Damascus University Journal for the Basic Sciences
Vol 41 No.4 (2025): 126 -138

مجلة جامعة دمشق للعلوم الأساسية
مجلد 41–عدد 4 (2025): 126 -138

Viscosity and Prediction of Melt Flow Curves for Polycarbonate (PC) and Polyacrylonitrile butadiene styrene (ABS): PC/ABS (30/70) and PC/ABS (60/40 mass ratio)

Douaa Subhi Alsaeed
[1]Assistant, Department of chemistry, Faculty of science, Laboratory of Materials Rheology, University of Damascus,
douaa9.subhi@damascusuniversity.edu.sy

Abstract
A study was conducted on a type of polymer blends based on polycarbonate (PC) and acrylonitrile butadiene styrene (ABS) in the molten state under the influence of shear stresses, shear rate, and temperature. Through the aforementioned transformations, a technique of Prediction curves was performed to determine the possibility of knowing the displacement and structure of flow curves and viscosity along the shear axis and viscosity by selecting a specific reference value for the shear rate $\gamma_{a\,(ref)}$ and its ratio to the experimental shear rate $\gamma_{a\,(T)}$ Then, the slip coefficient α_T was determined, resulting in a main composition curve where the curves converge. This technique helps in determining the expected production conditions to be applied in various fields..

Received :19/01/2024
Accepted: 07/05/2024

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Key words : Polymer blends of polycarbonate (PC) and acrylonitrile butadiene styrene (ABS), Rheological and Prediction.

ISSN (online): 2789-6366
http://journal.damascusuniversity.edu.sy/index.php/index/index

اللزوجة والتنبؤ بمنحنيات تدفق الجريان للبوليكربونات (PC) وبولي أكريلونيتري لبوتادين ستايرين (ABS): PC/ABS (30/70) و PC/ABS (نسبةالكتلة 40/60).

دعاء صبحي السعيد

[1]عضو هيئة فنية، هندسة بتروكيميائية (قسم هندسة بترولية)، قسم الكيمياء، كلية العلوم، مخبر ريولوجيا المواد، جامعة دمشق، douaa9.subhi@damascusuniversity.edu.sy

الملخص

تم دراسة نوع من المزائج البوليميرية التي أساسها البولي كربونات (PC) والبولي اكريلو نتريل بوتاديين ستايرن (ABS) في الحالة المنصهرة تحت تأثير إجهادات القص ومعدلات سرعة القص والحرارة. ومن خلال التحولات السابقة قمنا بإجراء تقنية منحنيات التنبؤ Prediction لبيان إمكانية معرفة الإزاحة والتركيب لمنحنيات الجريان واللزوجة على طول محور القص واللزوجة باختيار قيمة معينة مرجعية لمعدل سرعة القص $\gamma_{a\ (ref)}$ ونسبتها إلى معدل سرعة قص تجريبية $\gamma_{a\ (T)}$. ثم تعيين معامل الانزلاق α_T و بالتالي الحصول على منحني تركيب رئيسي تتقارب فيه المنحنيات من بعضها، حيث تساعد هذه التقنية على إمكانية تحديد شروط الإنتاج المتوقع العمل بها في مجالات مختلفة.

تاريخ الإيداع: 2024/01/19
تاريخ الموافقة: 2024/05/07

حقوق النشر: جامعة دمشق – سورية، يحتفظ المؤلفون بحقوق النشر بموجب الترخيص CC BY-NC-SA 04

الكلمات المفتاحية: مزائج بولي كربونات (PC) وبولي اكريلو نتريل بوتاديين ستايرن (ABS)، الريولوجيا، التنبؤ

INTRODUCTION:

Understanding the melt viscosity of thermoplastic polymers across different temperatures and shear rates is crucial for plastics engineers involved in designing polymer processing machinery or establishing processing parameters for plastic material production. This information is equally important to the producer of polymeric materials and to the applied polymer rheologist. In recent years, significant research has been carried out on the formulation of polymer blends, especially in polymer processing industries. These efforts appear to arise from both economic and scientific imperatives. Specifically, blending polymers with different molecular weights and distributions appears to offer a cost-effective means of achieving desired physical properties in the final product, rather than creating entirely new polymers for the same purpose.[1].

To achieve these objectives effectively, the development of mixing laws capable of predicting the rheological properties of molten mixtures based on the mixing ratios and rheological properties of the individual components would be immensely beneficial. Previous attempts have been made to establish such laws, but with limited success. In particular, previous studies focused on blends comprising two polymers with identical molecular structures but with different molecular weights and distributions. Another area of interest is mixtures formed by two polymers with different molecular structures. [2-3]. This category is intriguing due to the inherent incompatibility between chemically different polymers in the molten state, making it a pertinent topic for practical exploration. This work presents the experimental curves of various prediction methods, the flow curves of various polymers at any desired temperature from experimental data for those polymers as a temperature. This prediction of flow behavior at various temperatures is achieved by a shear rate-temperature superposition method valid for many polymers. [4-6].

ABS is a thermoplastic polymer that can be recycled and reshaped, and it finds applications in the manufacturing of lightweight and strong tools such as musical instruments, sports equipment, special ink cartridges with gloss properties, some car parts, and other important applications. However, one of the main areas where ABS is used is in the production of sewer pipes. This is because ABS exhibits corrosion resistance, which solves the corrosion problem commonly faced by other materials used in sewer pipe manufacturing. [7-8].

One of the key mechanical properties of ABS is its impact resistance and hardness. By adjusting the ratio of its primary components, the impact resistance, hardness, and heat resistance of ABS can be enhanced. On the other hand, PC (polycarbonate) is an important synthetic polymer widely used in the manufacturing of household appliances, office equipment, and industries that require a polymer with high impact strength and heat resistance. [9]. PC is also utilized in the production of sunglasses lenses, prescription eyewear lenses, shatter-resistant glasses, CD/DVD discs, musical instruments, laboratory and medical equipment. Additionally, due to its high impact strength, PC is used in the manufacturing of bullet-resistant windows. It is also used in the production of food storage containers due to its low migration into food environments. [10-14].

PC possesses excellent mechanical properties, including high hardness, significant heat resistance, and high impact resistance, making it one of the strongest polymers available. Recognizing the strengths of both ABS and PC, the PC/ABS blend aims to achieve strength, durability, and cost-effectiveness in the final product by combining the properties of these two polymers. ABS exhibits good mechanical properties and ease of forming, while PC has excellent mechanical properties. Therefore, this blend can solve the challenges faced by using ABS alone or PC alone [15-17].

Our work aims to study the rheological properties of PC/ABS blends in the molten state under the influence of shear stress and temperature using the Davenport viscosity scale. The mixing process was performed using a brabender mixer at a temperature of 25°C. We aim to assess the applicability of the displacement, composition, and slip coefficients on the studied blends to determine if they are suitable. If successful, this technique, which has been applied in previous research on different materials, will provide valuable information for determining production conditions. [18-19].

MATERIAL:

Polyacrylonitrile butadiene styrene (ABS) [density 0.987 g/cm^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).

1- EXPERIMENTAL:

A simple blend of PC/ABS(30/70) and PC/ABS(60/40 mass ratio) 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 includes a fluted mixing device positioned before the metering zone, which can enhance the compounding capability of the SSE. In this mixer type, the material is compelled to pass through high shear stress conditions. This introduces a certain level of dispersing action, in addition to reorienting the interfacial area and increasing the overall applied strain. The fight depth of screw in the metering zone was 1.5 mm and the helix angle 17.7°[20-22] . 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 a die with multiple holes (3 mm). Subsequently, the extrudate was fed into a granulator, which transformed it into granules. The resulting granules were dried at 70°C for 6 hours before being studied..

2- Rheological Properties:

Rheological properties of the blends were studied using a capillary Rheometer (Dvenport 3/80 , the rheological experiments were carried out at temperatures (220, 226, 232, 238, 244°C). shear stress(1.2 x 10^4, 2.13x 10^4, 3x 10^4, 3.74 x 10^4, 3.8 10^4Pa) and by using L/R= 15.25 and 35 capillaries Bagley's correction was performed using the data from the four capillary dies .The apparent shear rate (Υ_a) is given by [23-25]:

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

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

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

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

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

Where n is the non – Newtonian index depending on temperature , the term ($\frac{3n+1}{4n}$) was the Rapinowitsch correction factor[23].

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 [26-28] :

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

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

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

Flow Curves:

Typical flow curves (log τ_a Vs. log Υ_a) at temperatures from 220 to 244 (°C) for PC/ABS (30/70 mass ratio) and PC/ABS (60/40 mass ratio) are shown in Figures 1,2,3and4:

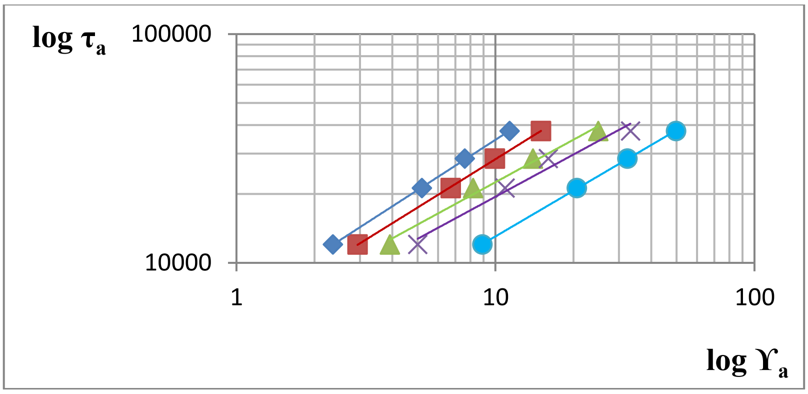

Fig1. **log τ_a VS log Υ_a for PC/ABS(30/70 mass ratio)**
T(C°) [(♦)220,(■)226,(▲)232,(+)238,(●)244]

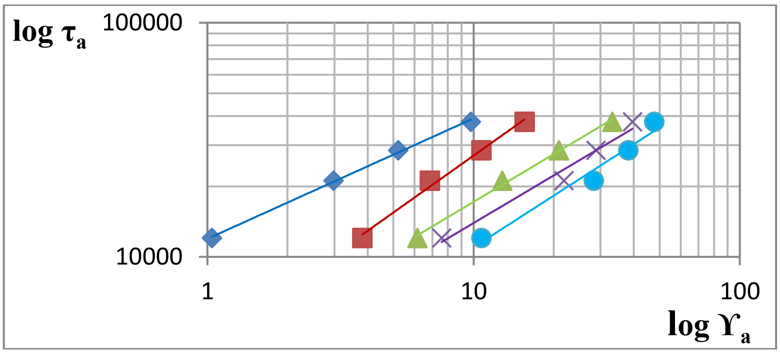

Fig 2. **log τ_a VS log Υ_a for PC/ABS(60/40 mass ratio)**
T(C°) [(♦)220,(■)226,(▲)232,(+)238,(●)244]

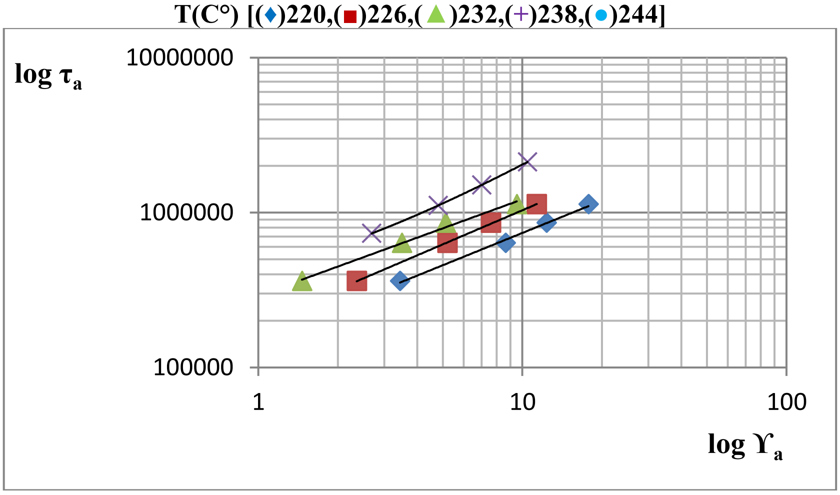

Fig3. **curves of pressure versus capillary length to radius ratio for PC/ABS (30/70) each straight line corresponds to constant shear rate $\Upsilon_a(s^{-1})$.(L/R) [(♦)8,(■)15,(▲)25,(+)36]**

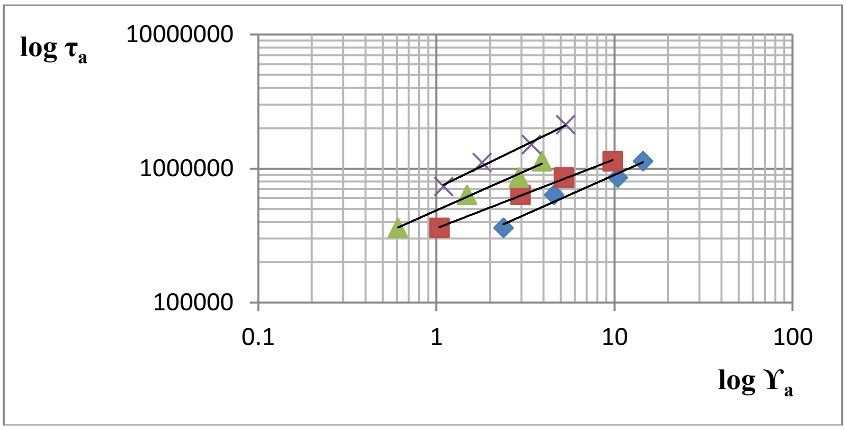

Fig4. curves of pressure versus capillary length to radius ratio for PC/ABS (60/40) each straight line corresponds to constant shear rate ϒa(s^{-1}). (L/R) [(♦)8,(■)15,(▲)25,(+)36]

It seems from figures 1,2,3 and 4 that the relationship between shear stress and shear rate is linear, thus obeying the power law [29-31] :

$$\tau = K.\, yn \qquad (6)$$

where K represents the consistency index, while n stands for the non-Newtonian index. These values can be determined by analyzing the slopes of the lines depicted in Figures 1,2,3 and 4 which indicate the values of n for PC/ABS (30/70) and PC/ABS (60/40 mass ratio). Observing Figures 1,2,3 and 4 reveals that the values of n for the blended melts are below1, suggesting that the melts of the blends exhibit pseudo plastic behavior[32-34].
The n presented in Table (1*)

Table 1* values of n for PC/ABS(30/70) and PC/ABS(60/40)

Temperature (C)°	n for PC/ABS (30/70)	n for PC/ABS (60/40)
220	0.73	0.51
226	0.70	0.72
232	0.61	0.67
238	0.61	0.67
244	0.69	0.73

The parameter n characterizes the departure from Newtonian fluid behavior regarding flow characteristics, hence often referred to as the flow behavior index. A higher n value indicates a lesser impact of shear rate on flow behavior. Essentially, this suggests that variations in viscosity with changing shear rates are less pronounced, implying that the flow behavior of the blended melts is more responsive to shear compared to the homopolymers.

3- Superposition Shift Factors:

The flow curves can be shifted along the shear rate axis to align, at a constant shear stress, with a single master curve corresponding to a chosen reference temperature. For the blend polymers, shear rates at constant shear stress of ϒr (sec^{-1}) 4, 8, 15, and 20 were used, with a reference temperature of 232°C. The horizontal shift factors α_T were determined by selecting the appropriate shear rates at constant shear stress.
The values of α_T were calculated based on the equation [35-37] :

$$\alpha T = ϒa\,(ref) / ϒa\,(T) \quad (const.\ \tau a) \qquad (7)$$

To minimize errors caused by reading graphs, the values of α_T corresponding to 4, 8, 15, and 20 (sec^{-1}) at the reference temperature were averaged for each temperature. Note that equation (7) can instead be expressed as:

$$\alpha T = \eta a\ (T)\ /\ \eta a\ (ref) \quad (const.\ \tau a) \qquad (8)$$

This is the reduced variable viscosity's commonly used approximation. Tables 1 and 2 provide a summary of the shift factor values for PC/ABS (30/70) and PC/ABS (60/40 mass ratio). To determine whether these shear rate temperature superposition shift factors are applicable, The master flow curves in Figures 3 and 4 were created using the αt that was provided in Tables 1 and 2:

Table(1) Superposition shift factors for(232°C) reference temperature. α_T for PC/ABS(30/70)

τ	ϒ (ref)	Temperature(°C).PC/ABS(30/70 mass ratio)				
Pa	Sec^{-1}	220	226	232	238	244
12030.27	4	1.69	1.30	1	0.78	0.43
21173.77	8.3	1.56	1.22	1	0.75	0.39
28563.55	15	1.93	1.45	1	0.85	0.45
37698.73	19.8	2.00	1.56	1	0.73	0.55

Table(2) Superposition shift factors for(232°C) reference temperature. α_T for PC/ABS(60/40)

τ	ϒ (ref)	Temperature(°C).PC/ABS(60/40 mass ratio)				
Pa	Sec^{-1}	220	226	232	238	244
12030.27	4.6	5.63	1.63	1	0.82	0.51
21173.77	10	4.50	1.92	1	0.67	0.52
28563.55	16	3.81	1.68	1	0.53	0.53
37698.73	22.4	3.23	1.77	1	0.80	0.66

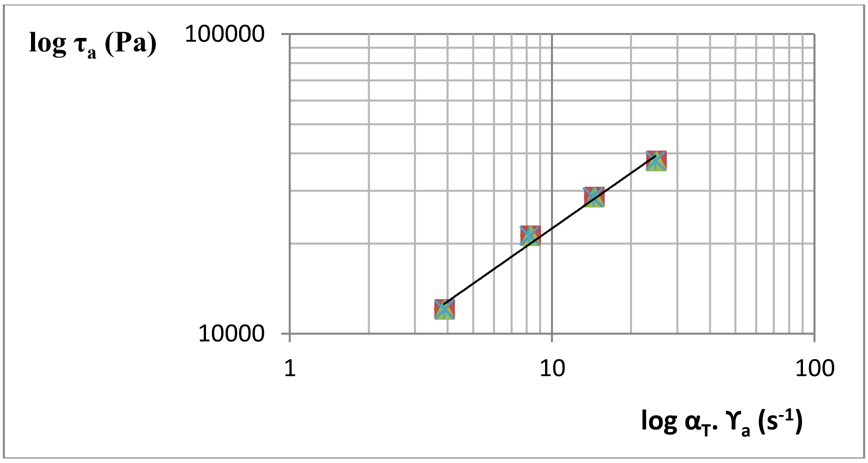

Fig 5. log τ_a VS log α_T.$ϒ_a$ for PC/ABS (30/70 mass ratio)
T(C°) [(♦)220,(■)226,(▲)232,(+)238,(●)244]

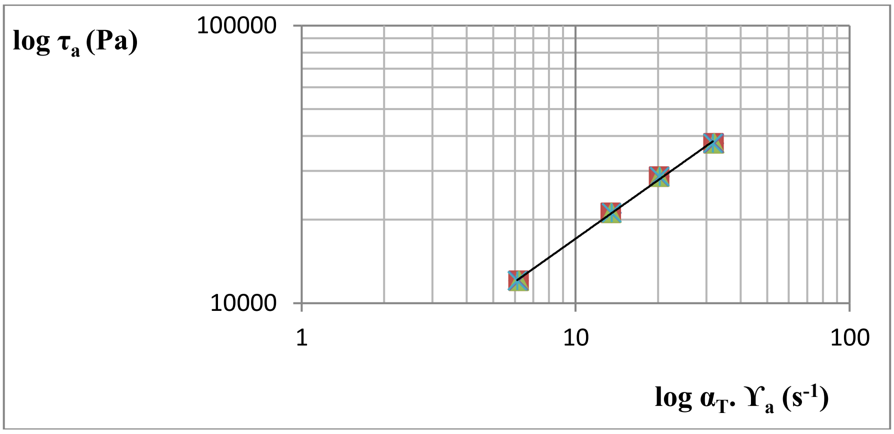

Fig 6. log τ_a VS log $\alpha_T.\Upsilon_a$ for PC/ABS (60/40 mass ratio)
T(C°) [(♦)220,(■)226,(▲)232,(+)238,(●)244]

The resulting master curves for PC/ABS (30/70) and PC/ABS (60/40 mass ratio) are displayed in figures 5 and 6 and amply demonstrate the applicability of the superposition method .It should be noted that the values of α_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. After that, the temperature dependency on the shift factors was examined in conjunction with an Arrhenius-type, or simple exponential, equation of the following form:

$$\alpha T = B \cdot \exp (Ea / RT) \qquad (9)$$

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 :

$$\text{Log } \alpha T = \text{Log } B + Ea / 2.303 RT \qquad (10)$$

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 . 10^3 (K^{-1}) observed for each blend polymer .

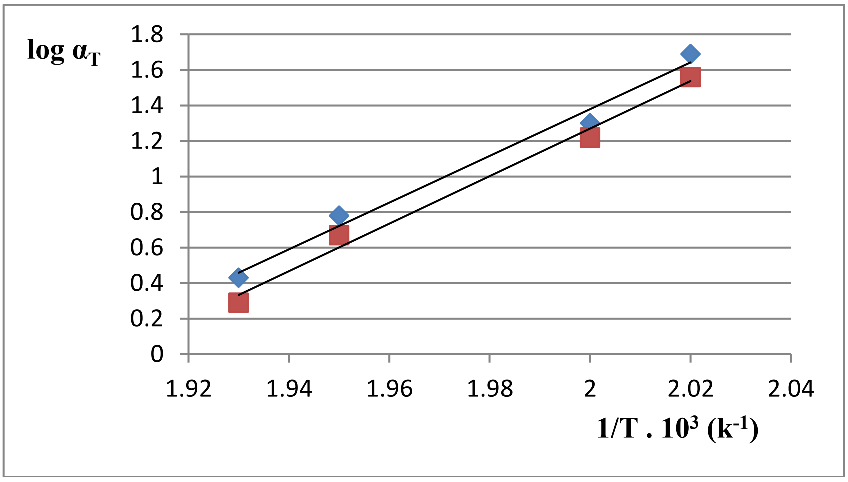

Fig 7. Log α_T VS 1/T.10^3 (K^{-1}) 232°C reference temperature for PC/ABS (30/70 mass ratio)

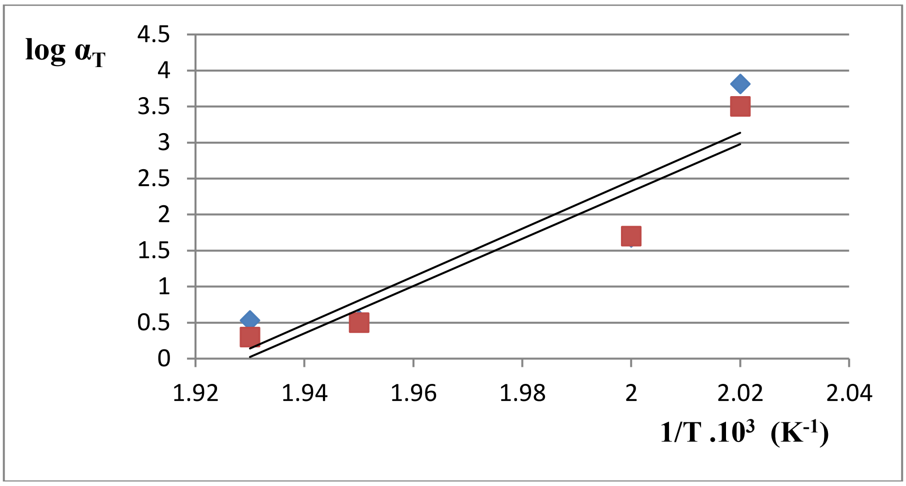

Fig 8. **Log α_T VS 1/T. 10^3 (K^{-1}) 232°C reference temperature for PC/ABS (60/40 mass ratio)**

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

Table(3)Summary of shift factors temperature equation constants (232°C reference temperature) for PC/ABS (30/70 mass ratio)

τ_a (Pa)	E_{at} (Kcal/mol)	B	B`	C
12030.27	12.731	0.7702	-0.113	$2.782x10^{-3}$
21173.77	13.197	0.3850	-0.414	$2.883x10^{-3}$

Table(4)Summary of shift factors temperature equation constants (232°C reference temperature) for PC/ABS (60/40 mass ratio)

τ_a (Pa)	E_{at} (Kcal/mol)	B	B`	C
12030.27	12.692	0.8157	-0.088	$2.773 x10^{-3}$
21173.77	13.790	0.6658	-0.176	$3.013x10^{-3}$

Viscosity curves represent the relation between apparent shear viscosity and apparent shear rate at different temperature. figures 7 and 8 show the viscosity curves of samples meet at 220-232°C. It could be noted from figures7 and 8 that the apparent shear viscosity of the sample melts decrease with increasing shear rate, this behavior was attributed to the alignment or arrangement of chain segments in the direction of applied shear stress [38-42].
It could be noted from figures9 and 10 that the reduced viscosity η_a/α_T VS $\Upsilon_a .\alpha_T$ decrease with increasing factor $\Upsilon_a. \alpha_T$. It means that the reduced viscosity curves could be superimposed if arbitrary shift along the shear rate or shear stress axis were allowed. Moreover, the resulting curves had shapes which were similar to a number of theoretical master curves calculated for the Zimm-Sehuls molecular- weight distribution [43-48]

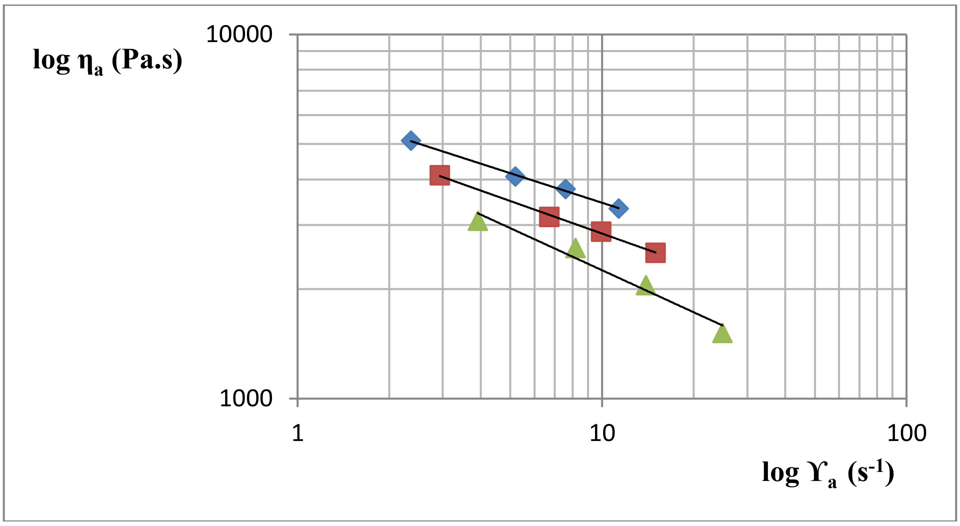

Fig9.log η_aVs log Υ_a for PC/ABS (30/70)
T(C°) [(♦)220,(■)226,(▲)232]

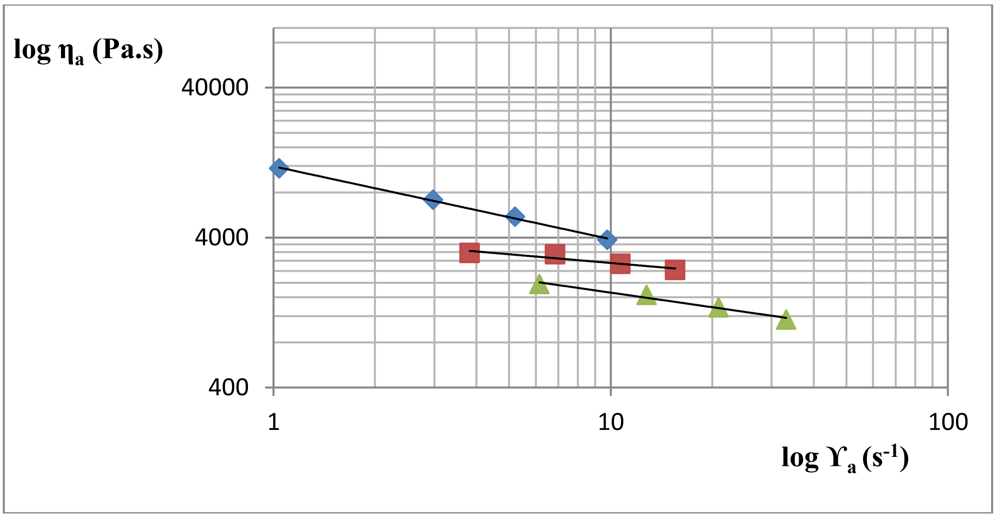

Fig10.log ηaVs log ϒa for PC/ABS (60/40)
T(C°) [(♦)220,(■)226,(▲)232]

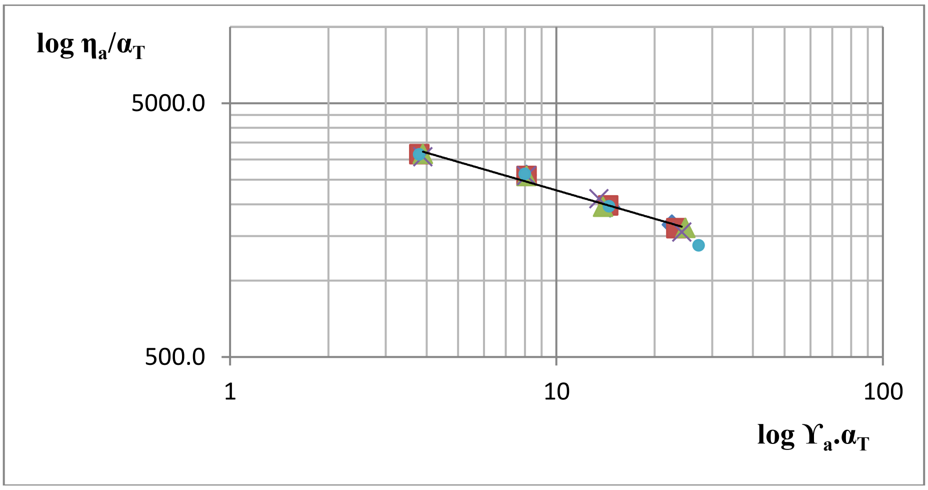

Fig11.log η_a/α_TVs log Υ_a. α_T for PC/ABS (30/70)
T(C°) [(♦)220,(■)226,(▲)232,(+)238,(●)244]

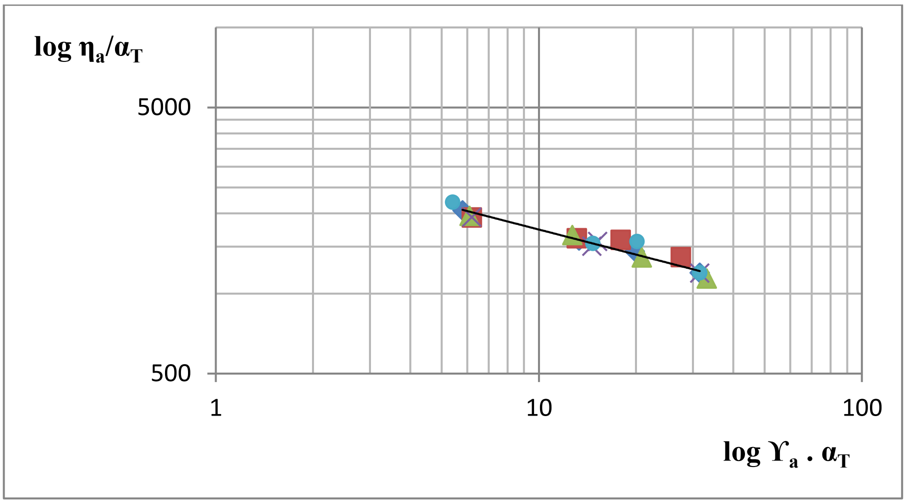

Fig12.log η_a/α_T Vs log $\Upsilon_a . \alpha_T$ for PC/ABS (60/40)
T(C°) [(♦)220,(■)226,(▲)232,(+)238,(●)244]

4- CONCLUSION:

1. The shift factor (α_T) increases for PC/ABS (30/70) as the shear stress (τ) increases.
2. The shift factor (α_T) increases for PC/ABS (60/40) as the shear stress (τ) increases.
3. The flow activation energy increases for PC/ABS (30/70) as the shear stress (τ) increases.
4. The flow activation energy increases for PC/ABS (60/40) as the shear stress (τ) increases.
5. The displacement technique can be applied to PC/ABS (60/40) and PC/ABS (30/70) blends by obtaining a single curve. This facilitates the selection of forming conditions in the production process based on the technician's skill and ability.

We would like to express our gratitude to Professor Dr. Fawaz Deri from the Materials Rheology Laboratory for his assistance and advice.

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