Rheological and Prediction of melt viscosity flow curves for blend of Polycarbonate (PC) and Polyacrylonitrile butadiene styrene (ABS)

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Abstract : A   knowledge of the variation of melt viscosity of thermoplastic polymers with both shear rate and temperature is of considerable importance to plastics engineers as well as to polymer rheologists.

The Actual measurement of melt viscosity at large number of temperatures and shear rates is frequently a tedious and time-consuming task. The experimental validity for superimposing Log shear stress – Log shear rate curves at different temperatures along the log shear rate axis has been established for the mixture of (polycarbonate and polyacrylonitrile butadiene styrene). The temperature dependence of the resultant shift factors has been determined to predict viscosities as a function of temperature and shear rate is discussed.

Keywords : PC, ABS polymer blends. Rheological and prediction.

Introduction

Knowledge of the melt viscosity of thermoplastic polymers at various temperatures and shear rates is important to plastics engineers who must design polymer processing equipment or specify the processing conditions for fabrication plastic materials. Such information is equally important to the producer of polymeric materials and to the applied polymer rheologist.

Experimental Material and

Polyacrylonitrile butadiene styrene (ABS) [density 0.987 g/cm$^{\overline{3}}$), M_v 43600; MFI 10.2 g/10min was supplied by bright china industrial company , Lid (shenzen , china). The selected grade is an extrusion material , it was dried at 70°C for 6 h before using. Polycarbonate (SABIC_K.S.A).[density=1.21 g/cm^3 ; MFI=11 g/10min ; M_v =28000] was applied by(K.S.A) . A simple blend of PC/ABS (10/90) was prepared using a single screw extruder (SSE) (D=20 mm , L/D=25) . it could be operated at different speeds varied from 0 to 100 (rpm).

The screw has a fluted type mixing device located before the metering zone [24] , which can be extend the compounding ability of the SSE , in this type of mixers the material is forced to pass at high shear stress. This brings in some level of dispersing action besides reorienting the interfacial area and increasing the imposed total strain.

The fight depth of screw in the metering zone was 1.5 mm and the helix angle 17.7°[1-3] . The screw was set at 70 (rpm) in the blends preparation, and the extruder temperature profile along the barrel was 180, 190, 200, 210 °C (from feed zone to die) . the blends were extruded through multi holes die (3 mm) , the extrudate were then fed into a granulator, which converted them into granules. The obtained granul was dried at 70°C for 6 h before studying .

Rheology

Rheological properties of the blends were studied using a capillary Rheometer (Dvenport 3/80), the rheological experiments were carried out at temperatures from 220°C to 244°C. shear stress from $1.2 \; 10^4$ to $3.8 \; 10^4$ (Pa) and by using L/R= 15.25 and 35 capillaries Bagley's correction [25.26] was performed using the data from the four capillary dies .

The apparent shear rate (Υ_a) is given by [4-6]:

$$\Upsilon_a = 4 \; Q \; / \; \pi \; R^3 \qquad (1)$$

Where R is the capillary radius ; and Q is the volumetric flow rate . The true shear rate (Υ_r) is given by :

$$\Upsilon_r = \frac{3}{4} . \frac{4 \, Q}{\pi R3} + \frac{1}{4} . \frac{4 \, Q}{\pi R3} . \frac{d \, (log \Upsilon a)}{d(log \tau a)}$$

$$\Upsilon_r = (\frac{3}{4} + \frac{1}{4} . \frac{1}{n}) \frac{4 \, Q}{\pi R3}$$

$$\Upsilon_r = \frac{3n+1}{4n} . \frac{4 \, Q}{\pi R3} \qquad (2)$$

Where n is the non – Newtonian index depending on temperature , the term $(\frac{3n+1}{4n})$ was the Rapinowitsch correction factor [4].

The apparent shear stress (τ_a) is given by :
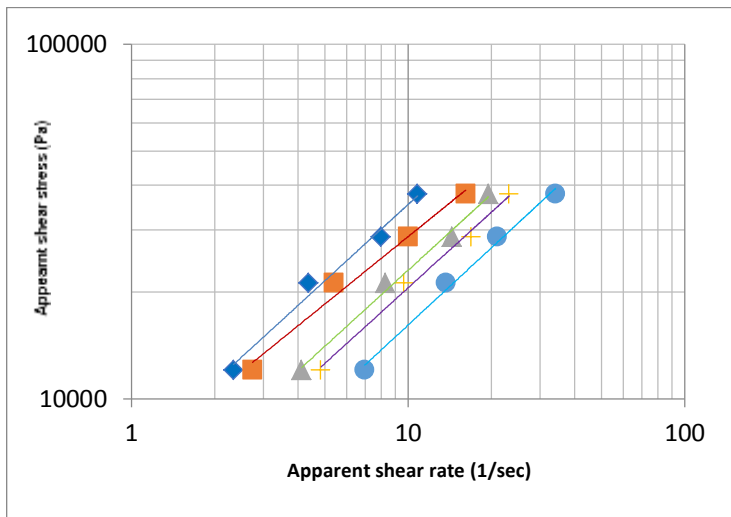
$$\tau_a = \Delta \; PR \; / \; 2 \; L \qquad (3)$$

where the ΔP is the pressure at the Capillary entrance, and L is the Capillary length . The true shear stress (τ_r) is given by [7-9] :

$$\tau_r = \frac{\Delta P}{2 \, (\frac{L}{R}+e)} \qquad (4)$$

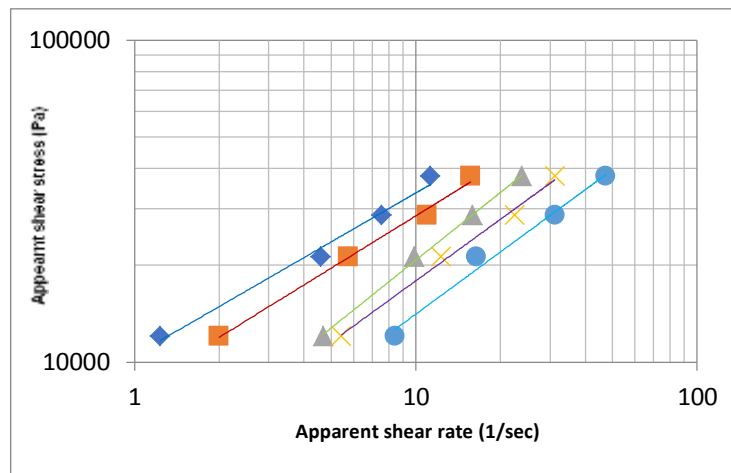Where (e) is the Bagley's correction the true viscosity (η_r) is given by :

$$\eta_r = \frac{\tau r}{\Upsilon r} \qquad (5)$$

typical flow curves (log τ_a Vs log Υ_a) at temperatures from 220 to 244 (°C) for PC/ABS (10/90) and PC/ABS (50/50) are shown in Figures 1 and 2.

Fig1. log τ_a VS log Υ_a for PC/ABS (10/90) T(C°) [(♦)220,(■)226,(▲)232,(+)238,(●)244]

Fig 2. log τ_a VS log Υ_a for PC/ABS (50/50) T(C°) [(♦)220,(■)226,(▲)232,(+)238,(●)244]

It seems from fig 1 and 2 , that the relationship between shear stress andshear rate is linear , thus obeying the power law [10-12] :

$$\tau = K \cdot y^n \qquad (6)$$

where K is the consistency index and n is the non – Newtonian index which can be calculated from the slope of the lines in Figures 1 and 2 shows the value of n for PC/ABS (10/90) and PC/ABS (50/50). It could be noted from figures 1 and 2 that the values of (n) for blends melts less than 1, implying that blend's melt were pseudo plastic [13-15] .

The value of n describes the deviation from the Newtonian Fluids about flow behaviour, so it also called the flow behaviour index . A higher value of n reveals less influence of shear rate on flow behaviour . In other words the changes in viscosity upon shear rate are not obvious, so it could be said that the flow behaviour of the blend melts is more sensitive to shear as compared with the homopolymers .

The flow curves may be shifted along the shear rate axis, i.e, at constant shear stress for each point or curve, to superimpose on the single master curve corresponding to arbitrarily chosen reference temperature . The arbitary reference used for blend polymers was Υ_r (sec^{-1}) 4,8,15, and 20 , and reference temperature was 232°C. The horizontal shift factors α_T were obtained by choosing the shear rates (at constant shear stress) . The values of α_T were calculated from[16-18] :

$$\alpha_T = \Upsilon_a(ref) / \Upsilon_a(T) \; (const. \; \tau_a) \qquad (7)$$

and for each temperature, the values of α_T corresponding 4,8,15 and 20 (sec^{-1}) at the reference temperature were averaged to reduce errors due to reading graphs . It should be noted that Eq.(7) may also be written :

$$\alpha_T = \eta_a(T) \ / \ \eta_a(ref) \quad (const. \ \tau_a) \quad (8)$$

which is the frequently used approximate for of the reduced variable viscosity.

The values of shift factors for PC/ABS (10/90) and PC/ABS (50/50) are summarized in tables 1 and 2 . in order to test the applicability of these shear rate temperature superposition shift factors . The α_T presented in table 1 and 2 were used to construct master flow curves Figure 3 and 4 :

Table(1) superposition shift factors for(232°C) Reference temperature . α_T

τ	Υ(ref)	Temperature(°C). PC/ABS(10/90)				
Pa	Sec^{-1}	220	226	232	238	244
12030.27	4	1.66	1.53	1	0.83	0.57
21173.77	8.3	1.97	1.56	1	0.84	0.58
28563.55	15	1.87	1.15	1	0.88	0.69
37698.73	19.8	1.65	1.23	1	0.84	0.56

Table(2) superposition shift factors for(232°C) Reference temperature . α_T

τ	(ref) Υ	Temperature(°C). PC/ABS(50/50)				
Pa	Sec^{-1}	220	226	232	238	244
12030.27	4.6	2.19	1.76	1	0.84	0.54
21173.77	10	2.22	1.75	1	0.74	0.58
28563.55	16	2.13	1.40	1	0.73	0.51
37698.73	22.4	1.96	1.41	1	0.72	0.45
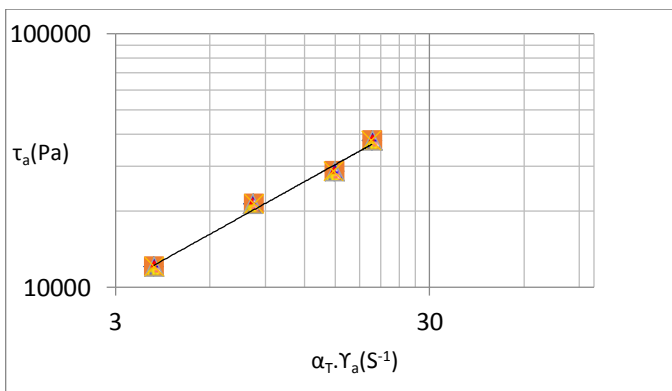
Fig 3. log τ_a VS log $\alpha_T.\Upsilon_a$ for PC/ABS (10/90) T(C°) [(♦)220,(■)226,(▲)232,(+)238,(●)244]
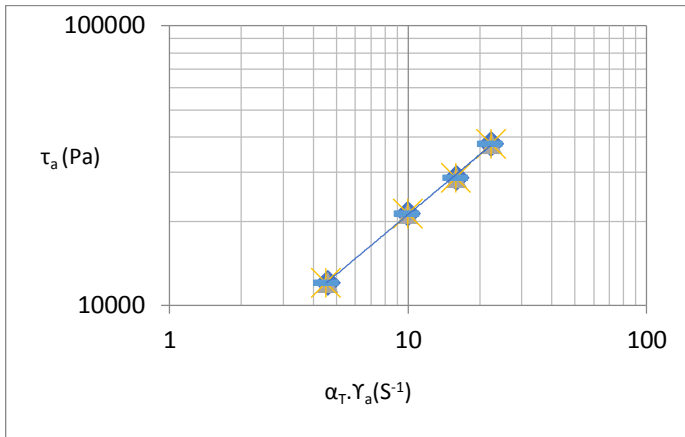
Fig 4. log τ_a VS log $\alpha_T.\Upsilon_a$ forPC/ABS (50/50) T(C°) [(♦)220,(■)226,(▲)232,(+)238,(●)244]

The resultant master curves shown in Figure 3 and 4 clearly illustrate the validity of the superposition method for PC/ABS (10/90), PC/ABS (50/50).   It should be noted that the values of $\alpha_T$for blend's polymers decrease with increasing the temperatures, and the method of construct the Master Curve at arbitrary chosen reference temperature becomes more difficult . The temperature dependence on the shift factors was next investigated together with a simple exponential, or Arrhenius – type equation of the form :

$$\alpha_T = B \cdot \exp (E_a / RT) \qquad (9)$$

where T is the absolute temperature and E_a is the "shift factor activation energy", was found to give an excellent fit for each of the blend polymer over the appropriate temperature range covered . Equation(8) may be rewritten as :

$$\text{Log } \alpha_T = \text{Log } B + E_a / 2.303 \text{ RT} \quad (10)$$
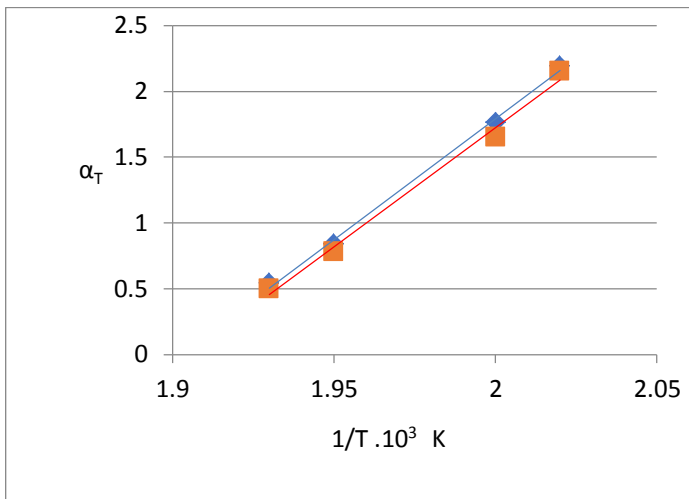
Or, simplifying:

$$\text{Log } \alpha_T = B´+ C / T \qquad (10\text{-a})$$

The Figures 5 and6 show the linear plots of log α_T Vs 1/T observed for each blend polymer .
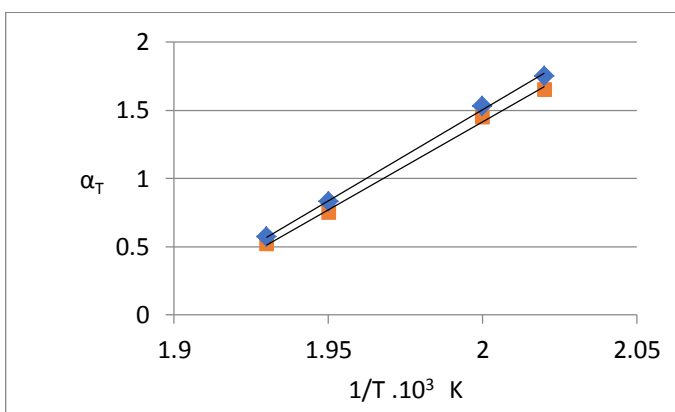
Fig 5.Log α_T VS 1/T 232°C REF. TEMP for PC/ABS (10/90)

Fig 6. Log α_T VS 1/T 232°C REF. TEMP for PC/ABS (50/50)

The various sets of log α_T Vs 1/T data were fitted by a least – squares procedure to allow calculation of the constants in Eq.(9-10a) . These are summarized in tables 3 and 4 .

Table(3) summary of shift factors temperature equation constants (232°C Ref. temp) for PC/ABS (10/90)

τ_a Pa)(	E_{at} (Kcal/mol)	B	B´	C
12030.27	12.240	0.0301	-1.521	2.674×10^3
21173.77	13.813	0.0267	-1.573	3.018×10^3

Table(4) summary of shift factors temperature equation constants (232°C Ref. temp) for PC/ABS (50/50)

τ_a Pa)(	E_{at} (Kcal/mol)	B	B´	C
12030.27	18.418	0.0428	-1.368	4.024×10^3
21173.77	12.188	0.0664	-1.177	2.633×10^3

The forgoing experimental results provide the basis for a rather general technique for predicting melt viscosity flow curve data at various temperature . It is apparent Eq.(7) may be rewritten in terms of the shear rate at any temperature ,T, as follows :

$$\Upsilon_a(T) = \Upsilon_a(ref) / \alpha_T \qquad (11)$$

Where the corresponding shear stress is the same at two shear rates, thus, given a set of shear stress – shear rate data reference temperature, it is possible to construct sets $\tau_a - \Upsilon_a - \eta_a$ data at any desired temperature, it is not even necessary that the known data set be available at the reference temperature since, assuming data to be known at T1 and desiring data at T2, elimination Υ_a(ref) from Eq.(8) yield .

$$\Upsilon_a(T2) = \alpha_{T1}. \Upsilon_a(T1) / \alpha_{T2} \qquad (12)$$

Appropriate values of α_t are obtained from Eq.(10-a) using the values of B` and C given in tables 3 and 4 .

Finally it must be noted that Eq.(7), (11) and (12) are equally valid for true shear rates, i.e , shear rates corrected for non – Newtonian flow. Thus, the same calculation scheme may be applied to predict corrected flow curves, given only that initial set of data are for a corrected flow curve [19-21] .

It may be shown that the Rabinowitsch correction to the shear rate does not affect the values of the shear rate – temperature superposition shift factors in the following manner :

Let R and T refer to reference temperature and any other temperature, respectively, and subscript t refer to "true" shear rate corrected for non – Newtonian flow .

Then :

$\alpha_T = \Upsilon(R) / \Upsilon(T)$ (const. τ)

and:

$\alpha_T{'} = \Upsilon_t(R) / \Upsilon_t(T)$ (const. τ)

define the shift factors in the uncorrected and corrected cases, respectively . The Rabinowitsch correction may be written :

$\Upsilon_t = \Upsilon\left(\frac{3n+1}{4n}\right)$

Where $n = d \log \tau / d \log \Upsilon$

Then :

$\alpha_T{'} = \Upsilon(R)\left[\frac{3n(R)+1}{4n(R)}\right] / \Upsilon(T)\left[\frac{3n(T)+1}{4n(T)}\right]$

$\eta = \alpha_T \left[\frac{3n(R)+1}{4n(R)}\right] / \left[\frac{3n(T)+1}{4n(T)}\right]$

However, since it is a necessary condition for superposition that the slopes of the curves at constant shear stress be equal, i.e. , n(R) = n(T), it follows that $\alpha_T{'} = \alpha_T$

Thus α_T is independent of the Rabinowitsch correction .

Conclusion

The general validity of a shear rate-temperature superposition of Log shear stress VS Log shear rate flow curves have been demonstrated for blend polymers (PC/ABS)

The temperature dependent on the resultant shift factors has been shown to be capable of representation by an Arrhenius type equation of the generic system .

It should be noted that the value of α_T for blend's polymers decrease with increasing the temperature and the method of construct Master Curve atarbitrary dependence become more difficult .

Moreover the technique of shear rate – temperature superposition and the shift factor temperature dependence to predict flow curve at various temperature allow us to determine the shear stress that is necessary for desired temperature at shear rate constant.

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