Studying the Effect of Addition of Carbon Black on Rheological Properties of Polypropylene and Polycarbonate

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Received on: 3/1/2012 & Accepted on: 8/1/2013

ABSTRACT

In the present research the rheological properties of polymer melt composed of (polypropylene- polycarbonate) unfilled_ filled with different amounts of Iraqi carbon black (2 – 7) wt% was studied. Single screw extruder was used for development of these blends . The rheological behaviour of these blends was investigated by using rotational concentric type rheometer .

The rheological properties shear rate($\dot{\gamma}$) , apparent viscosity (η_a), dynamic viscosity(ή), shear stress (τ) and angular frequency (ω),shearing flow at various temperatures (220 ˚C, 240˚C and 260 ˚C) were studied and found to be increase with increasing the amount of filler and decrease with increasing temperature. The flow curves were determined in the range of shear rate from about (10 to10^2) s^{-1}. The activation energy was also measured, the values of activation energy varied from(11.939 to 20.892) KJ/Mole for different formation.

Keyword: Melt rheology ,Composite ,Power law index, Polypropylene , Polycarbonate, Filler.

دراسة تأثير إضافة الكاربون الاسود على الخواص الانسيابية لبولي بروبيلين والبولي كاربونات

الخلاصة

في هذا البحث تم تحضير منصهر بوليمري من بولي برولين وبولي كاربونات المدعمة بنسب وزنيه مختلفة من الكاربون الاسود(السخام) العراقي %(7 – 2) باستخدام جهاز الباثقة الأحادية. وبعد ذلك جرت دراسة الخواص الانسيابية باستخدام جهاز لقياس الانسيابية ثنائي المركز.

تم التوصل الى ان الخصائص الانسيابية التي تم دراستها في تدفق القص والمتضمنة معدل القص ($\dot{\gamma}$) ,اللزوجة الظاهرية (η_a) ، اللزوجة الديناميكية (ή) ، إجهاد القص (τ)والتردد الزاوي (ω)،

https://doi.org/10.30684/etj.31.5A13
2412-0758/University of Technology-Iraq, Baghdad, Iraq

كانت متذبذبة في درجات حرارة المختلفة (220 ˚C, 240˚C and 260 ˚C) حيث تزداد بزيادة كميه الماده المدعمه وتقل مع زيادة درجه الحرارة وتم تحديد منحنيات التدفق في نطاق معدل القص من حوالي(10 إلى 10^2) لكل ثانيه فضلا عن طاقة التنشيط تفاوتت من (11.939 إلى25.368) كيلو جول /مول للخلطات المختلفة.

INTRODUCTION

The rheology is defined as the science of the deformation .Composite materials are formed when two or more materials are joined to give a combination of properties that cannot be attained in the original materials [1-3].Several workers were carried out their work in the field of composite and its rheological properties.

Minagawa and White [4] ,studied the melt viscosity for low density polyethylene (LDPE), containing various amounts of titanium as filler versus shear rate. It was observed that as the amount of filler particles is increased, the melt viscosity increases rapidly, in particular at low shear rates.

Lobe and White [5], studied the relation between melt viscosity for polystyrene (PS) containing various amounts of the carbon black as filler versus shear rate. They observed that as the amounts of carbon black are increased, the melt viscosity increases, in particular at law shear rates.

Viz. and Utracki [6], studied the relation between melt viscosity for polyethylene – terephalate (PET), poly amide-6 (PA) versus shear rate .They noticed that the range of the Newtonian behavior was observed to be significantly larger for pure polymers than for the blends. In the blends, transitions from the Newtonian to slightly pseudo plastic flow has occurred . In general, the transition from Newtonian behavior occurs at lower shear rates Abdel – Khalik and Hassager[7], studied the relation between apparent viscosity versus shear rate for three polymer melts as following :-

Poly styrene at 453°k, high density polyethylene at 443 °k and (phenoxy – A) at 485 °k .The slop of the relation of apparent viscosity versus shear rate equal to(n-1) from which the value of (n) :power – low index was determined .It was found for the previous three polymers that the values of (n) are < 1 which means the behavior of flow is pseudo plastic.

Leonov and Malkin [8], investigated the relation between apparent viscosity and dynamic viscosity where $\left| \acute{\eta} \right|(c\omega)= \eta_a (\dot{\gamma}) \Big|_{c\omega=\dot{\gamma}}$ then$(\dot{\gamma}) = C(\omega)$.The value of (C) increases somewhat with increasing rate of shear rate and frequency, if the value of C within the range of (1 – 4) then $\eta_a=\acute{\eta}$.

Krieger and Dougherty [9], studied the relation between apparent viscosity versus shear stress, for suspensions of glass beads in polybutane (indopol L100). They noticed that over the range of shear stresses investigated, as shear stress decreases, the apparent viscosity rapidly increases.

Chapman and Lee[10], studied the flow properties of mica – reinforced polypropylene melts using the weissenberg Rheogoniometer at two temperatures (180ºC and 220ºC). It was observed that the viscosity of the composite decreases with increasing shear rate. This behavior is explained by flake interactions, which is tend to draw the flakes into orientations unfavorable for flow, leading to high viscosity at low shear rates; but at high shear rates the viscous stresses predominate over particle interactions, alignment is greater and the viscosity is less .At 180ºC as the mica content is high, the flakes tend to agglomerate in to a network structure which is readily destroyed by shear.

In this work the rheological properties of polymer melt composed of filled and unfilled polypropylene/polycarbonate(PP-PC) with different amounts of C.B. was studied using rotational type rheometer . The flow curves were determined ,as well as activation energy was also calculated.

EXPERIMENTAL WORK

Raw materials

Matrix phase

Polypropylene(PP)

Commercial polypropylene was used, it was supplied by Saudi Arabia SABIC Company .The general properties of this type of polypropylene are shown in the Table(1).

Table (1) Properties of PP.

Specifications	Value
Melt index	11 gm/10 min
Density	0.908 gm / cm^3
Molecular weight	254 gm/ mol

Polycarbonate (PC)

Commercial polycarbonate was used, it was supplied by Germany BASF Company. The general properties of this type of polycarbonate are shown in the Table (2).

Table (2) Properties of PC.

Specifications	Value
Melt index	2.1 gm/10 min
Density	1.20 gm / cm^3
Molecular weight	420.7 gm / mol

Filler(Carbon black)

The carbon black used in this work was produced by Iraqi Asala Company .The general properties of this type of Carbon Black are shown in the Table (3).

Table (3) Properties of C.B.

Specifications	Value
Particle size	66.21 μm
Blackness index	90
Surface area	33 m^2/g

PROCEDURES

Extrusion procedure

(PP), (PC) and (C.B) samples were kept in an air circulation dry oven at 80°C for 4 hr then 10 wt% of PP, 90 wt% of PC and different amounts of carbon black (2 – 7) wt% were measured by using digital balance (Sartorious – Germany) and mixed. Various formulation were prepared for unfilled- filled PP/PC blend with different amounts of carbon black as shown in Table (4).A weighed samples were transferred to single – screw machine at temperature ranging (210 – 220)°C with rotation (30) rpm. The compounding time involved was less than (5min). The extradites produced in the form of about (1.5 – 2)mm diameter sheet were cooled in water at room temperature and cut well in suitable forms for each test.

Table (4) Extrusion parameters of Polymer blend with Carbon black.

No.	Formulations PP/PC/C.B ,(wt%)	Temperature, °C Zone (1)	Zone (2)	Zone(3)	Screw speed, (r.p.m)
1	10/90/0	210	220	220	30
2	10/90/2	210	220	220	30
3	10/90/3	210	220	220	30
4	10/90/4	210	220	220	30
5	10/90/5	210	220	220	30
6	10/90/6	210	220	220	30
7	10/90/7	210	220	220	30

Procedure of molding process.

The homogenous mixture was then pressed in the hydraulic press applying temperature and pressure at the same time. The temperature 200°C was applied to the upper and lower sides of mold while the samples were still under the applied pressure. The sample sheet with dimensions 15cm * 5cm * 4mm was obtained. The specimen were prepared from this sheet.

Rheometer

Coaxial – cylinder Rheometer type (VEB MLW prÜ fgerate – Wark) Company, was used to measure viscosity at different temperatures ranging from (220 – 260) °C. This apparatus has four rotational speeds (16, 37, 77 and 150) rpm. An electrical motor drives the rotor. The shear stress (scale reading) is determined, as a function of shear rate from (the rotational speed). This instrument consists of two cylinders, first, the inner is moved and second, the outer is fixed. The Rheometer dimensions are as follows:

r_i = radius of inner cylinder = 11.5mm
r_o = radius of outer cylinder = 19mm
h = height of immersed cylinder = 26mm

$$\omega = 2\pi N / 60 \ (S^{-1}) \qquad \text{... (1)}$$

Where

π=constant

ω = angular frequency (S^{-1})

N = rotational speed (rpm)

Procedure of rheology test

The samples were cut into small pieces and placed in fixed cylinder under suitable temperature .The factor (α) was obtained from the rheometer, it is proportional with shear stress, The shear rate is a function of rotational speed as follows:

$$\tau = z.\ \alpha \qquad \text{... (2)}$$

where

τ = shear stress (dyne/cm^2.skt)

z = constant

α = scale reading (skt)

$$\dot{\gamma} = \frac{\omega r_0^2}{r_0^2 - r_i^2} \qquad \text{.....(3)}$$

Where

$\dot{\gamma}$ =shear rate(s^{-1})

Then :

$$\eta = \frac{\tau}{\dot{\gamma}} * 100 \qquad \text{.....(4)}$$

Where

η=Viscosity (CP)

RESULTS and DISSCUSIONS

Effect of carbon black and temperatures on:

Apparent viscosity (ηa)

Figures (1-7) show the relation between apparent viscosity of PP/PC = 10/90 unfilled – filled with different amounts of carbon black (2 – 7) wt% versus shear rate at different temperatures (220ºC, 240ºC and 260ºC). It is clearly seen that as the amount of filler particles increased, the apparent viscosity increases rapidly, in particular at low shear rate. This behavior is explained in the light of filler particle interactions, which tend to draw the particle of fillers into orientations unfavorable for flow, leading to high viscosity. At low shear rates the composite viscosity is more influenced by the strength of bonding in the network structure, which appears to be relatively independent of temperature. These results are in good agreement with the results obtained by Chapman [10], Minagawa [4] and Lobe [5].

The effect of temperature at high shear rates on composite viscosity may be illustrated as follows, when the temperature is increased, polymeric composite does not soften immediately ,but develop gradually. When the temperature is above the glass transition region, chain rotation and uncoiling can take place with relatively little viscous effect, thus the rubber like behavior is observed. In this region (rubbery) the stiffness of materials is considerably less than the glass region which leads to decrease the adhesion force, thus the viscosity will decrease. As the temperature is increased, the viscosity decreases, because the viscous stresses predominate over particle interactions, alignment is greater and the viscosity is less. These results are in good agreement with the results obtained by Lockett [11] and Chapman [10].

Figures (1-7) it indicate that at low shear rate the behaviour of flow was Newtonian for unfilled pure polymer blend ,when the shear rate increases the behaviour is pseudo plastic.

The (n – 1) value was obtained from the slop of the relation between obtained apparent viscosity versus shear rate . The value of n (power – law index) was obtained, the value of (n) obtained equals (0.389-0.936)which in lower than one indicate that the flow is pseudo plastic confirming that transition is occurred from Newtonian to pseudo plastic These results agree well with the results obtained by Hassager [7].

Dynamic viscosity (ή)

Figures (8-14) show the relation between the dynamic viscosity versus angular frequency for PP/PC = 10/90 unfilled – filled with different amounts of carbon black (2 – 7) wt% at three temperatures (220ºC, 240ºC and 260ºC). It is clearly seen that the behavior is similar to that observed with apparent viscosity versus shear rate.When the amounts of filler particles is increased, the dynamic viscosity increases rapidly, in particular at low angular frequency. At high angular frequency, the dynamic viscosity is decreased, also with different temperatures. This occurs $\eta_a(\dot{\gamma})=\acute{\eta}(\omega)$, when$(\dot{\gamma})$ = C(ω), where $\left(C = \frac{r_0^2}{r_0^2 - r_i^2} \text{ is a constant} \right)$.

The obtained value of (C) (1.578) is within normal range which is (1 – 4) mentioned by Leonov and Malkin [8].

Shear rate ($\dot{\gamma}$)and shear stress (τ).

Figures (15-21) show, the relation between the shear rate and shear stress for PP/PC = 10/90 with unfilled – filled different amounts of carbon black (2 – 7) wt% at three temperatures of (220ºC, 240ºC and 260ºC). It is clearly that the shear stress increased with increasing amounts of carbon black (2 – 7) wt% at temperature of (220ºC); but above this temperature, the sequence of increases is as follows:-

(220ºC>240ºC>260ºC)

This is due to the decreasing of viscosity with increasing the temperature. These results agree well with the results obtained by Villamizar and Han [12].

Interaction between filler (carbon black) and matrix (PP/PC).

Figures (22-25) show the relation between apparent viscosity and different amounts of carbon black (2 - 7) wt%, at three temperatures of (220ºC, 240ºC and 260ºC) as the shear rate is constant.

The shape of apparent viscosity to be straight line which indicates that there was little interaction between reinforcement phase and matrix phase and this is attributed to lower percent of filler used. In the literature as the amount of filler increases the shape of the relation will be curve instead of straight line indicating higher interaction .These results are in good agreement with the results obtained by Uemura and Takayanagi [13].

Torque behavior (T).

Figures (26-29) show, the relation between torque and different amounts of carbon black (2 – 7) wt% at three melt temperatures of (220ºC, 240ºC and 260ºC) and at four rotor speeds (16, 37, 77 and 15) rpm.

It is observed that the torque value increased with increasing amounts of carbon black (2 – 7) wt 220ºC and decrease with increasing melt temperatures (220ºC, 240ºC and 260ºC). These results in good agreement with the results obtained by Folt[14].

Flow activation energy (Eη).

Determination flow activation energy (Eη).

Figure (30) shows the relation between logarithm of the zero – shear viscosity (η_0) and the reciprocal of absolute temperature (1/T), known as Arrhenius plots, for pp/pc = 10/90 unfilled – filled with different amounts of carbon black at three melt temperatures of (220ºC, 240ºC and 260ºC).

It is noticed in Fig. (30) that from the slope of Arrhenius plot, the activation energy was calculated. The results are reasonable agreement with the results obtained by Ferry [15] and westover [16].

Behavior of flow activation energy (Eη).

Figure (31) shows, the relation between flow activation energy calculated from Fig. (30) and different amounts of carbon black (2 – 7) wt%.

It is clearly seen that the flow activation energy varies linearly with increasing amounts of carbon black as filler of (2 – 7) wt% as shown in Table (5). As the amounts of carbon black increase, the activation energy increases which means more energy is needed to break the samples. These results are in good agreement with the results obtained by Ferry [15] and Utracki [6] .

Table (5) The flow activation energy for PP/PC unfilled – filled with Different amounts of Carbon black (2-7) wt% (calculated by using Arrhenius equation).

No.	Composite compositions PP/PC/C.B (wt%)	flow activation energy Eη (KJ/mol)
1	10/90/0	11.939
2	10/90/2	14.184
3	10/90/3	16.447
4	10/90/4	18.654
5	10/90/5	20.892

CONCLUSIONS

At the end of this work on polymeric blends, the following conclusions are reached.

1.The apparent viscosity (ηa), dynamic viscosity (ή), shear stress (τ) and flow activation energy (Eη) are :-

- Increase by increasing the amount of filler used from (2 – 7) wt%.
- Decrease when the temperature increases from 220ºC to 260ºC.

2.The torque value (T) has been calculated experimentally from mathematical model. The calculated torque has been plotted versus different amounts of carbon black (2 – 7) wt%. It was observed that it increases gradually with increasing the amounts of carbon black.

3.The type of interaction between the matrix and reinforcement phase has been observed and proved to be weak.

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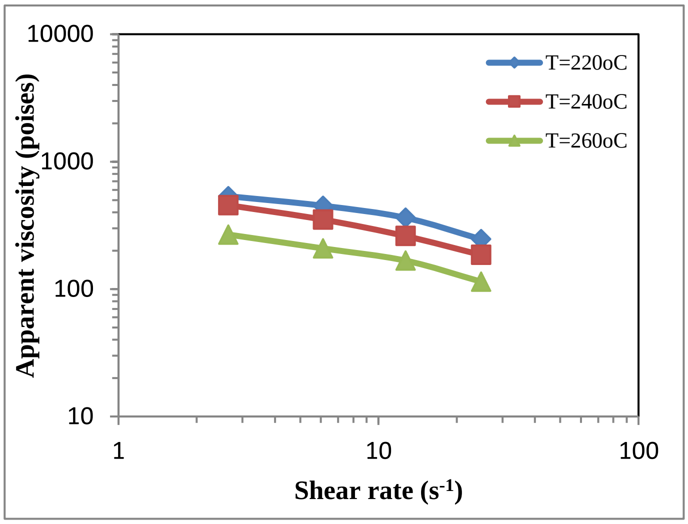


Figure (1) Apparent viscosity of pp/pc = 10/90 blend versus shear rate at different temperatures are (220ºC ,240ºCand 260ºC).

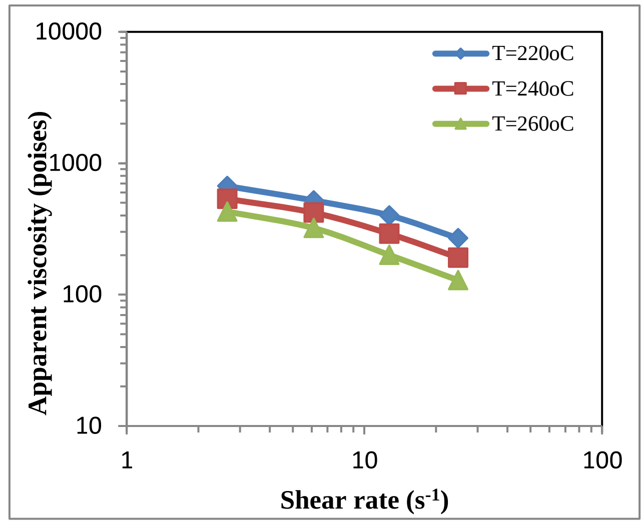


Figure (2) Apparent viscosity of pp/pc= 10/90 filled with carbon black (2wt%) versus shear rate at different temperatures are (220ºC ,240ºCand 260ºC).

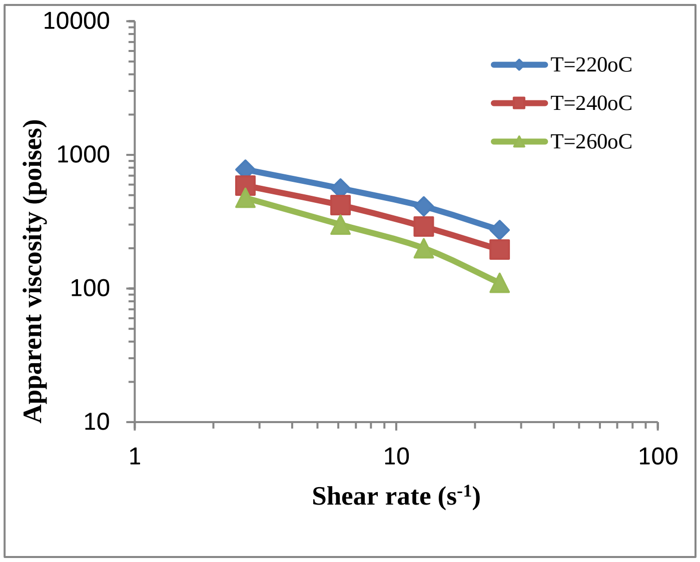


Figure (3) Apparent viscosity of pp/pc = 10/90 filled with carbon black (3wt%) versus shear rate at different temperatures are (220°C ,240°Cand 260°C).

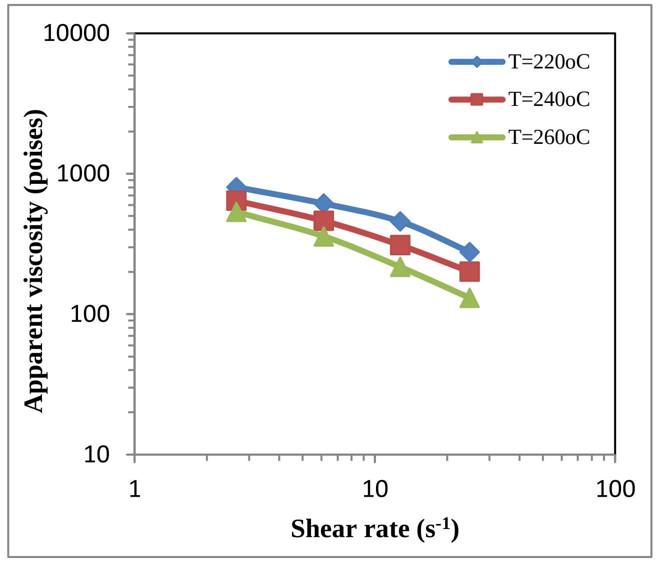


Figure (4) Apparent viscosity of pp/pc = 10/90 filled with carbon black (4wt%) versus shear rate at different temperatures are (220°C ,240°Cand 260°C).

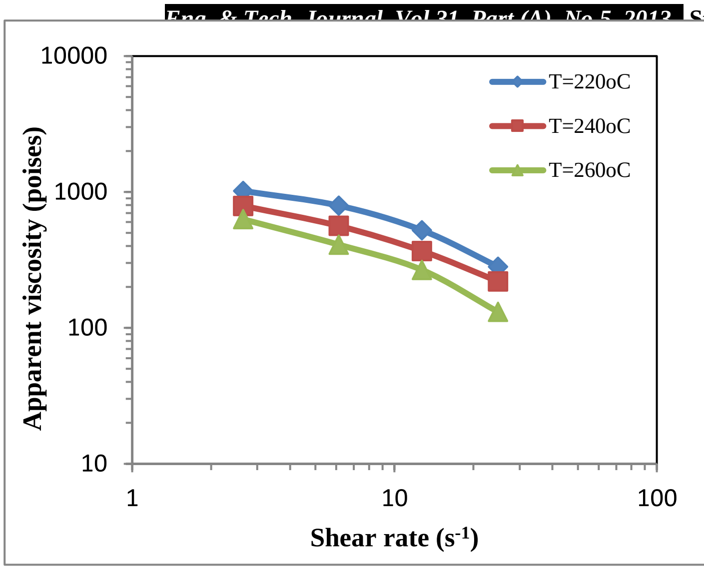


Figure (5) Apparent viscosity of pp/pc = 10/90 filled with carbon black (5wt%) versus shear rate at different temperatures are (220ºC ,240ºCand 260ºC).

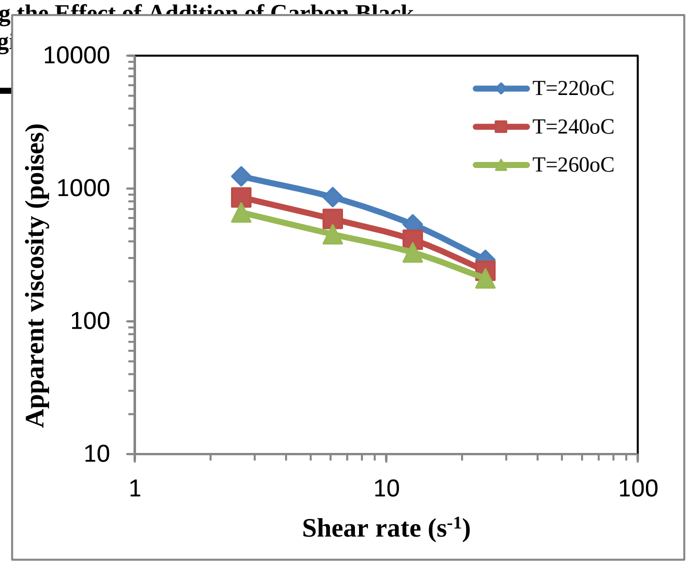


Figure (6) Apparent viscosity of pp/pc = 10/90 filled with carbon black (6wt%) versus shear rate at different temperatures are (220ºC ,240ºCand 260ºC).

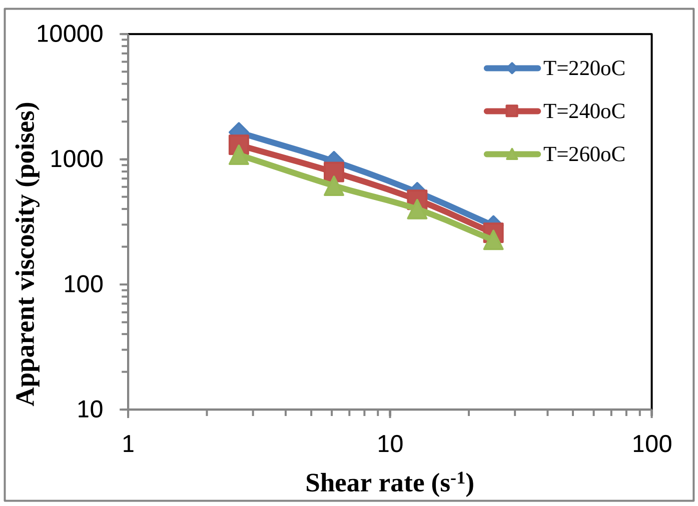


Figure (7) Apparent viscosity of pp/pc = 10/90 filled with carbon black (7wt%) versus shear rate at different temperatures are (220ºC ,240ºCand 260ºC).

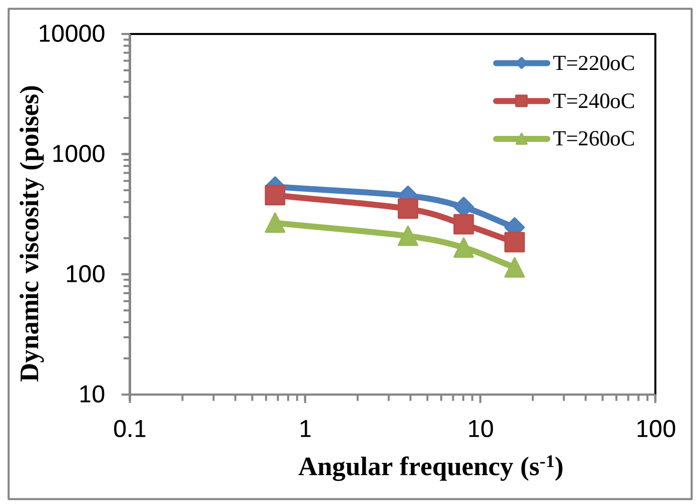
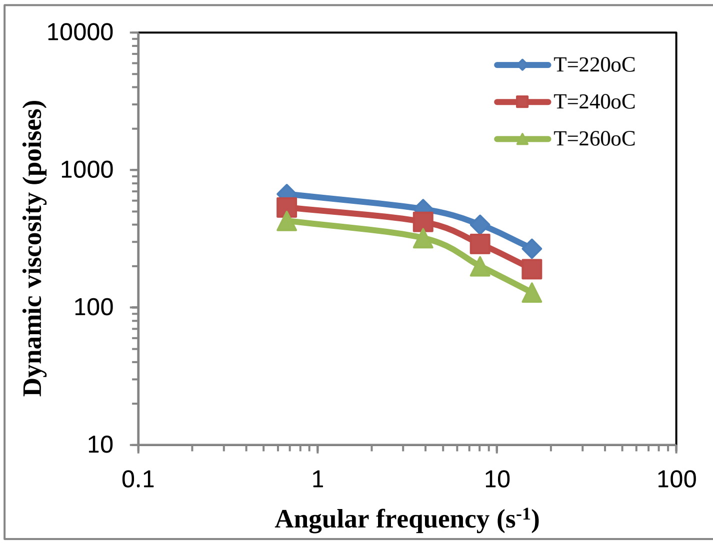


Figure (8) Dynamic viscosity of pp/pc = 10/90 versus angular frequency at different temperatures are (220ºC ,240ºCand 260ºC).



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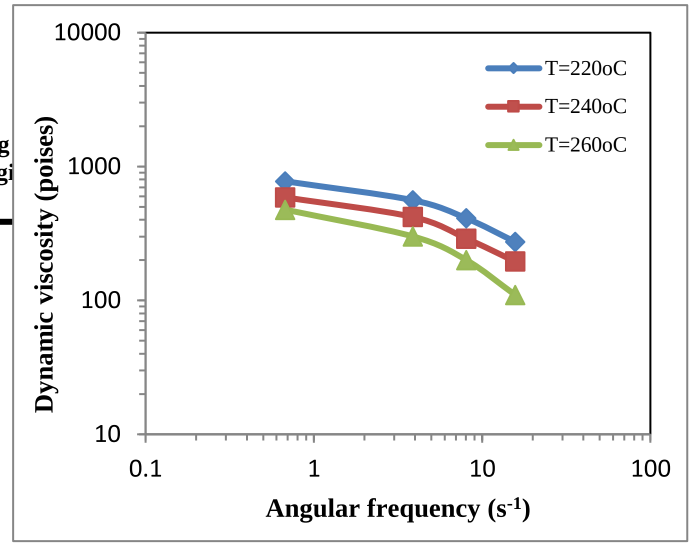
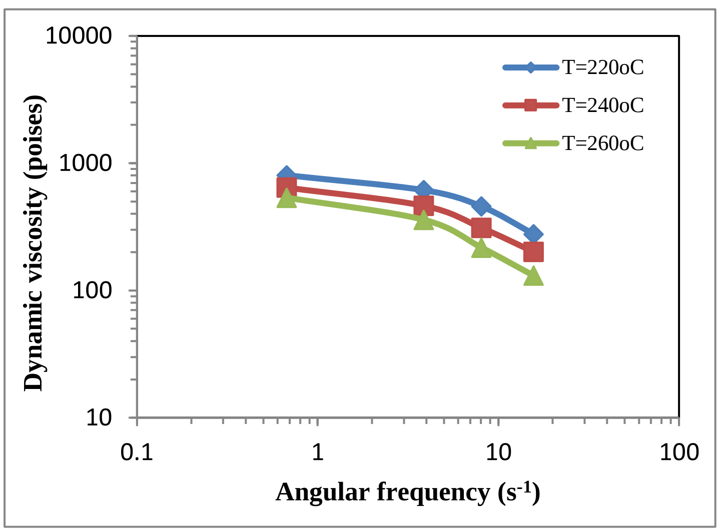


Figure (9) Dynamic viscosity of pp/pc = 10/90 filled with carbon black(2wt%) versus angular frequency at different temperatures are (220ºC ,240ºCand 260ºC).

Figure (10) Dynamic viscosity of pp/pc = 10/90 filled with carbon black(3wt%) versus angular frequency at different temperatures are (220ºC ,240ºCand 260ºC).



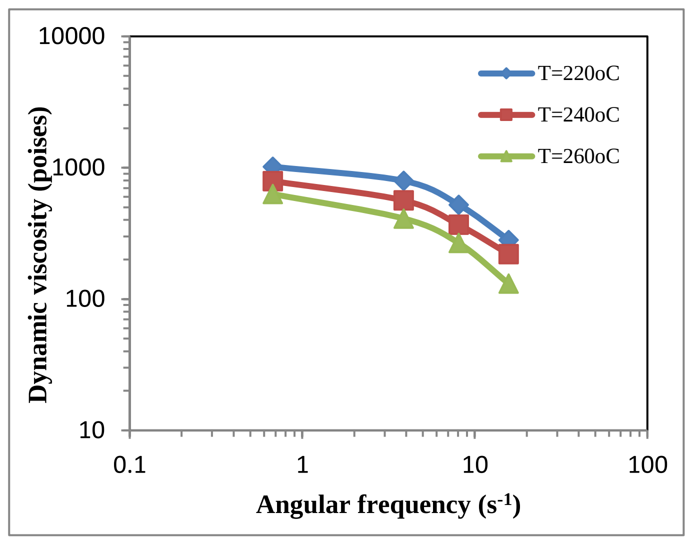
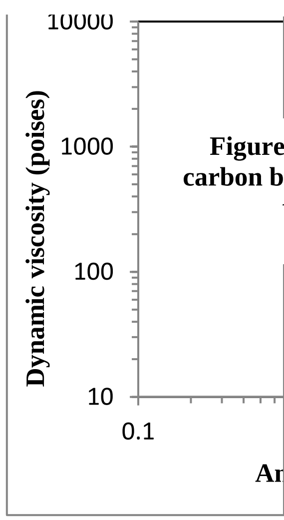


Figure (11) Dynamic viscosity of pp/pc = 10/90 filled with carbon black(4wt%) versus angular frequency at different temperatures are (220ºC ,240ºCand 260ºC).

Figure (12) Dynamic viscosity of pp/pc = 10/90 filled with carbon black(5wt%) versus angular frequency at different temperatures are (220ºC ,240ºCand 260ºC).

Figure (13) Dynamic viscosity of pp/pc = 10/90 filled with carbon black(6wt%) versus angular frequency at different temperatures are (220ºC ,240ºCand 260º



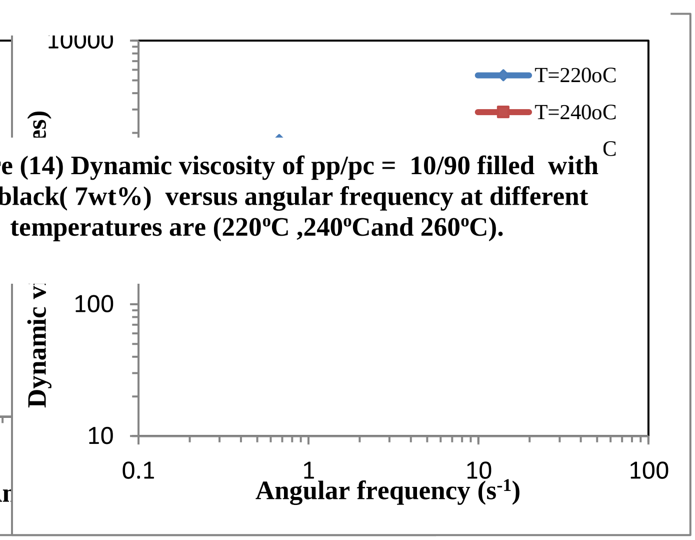


Figure (14) Dynamic viscosity of pp/pc = 10/90 filled with carbon black(7wt%) versus angular frequency at different temperatures are (220ºC ,240ºCand 260ºC).

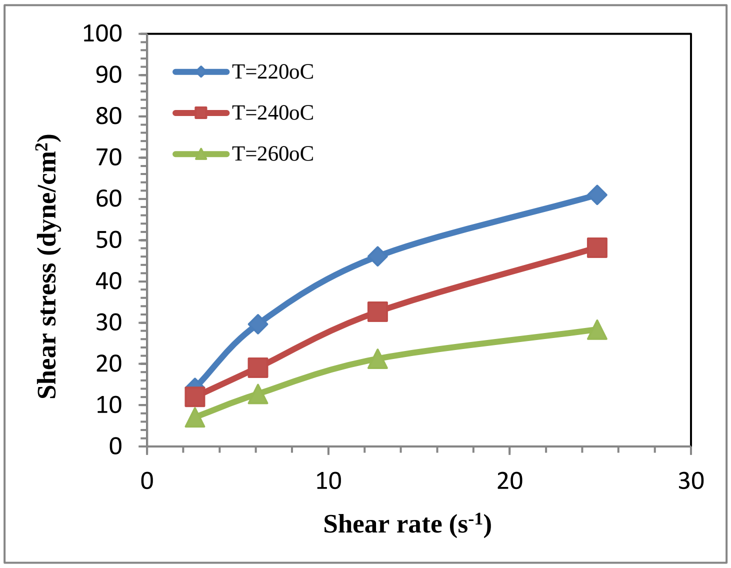


Figure (15) Shear rate versus shear stress for PP/PC = 10/90 at different temperatures are (220ºC,240ºC and 260ºC)

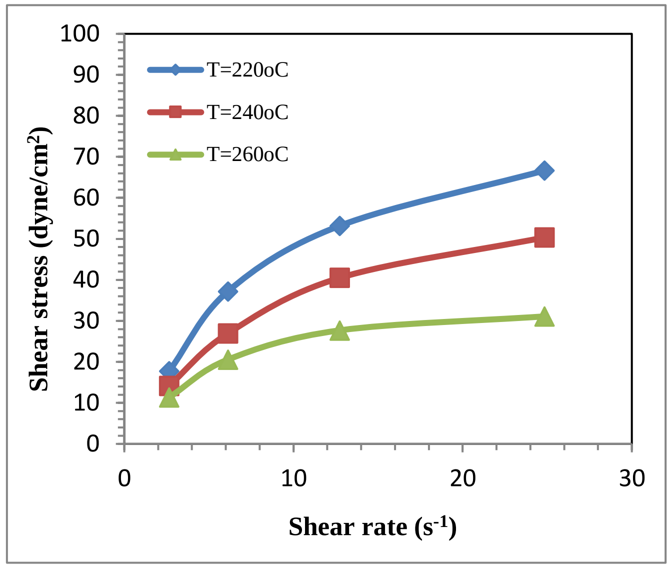
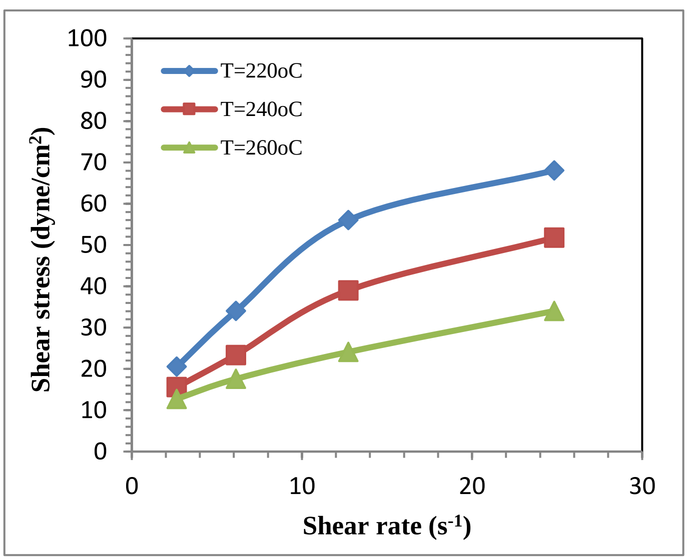


Figure (16) Shear rate versus shear stress for PP/PC =10/90 filled with carbon black (2wt%) at different temperatures are (220ºC,240ºCand 260ºC).



gure (17) Shear rate versus shear stress for PP/PC =10/90 filled with carbon black (3wt%) at different temperatures are (220ºC,240ºCand 260ºC).

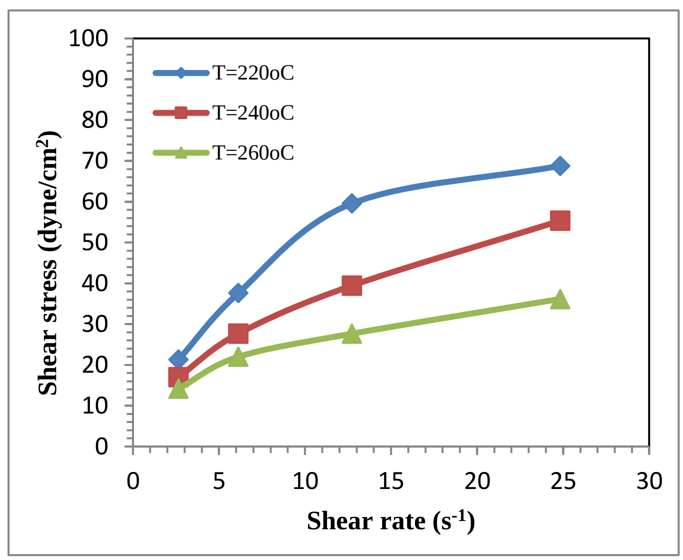


Figure (18) Shear rate versus shear stress for PP/PC =10/90 filled with carbon black (4wt%) at different temperatures are (220ºC,240ºCand 260ºC).

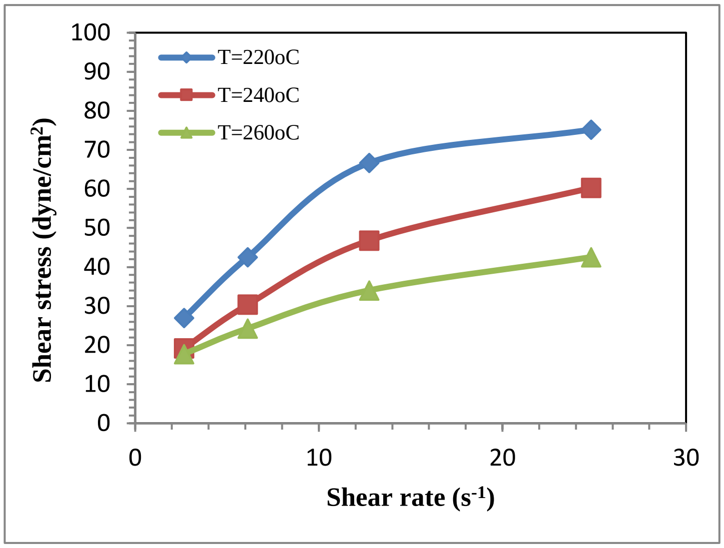


Figure (19) Shear rate versus shear stress for PP/PC =10/90 filled with carbon black (5wt%) at different temperatures are (220°C,240°Cand 260°C).

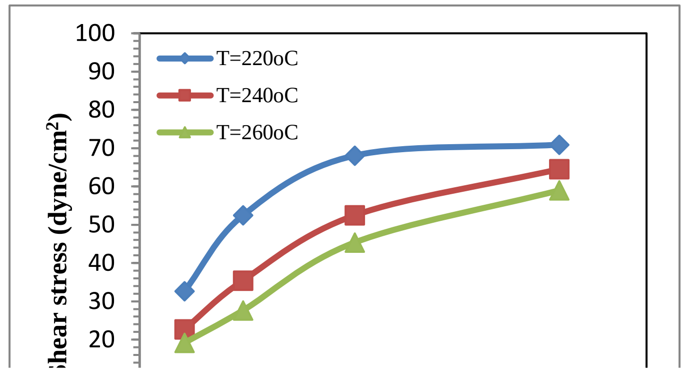


Figure (20) Shear rate versus shear stress for PP/PC =10/90 filled with carbon black (6wt%) at different temperatures are (220°C,240°Cand 260°C).

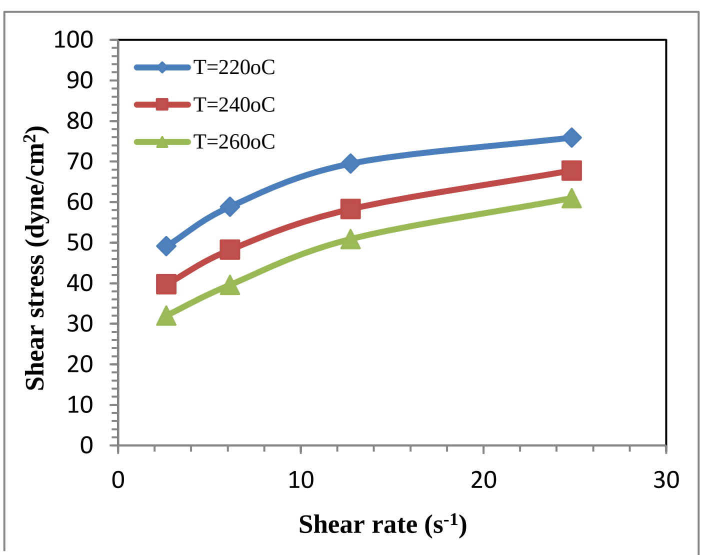


Figure (21) Shear rate versus shear stress for PP/PC =10/90 filled with carbon black (7wt%) at different temperatures are (220°C,240°Cand 260°C).

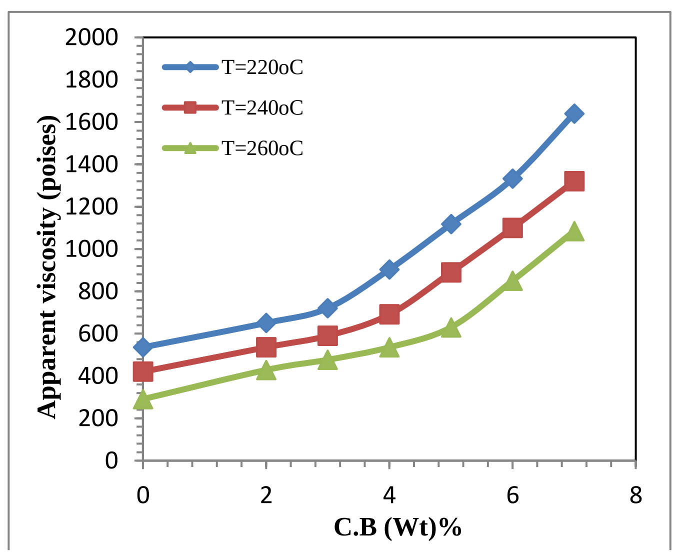
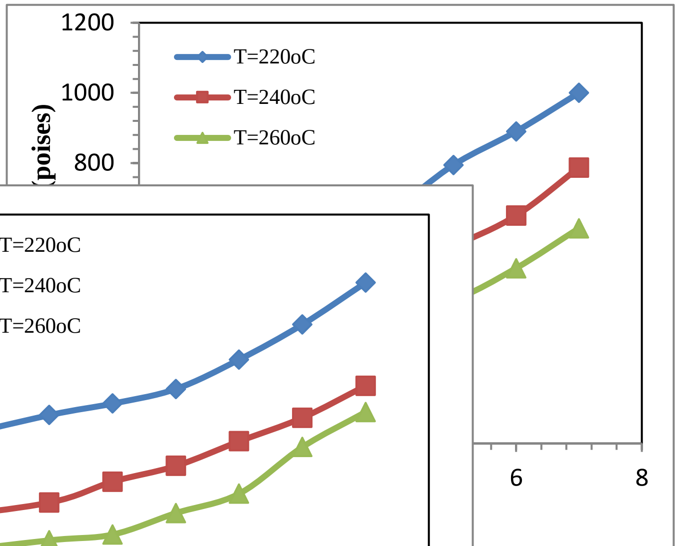


Figure (22) Apparent viscosity versus different amounts of carbon black (0, 2, 3, 4, 5, 6 and 7) wt% at three temperatures are (220°C240°Cand260°C) at constant shear rate = 2.648 (s^{-1})



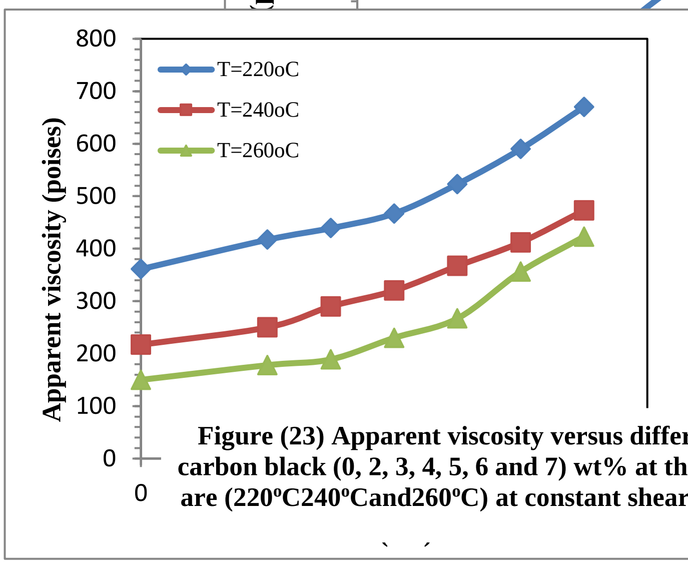
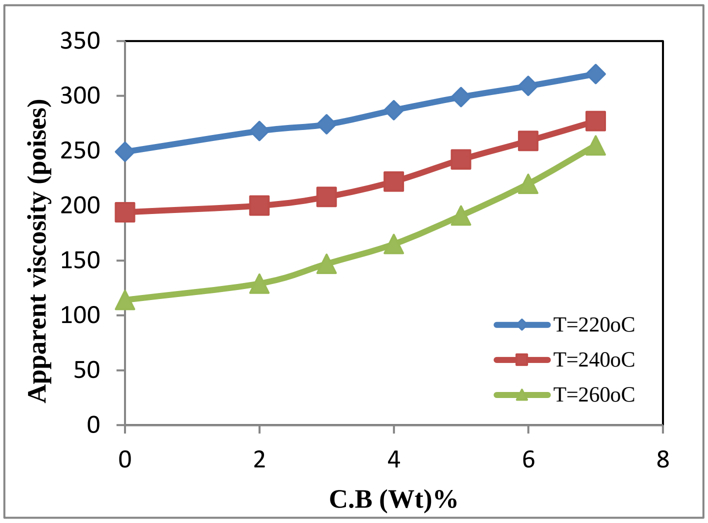
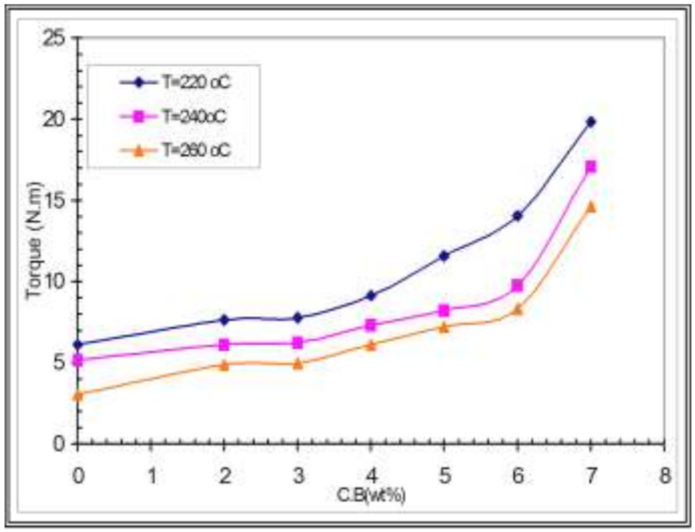


Figure (23) Apparent viscosity versus differen carbon black (0, 2, 3, 4, 5, 6 and 7) wt% at thre are (220ºC240ºCand260ºC) at constant shear ra

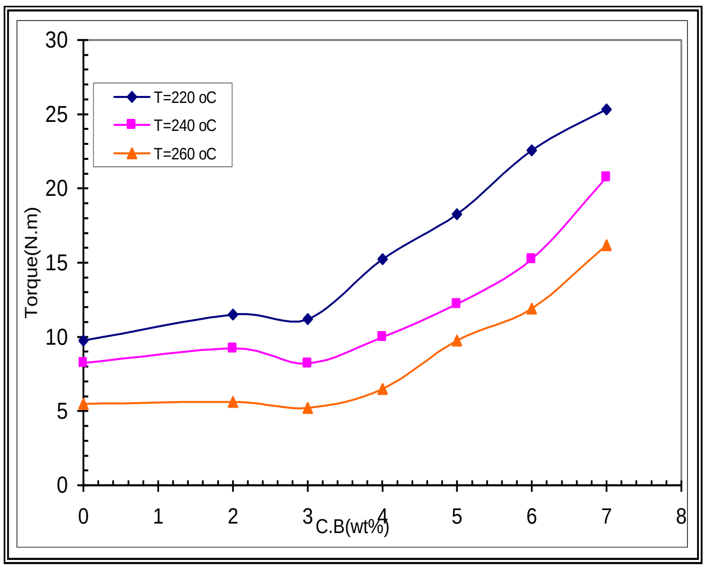
Figure (24) Apparent viscosity versus different amounts of carbon black (0, 2, 3, 4, 5, 6 and 7) wt% at three temperatures are (220ºC240ºCand260ºC) at constant shear rate = 12.733 (s^{-1})



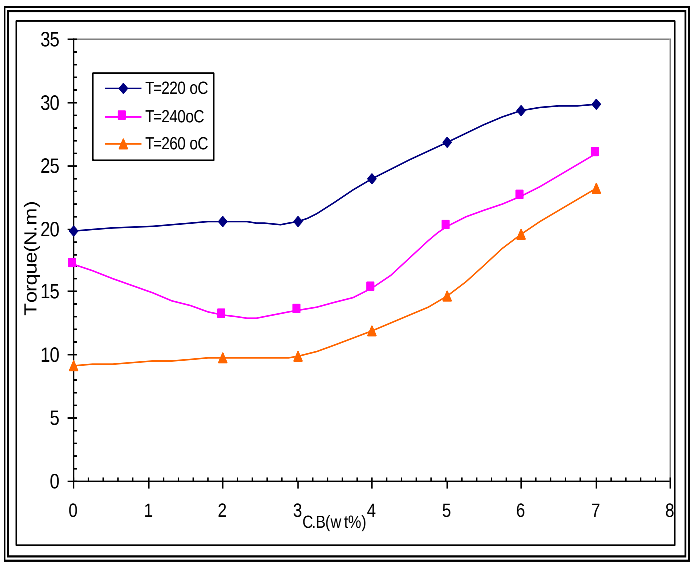
Figure(25) Apparent viscosity versus different amounts of carbon black (0, 2, 3, 4, 5, 6 and 7) wt% at three temperatures are (220ºC240ºCand260ºC) at constant shear rate = 24.388 (s^{-1})



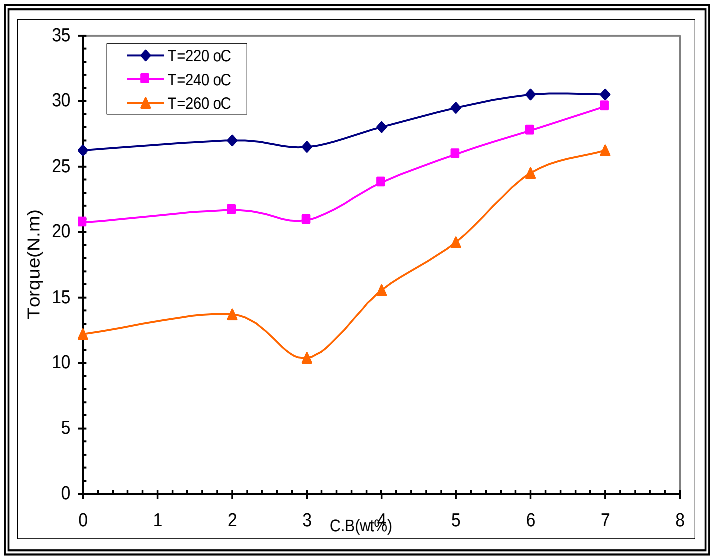
Figure(26) Torque versus different amounts of carbon black (0,2, 3, 4, 5, 6 and 7) wt% at three temperatures are (220ºC,240ºC and 260ºC) at rpm = 16



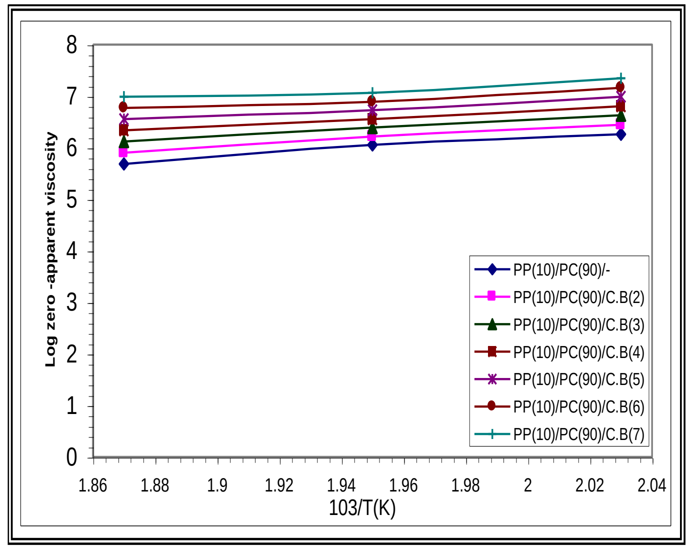
Figure(27) Torque versus different amounts of carbon black (0,2, 3, 4, 5, 6 and 7) wt% at three temperatures are (220ºC,240ºC and 260ºC) at rpm = 37



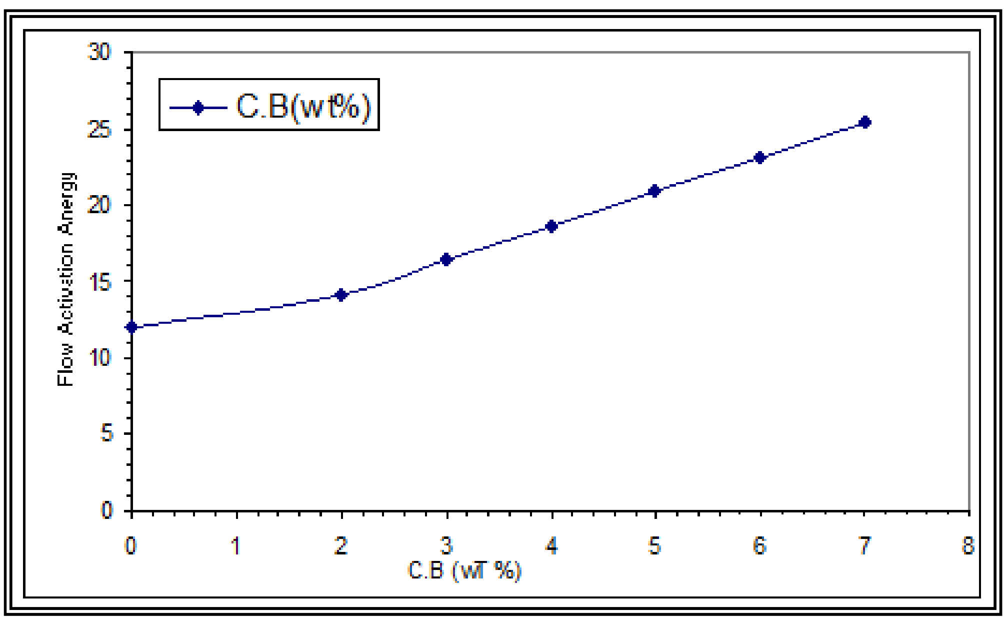
Figure(28) Torque versus different amounts of carbon black (0,2, 3, 4, 5, 6 and 7) wt% at three temperatures are (220ºC,240ºC and 260ºC) at rpm = 77



Figure(29) Torque versus different amounts of carbon black (0,2, 3, 4, 5, 6 and 7) wt% at three temperatures are (220ºC,240ºC and 260ºC) at rpm =150



Figure(30) Log η_oZero –apparent viscosity versus 1/T for the PP/PC filled with different amounts of carbon black are (0, 2, 3, 4, 5, 6 and 7) wt%



Figure(31) Flow Activation energy versus different amounts of carbon are (0,2,3,4,5,6 and 7) wt%