/NBR TPEs have been reported by Mousa et al. [19]. A Brabender Plasticorder has been used extensively for assessing the fusion characteristics, mechanical and thermal stability as well as processing characteristics of polymers [7-9]. Such an investigation has been carried out on PVC/NBR blends using a Brabender Plasticorder to check the processibility behaviour of the uncured PVC/NBR blends.

## EXPERIMENTAL

### Materials

Poly (vinyl chloride) (PVC) suspension grade in powder form, with a K-value of 65 and degree of polymerization of 920-1060 was supplied by Jordanian Petrochemical Industry. Nitrile butadiene rubber with 34 mole % acrylonitrile (NBR-34) was obtained from Bayer AG, Germany.

### Formulation

The formulations shown in Table 1 were used in this study.

### Sample Preparation

PVC was initially premixed with 3 phr lead stabilizer in a Jankel and Kunkel IKA Labortechnik Model RE 162/P at 300 rev/min for 10 min at 30 C. Melt mixing was performed using a computerized Brabender Plasticorder Model PLE 331 at various temperatures and

**Table 1.** Composition of the PVC/NBR TPEs (%).

Rubber (NBR)	Thermoplastic (PVC)	DOP
20	80	50
30	70	50
40	60	50
50	50	50

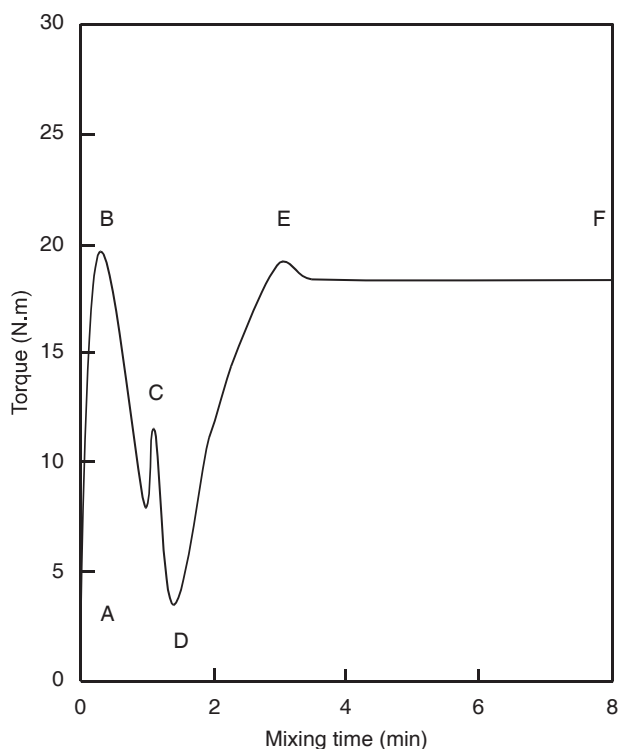
rotor speeds. The NBR was initially charged into the mixing chamber for 1 min to equilibrate followed by PVC and the plasticizer (DOP in this case). Mixing was allowed to proceed until constant torque was obtained [16-19]. The compound was removed from the mixer and sheeted on a cold two-roll mill. It was passed once through the nip to produce a 1-mm thick sheet. The sheets were cut into strips for further studies. Melt rheological properties of the prepared blends were evaluated using a Brabender Plasticorder at mixing speeds of 30, 40, 50, and 60 rev/min and mixing temperatures of 130, 140, 150, and 160 C. The torque and temperature were stabilized to constant values of 10-12 min at 30 rev/min and 8-10 min above 40 rev/min. This suggests that 40-50 rev/min as the optimum mixing shear, to keep the mixing time low further mixing was carried out at 50 rev/min and 150 C. The effect of shear heating ( $\Delta T$ ) in a Brabender Plasticorder results in temperature rise are given as :

$$\Delta T = \text{Melt temperature} - \text{Set temperature}$$

## RESULTS AND DISCUSSION

### Mixing Rheology

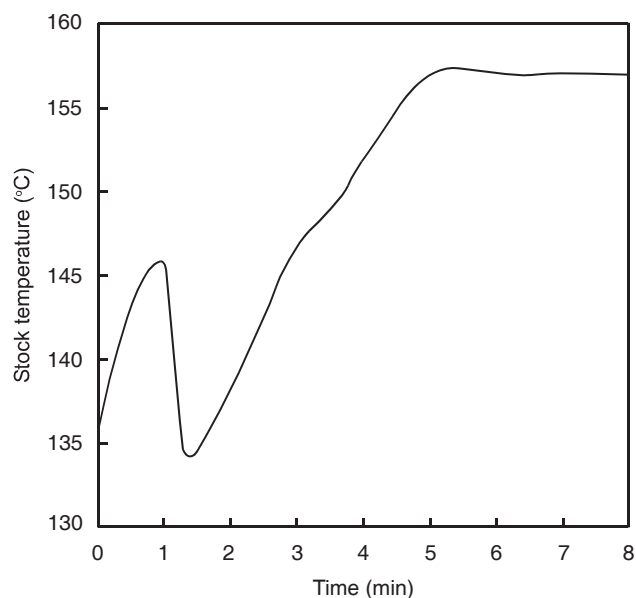
Figure 1 shows the plastogram of plastified PVC/NBR TPE at 150 C and 50 rev/min. Note that charging NBR into the mixing chamber in the region A, increases the torque up to B. Beyond point B the torque drops. This should be attributed to the homogenization of the NBR and temperature rise. The addition of PVC, followed by plasticizer was completed at C and D, respectively. The fusion process of the thermoplastic (PVC, in this case) is initiated at E where torque increases again. Recall that viscosity is a direct function of torque which accounts for the torque increment. Hence, the increase in viscosity coupled with shearing generates



**Figure 1.** Torque time curve of the plastified PVC/NBR TPEs at 150°C for 8 min.

frictional heat build-up. This is expected to increase the temperature of the melt. Therefore, the resistance of the material to shear (energy uptake) decreases. Thus, the fusion peak is observed at point F. Fusion continues until point G (i.e., 4 th min) after which the torque levels off. The melt was allowed to homogenize by further mixing until H. Similar trend was demonstrated also in our recent work devoted to the mixing rheology of dynamically cured PVC/ENR (epoxidized natural rubber) thermoplastic rubbers [16-18]. The progress of the stock temperature as a function of time is represented in Figure 2 for 70/30 blend. One can see that the stock temperature is lower than that of the mixing temperature (i.e., 150 C) at early stages of the mixing. This should be due to the quick addition of the NBR into the fused PVC.

However, the extensive shearing causes the stock temperature to rise steeply above the mixing temperature even at the end of the 4th min of the mixing time. As the mixing proceeds the stock temperature undergoes a gradual rise till a final steady value is attained. The maximum rise in stock temperature ( $\Delta T$ ) for the prepared sample at 150 C has been found to be 8 C. The attainment of steady values of torque and high



**Figure 2.** The effect of mixing time on the stock temperature of the PVC/NBR thermoplastic elastomer.

stock temperature indicates the completion of the exothermic mixing of the plasticized PVC/NBR blend in the Brabender Plasticorder as shown in Figures 1 and 2, respectively. This concurs a previous investigations on miscible blends of PVC/ ENR and PVC/NBR blends, respectively [2, 16-18].

### Rheological Behaviour

Rheological data obtained from the Brabender Plasticorder had been reported earlier based on the equation of the non-Newtonian flow behaviour [7-9]. The relationship obtained from the Brabender Plasticorder can be stated as:

$$M = CS^a \quad (1)$$

where  $M$  is the torque,  $S$  is the rpm, and  $C$  and  $a$  are constants. The above equation resembles the power law behaviour [7-9] which is given as:

$$\tau = K (\dot{\gamma})^n \quad (2)$$

where  $\tau$  is shear stress;  $K$ , constant;  $\dot{\gamma}$ , shear rate and  $n$ , non-Newtonian flow index. Based on the above two equations it can be inferred that the torque recorded on the Brabender Plasticorder is an indirect indication of the shear stress, while the rotor speed (rpm) is an indirect indication of shear rate. Thus, the viscosity that is

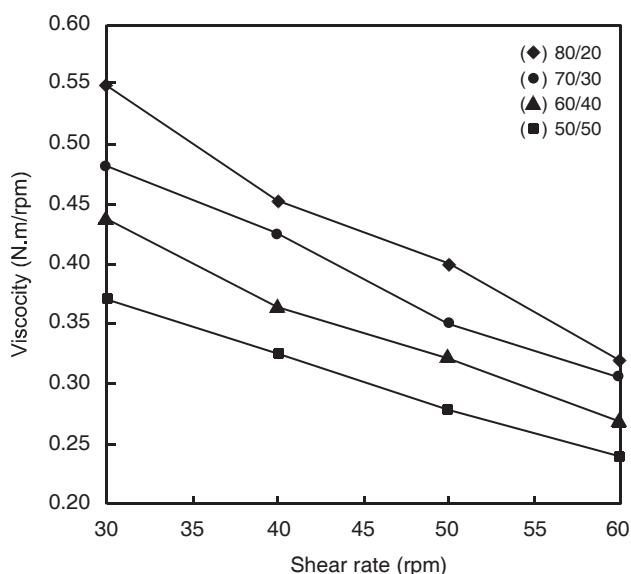
given as the ratio of shear stress to shear rate in the case of the Brabender Plasticorder can be obtained from the ratio of torque to rotor speed rpm. Hence, this could be used to estimate the power law index  $n$ .

### Power Law Index

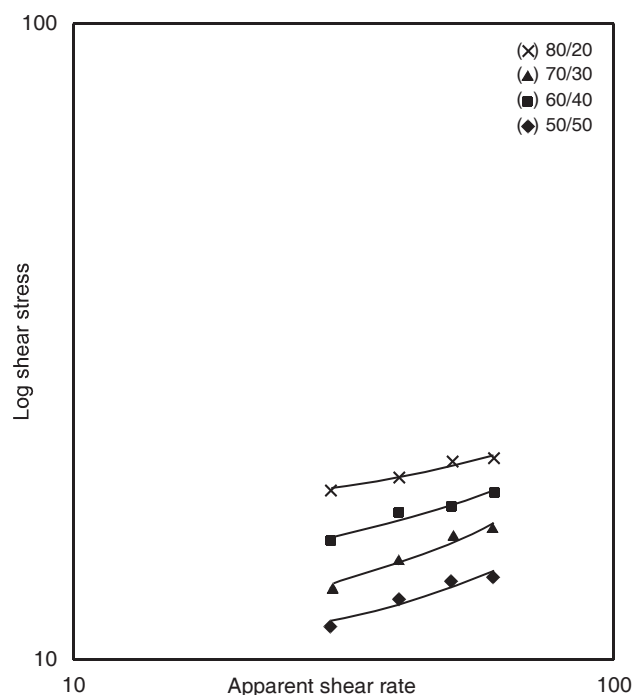
Figure 3 reflects the effect of shear rate on the apparent viscosity of PVC/NBR formulations at various amounts of NBR loading. It can be seen that two factors control the viscosity of the PVC/NBR TPEs. First, the viscosity decreases with increase in shear rate, second the viscosity is influenced with the blend composition. The viscosity decrease with increased shear rate indicates that the chains are easily deformed and their frictional resistance is not optimum. Furthermore, it is observed that at any shear rate the higher the PVC content the higher would be the viscosity. The increase in viscosity is due to the high viscosity of the PVC phase.

However, the effective decrease in the overall viscosity with the increase in NBR concentration might be related to plasticization role of NBR on PVC due to the dilution of the PVC viscosity phase. This is in agreement with our recent findings on PVC/ENR TPEs [16-19]. Similar trends on thermoplastic elastomers derived from PVC and NBR were reported by Mathew et al. [20].

The melt flow behaviour of the samples can be described by power law index. Figure 4 illustrates the



**Figure 3.** The effect of apparent shear rate on the viscosity of PVC/NBR TPEs at various amounts of NBR content mixed at 150°C.

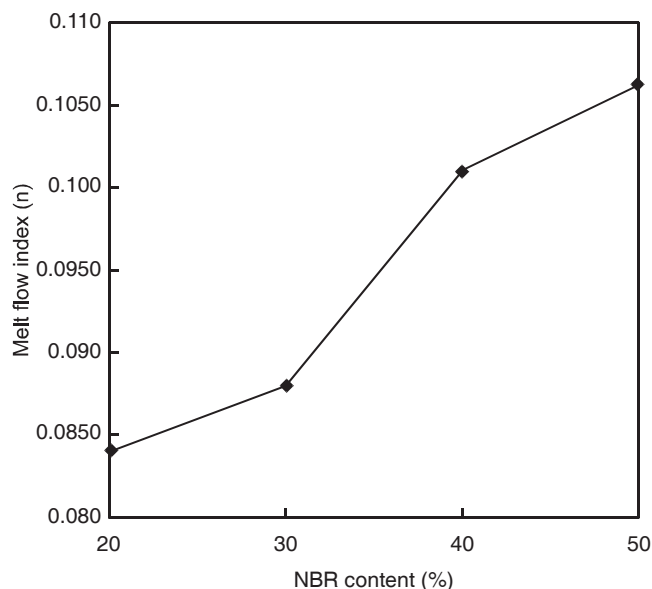


**Figure 4.** The effect of apparent shear rate on the apparent shear stress of PVC/NBR TPEs at various amounts of NBR content mixed at 150°C.

relationship between shear stress and shear rate of the PVC/NBR TPEs at various NBR concentrations as log-log graphs. It can be observed that in all cases the shear stresses increased linearly with shear rates albeit the fact that the rate of increasing shear stress was affected by NBR contents. The data shows that the behaviour of the melts is highly non-Newtonian. The slope of these straight lines used to estimate the value of the non-Newtonian flow index ( $n$ ). The variation of non-Newtonian flow index,  $n$  with NBR concentration is presented in Figure 5. Interestingly, the single power law index increases with increase in NBR concentration. The observed trend should be traced to the plastication effect of the NBR which is expected to improve the flow properties of the PVC. Hence the melts displayed a less non-Newtonian behaviour with increased NBR content. The values of  $n$  dictate the pseudoplastic nature of the PVC/NBR blends since  $n < 1$ , showing that the apparent viscosity decreases as shear rate increases.

### Flow Activation Energy

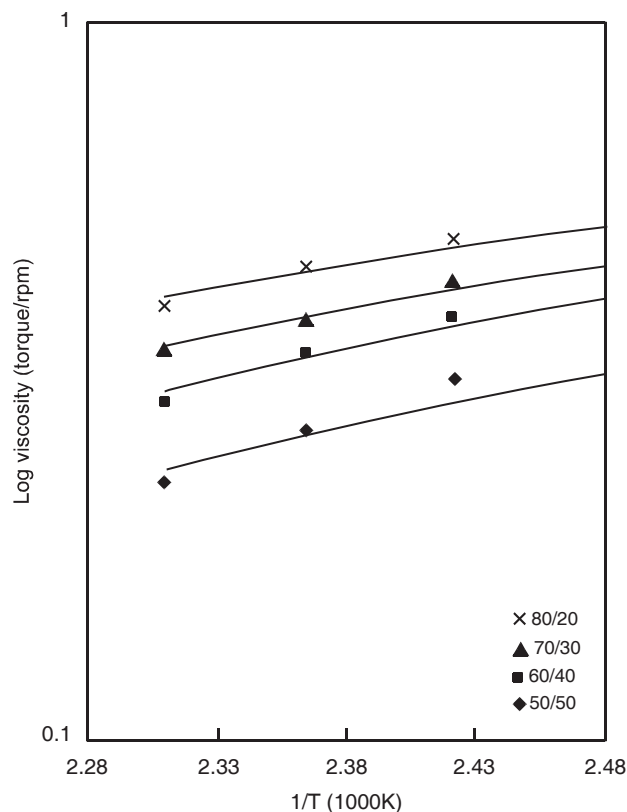
The temperature dependence of the viscosity was expressed in term of Arrhenius equation [7-9]:



**Figure 5.** The effect of NBR concentration on the flow index ( $n$ ) of PVC/NBR TPEs.

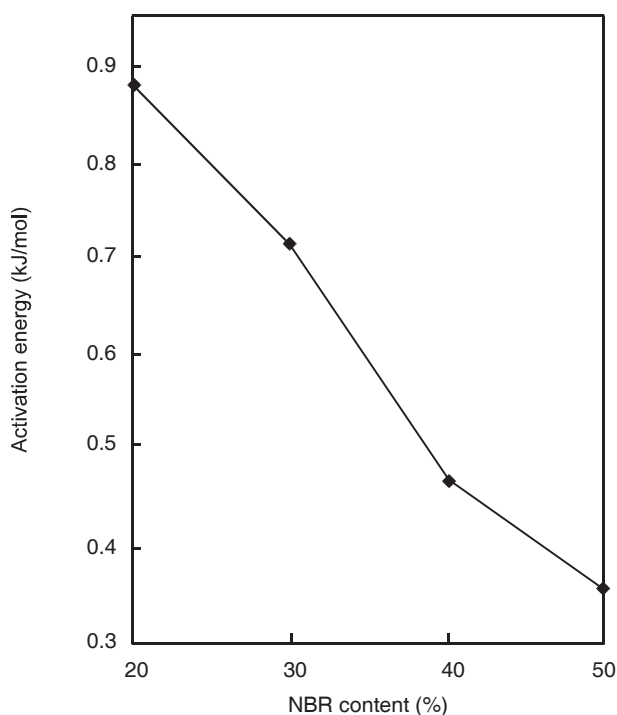
$$\eta = A \cdot e^{E_a/RT} \quad (3)$$

where  $\eta$ , viscosity (torque/rpm);  $A$ , constant;  $E_a$ , activation energy;  $T$ , absolute temperature; and  $R$ , Universal gas constant. As the ratio of torque to rpm can be used to represent the apparent viscosity of the blend,  $E_a$  can be calculated from the graph of log torque/rpm against the reciprocal absolute temperature  $1/T$ , as shown in Figure 6. The apparent shear viscosity of the PVC/NBR TPEs was calculated from torque values at shear rate of 50 rev/min for mixing temperatures ranging from 130-160 C. One can see that the viscosities of samples were lowered as mixing temperature increases. This is in line with the previous reports on the application of waste latex products in SBR as well as the rheological behaviour of the cross-linkable polyethylene and EPDM rubber with the help of torque rheometry [21-22]. Recall that the increase in the kinetic energy of the blend components was as a result of thermal energy transferred from the mixer wall as well as the friction between the samples and the mixer rotors. Thus, intermolecular bonds which hold the samples together will not be strong enough to prevent the blend components from flowing. Providing that the viscosity depends on the strength of intermolecular structure of the blend components. Hence, it is obvious that the incorporation of the NBR has facilitated the flow of PVC/NBR TPEs.



**Figure 6.** The effect of absolute reciprocal temperature on the viscosity of PVC/NBR TPEs at various amounts of PVC content.

Furthermore, the results obtained provide valuable information on the sensitivity of the materials towards the changes in temperatures which results in a better fusion of the PVC phase. Figure 6 permits the calculation of activation energies of viscous flow for PVC/NBR blends. In order to understand the temperature dependence of viscosity of the PVC/NBR TPEs at particular shear rate the flow activation energy using Arrhenius equation (eqn 3) was evaluated [8]. The flow activation energy which appeared in Figure 7 was calculated from the slope of the straight lines presented in Figure 6. It can be seen that the increase in rubber loading decreases the activation energy of the PVC/NBR formulation. This might have occurred predominantly from two factors: an overall tendency for the viscosity to decrease due to the rise in temperature as mentioned earlier and the tendency of the PVC phase to enhance the viscosity by melting. In addition to the plastification effect of NBR on PVC which results in softer and more elastic compositions, the observed trend agrees quite well with an earlier report



**Figure 7.** The effect NBR concentration on the activation energy of PVC/NBR TPEs at various amounts of NBR content.

on PVC/ENR thermoplastic elastomers [16].

## CONCLUSION

The melt processibility of the NBR/PVC thermoplastic TPEs can be studied using a torque rheometry. The single power law index of PVC/NBR formulations was found to be highly non-Newtonian and was affected by the NBR concentration. The linearity between log apparent shear stress and  $T^{-1}$  at particular shear rate confirms the Arrhenius type behaviour of the blend from which the flow activation energy was calculated. The estimated flow activation energy seems to be influenced by the plastification role of the NBR and the fusion of the PVC particles.

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