STUDY THE INTERACTION AND COMPATIBILITY OF LOW DENSITY POLYETHYLENE/ POLYACRYLIC ACID BLENDS BY RHEOLOGICAL BEHAVIOR AND FTIR MEASUREMENT [+]

دراسة التجاذب والانسجاميه لخليط ماليتد بولي اثيلين الواطىء الكثافه والبولي اكريلك بواسطة السلوك الانسيابي وقياسات طيف الاشعه تحت الحمراء

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Abstract:

Blends of low density polyethylene grafted with maleic anhydride (LDPE-g-MAH) and several ratios (1%, 3%, 5%, 7% and 10%) of poly acrylic acid (PAA) were prepared via melt mixer and their rheological properties was studied. Shear stress, shear rate, viscosity and die swell were calculated at temperatures 210 and 230 ^{o}C . All blends showed that shear stress reduce with increases shear rate .The pseudoplastic behavior for all blends was observed while the apparent viscosity decreases with increasing shear rate. Activation energy (E_a) for these blends was determined at temperatures 170,190,210 and 230 ^{o}C. The characteristic groups of MAH in LDPE, carboxylic acid in PAA, the interface between this functional groups were indicated by Fourier transform infrared spectroscopy (FTIR).The results show the disappear one of the maleic anhydride bands in the LDPE-g-MAH and appearance of strong band at 1730cm^{-1}approximately in the LDPE-g-MAH/PAA (90/10 wt/wt) blends spectrum.

المستخلص :

تمت في هذه الدراسة تحضير خلائط بوليمرية من البولي اثيلين واطئ الكثافة المطعم بحامض الماليك اللامائي مع نسب مختلفة (١%، ٣%، ٥%، ٧%، ١٠%) من البولي اكريلك عن طريق مزج المنصهر للبوليمرين . درست انسجامية الخلائط باستخدام جهاز قياس الصفات الانسيابية (جهد القطع ، سرعة القطع ، اللزوجة ، انتفاخ القالب) عند درجات حرارة ٢١٠ و ٢٣٠ درجة مئوية ، إذ أظهرت جميع الخلائط انخفاضاً في جهد القطع واللزوجة مع زيادة سرعة القطع . كذلك تم حساب طاقة التنشيط للخلائط المحضرة بدرجات حرارة مختلفة (١٧٠، ١٩٠، ٢١٠، ٢٣٠ درجة مئوية) حيث لوحظ أن زيادة نسبة البولي

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اكريلك في الخليط يؤدي إلى انخفاض في طاقة التنشيط . كما لوحظ أن زيادة نسبة البولي اكريلك بالخليط البوليمري أدى إلى انخفاض قليل لانتفاخ القالب خاصة عند درجة حرارة ٢٣٠ درجة مئوية . التداخل والتجاذب بين مجموعة حامض الماليك اللامائي المطعم على البولي اثيلين واطئ الكثافة ومجموعة حامض الاكريلك في البولي اكريلك ، تم الاستدلال عليها باستخدام تقنية الأشعة تحت الحمراء حيث اختفت إحدى حزم حامض الماليك اللامائي وظهرت حزمة قوية عند ١٧٣٠ cm^{-1} في طيف الخليط البوليمري ٩/١ (وزن/وزن) بولي اثيلين مطعم بحامض الماليك اللامائي / بولي اكريلك .

Introduction :

Mixing two or more polymers together to produce blends or alloys is a well-established strategy for achieving a specific combination of physical properties [1-2]

Normally blending is used to combine the properties of two or more polymers and is performed in mixers. However it is often found that the material properties are not as good as expected due to a poor interfacial adhesion between the minor and the major component. Therefore a need arises to look for ways to improve the material properties. Many polymers can be dissolved in a wide spectrum of monomers, even if the resulting polymers are incompatible. Monomers are mixed with an initiator and then absorbed in a polymer. After the temperature increases monomer polymerizes and is grafted on the polymer chains. Graft copolymers are formed, forming *in situ* an alloying agent in the minor phase, during the blending process.

So an essential process for the *in situ* production of an alloying agent is grafting or functionalizing the polymer chains of the dispersed phase. A popular route of functionalizing polyolefin is the use of unsaturated carboxylic derivatives. For free radical grafting some of the most interesting monomers are unsaturated carboxylic derivatives, such as maleic or itaconic anhydrides, and vinylic or acrylic substances containing a second functionality. Maleic anhydride (MAH) has superiority over other monomers because it can hardly homopolimerize, but is also reluctant to free radical grafting, due to a deficiency of electrons in its double bond. This is due to the electron-attracting nature of the carbonyl group, the symmetry of the double bond, and a steric hindrance due to di-substitution. Therefore various methods have been used to grafting MAH on polyethylene ,such as melt, solution[3], UV[4] and ultrasonic[5].Several research was publish on rheological properties of blends like LDPE/PP[6], Starch/LLDPE[7], PET/SBR[8] and LDPE/PA6[9]. In this study ,this MAH grafted on LDPE could be used a potential compatibilizer for LDPE /PAA blends , where the second component of the blends (PAA) could be a polar polymer since amore effective interaction between the blend components could occur. We used maleated low density polyethylene (LDPE-g-MAH) instead of LDPE alone and mixed with several ratio (1%, 3%, 5%, 7% and 10% wt/wt) from poly acrylic acid (PAA). For compatibility of blend between LDPE-g-MAH and PAA we study rheological properties (shear stress, shear rate, viscosity and die swell as well as activation energy) at different temperatures.

Experimental:

Polymers and Chemicals

The following materials were used:

Maleated low density polyethylene MFI=1.578 gm/10min , Density=0.9237 gm/cm^3 , maleic anhydride(%MAH)=9.8 from state company for petrochemical (SCPI) (Basrah – Iraq).Acrylic acid was obtained from BDH company and polymerized to polyacrylic acid which of viscosity average molecular weight (Mv)=11370-11376) .

Blends Preparation

All blends from LDPE-g-MAH and PAA were prepared in Haake Rheocord Torque Rheometer with a speed of 32 rpm , after LDPE-g-MAH melt at 165 °C several weight ratio (1% , 3% , 5% , 7% and 10% wt/wt) from polyacrylic acid was mixed with LDPE-g-MAH .

For rheological measurement used Instron capillary Rheometer machine (the capillary barrel diameter was 1.257mm , capillary length to diameter L/D ratio 80/9 , load weighing was constant 2000 Kg) .The blend products from LDPE-g-MAH / PAA were compression –molded as discs (2 cm diameter 2 mm thickness) for 9 min at 175 °C under a pressure 15 ton and prepared thin film about 0.05 mm thickness for Fourier transform infrared ray (FTIR) measurement which is done by Shimadzu FTIR-8400S for the samples .

Results and discussion :

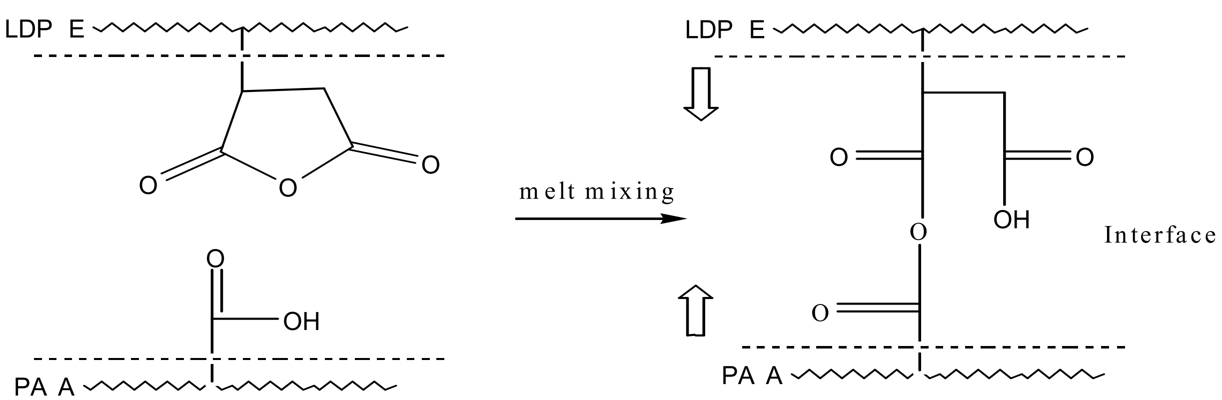
Mechanism of compatibility

Reasons for incompatibility of LDPE / PAA blends are poor interaction adhesion between the tow components (LDPE nonpolar , PAA polar polymers) .However , the phenomenon of compatibility can be induced in an immiscible binary system by modification the LDPE surface with polar group .Used grafted polymer (LDPE-g-MAH) reduce the interfacial tension between phases , increases the surface area of the dispersed phase ,promotes adhesion between the phase components , and stabilizers the dispersed phase morphology[10].

The LDPE-g-MAH was used instead off LDPE is based on tow factors : (1) the ester may be forming ability of anhydride group with hydroxyl group on PAA (scheme 1).(2) The hydrogen bond forming ability between carbonyl groups of MAH and its hydrolyzed with carboxylic acid on PAA.

FTIR spectra of the blends product and LDPE-g-MAH, PAA pure are shown in fig. (1-a) and (1-b), we observed from this figure PAA bands, 3232 cm^{-1} to –OH carboxylic acid stretching, 1728 cm^{-1} for C=O group and C-O bond vibration in 1288cm^{-1} .The LDPE-g-MAH spectrum show two small bands at 1890 and 1791 cm^{-1} corresponded to carbonyl anhydride group and 1724 cm^{-1} may be to carbonyl of hydrolyzed anhydride pendant groups on LDPE chains.

The spectra of blend LDPE-g-MAH/PAA in figure (1-b), all bands shifts to somewhat lower number wave. The carbonyl group at 1730cm^{-1} is stronger than that of PAA and LDPE-g-MAH spectra. The band at 1791 cm^{-1} for maleic anhydride (carbonyl symmetrical) disappear gradually with increase PAA percentage (>1%) besides the 3232cm^{-1} band characteristic of hydroxyl carboxylic acid group of the PAA was not observed in the spectrum of the blend perhaps due to forming ester linkage.



Scheme (1)

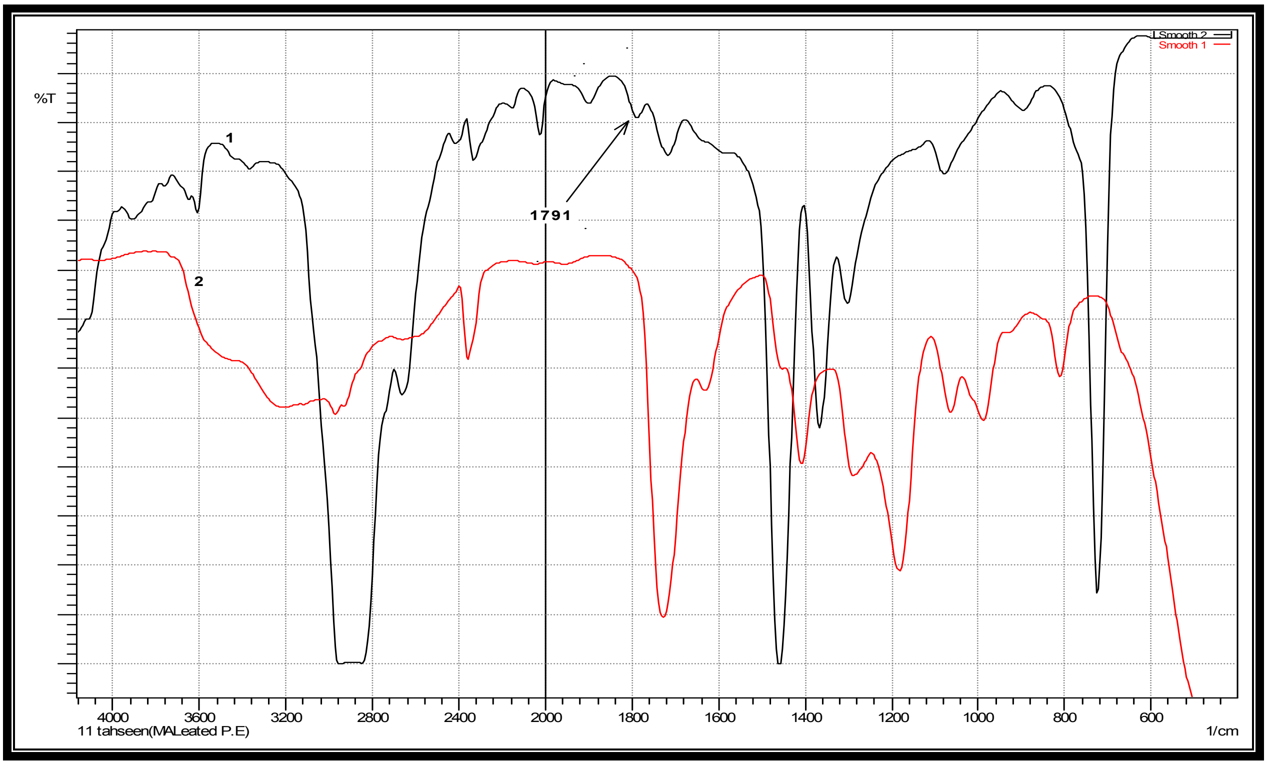


Fig. (1-a) FTIR spectra for 1- maleated polyethylene (LDPE-g-MAH) and 2- polyacrylic acid (PAA)

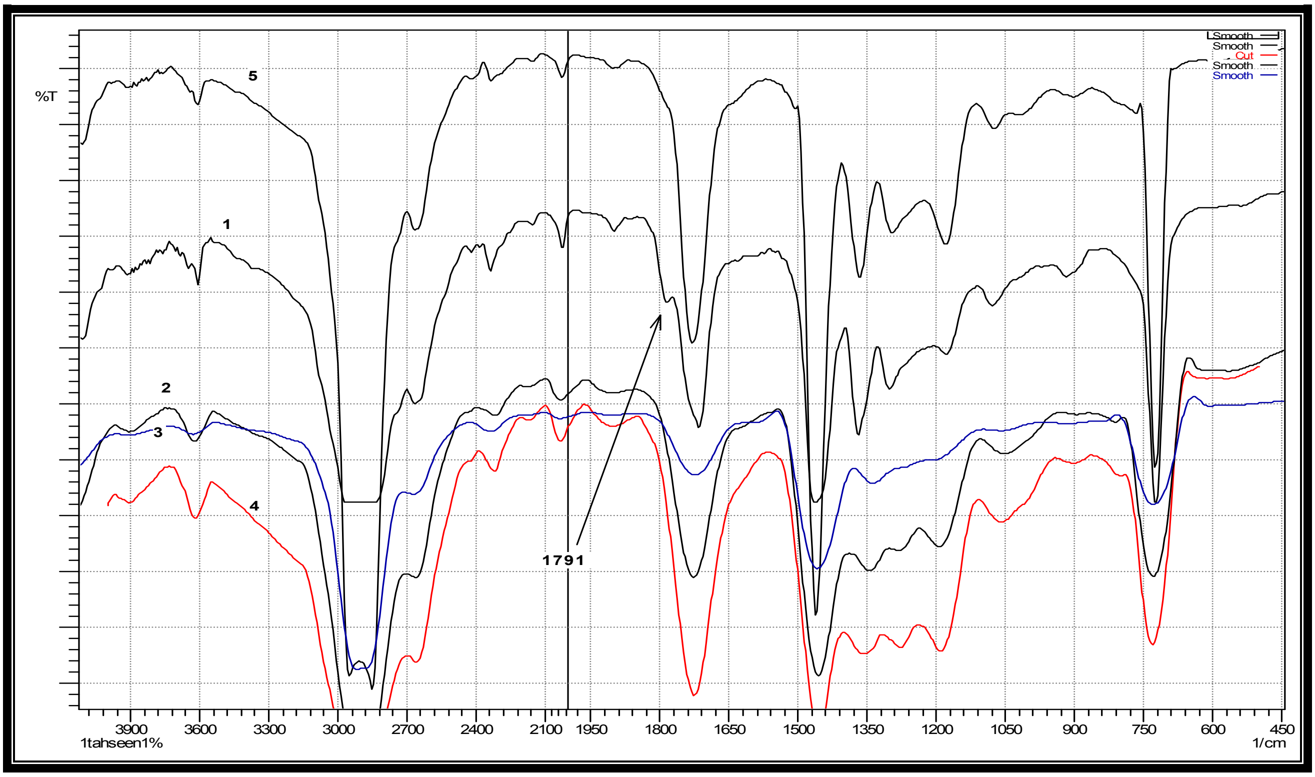


Fig (1-b) FTIR spectra for maleated polyethylene (LDPE-g-MAH) with various percentage (1) 1%, (2) 3%, (3) 5%, (4) 7% and (5) 10% from PAA

Rheology:

Compatibility refers to stabilizing polymer blends and closely related to its rheology [11], therefore, several data was calculated for LDPE-g-MAH/PAA blends:

1) The wall shear stress was calculated from relationship:

$$\tau_w = 3.44*10^5*F\ dc/L$$

Where τ_w is the wall shear stress (K.pa.), F plunger force (Kg), dc is capillary diameter (cm), and L is the length of the capillary (cm).

2) Shear rate was calculated from the following equation:

$$\gamma_w = 0.133[(3n+1)/4n]\ V_{XH}(dB^2/dC^3)$$

where γ_w is the Shear rate (sec^{-1}) , n is the slope from the graph of Ln τ_w against Ln(8V/dc) ,V speed of the flow of the fluid , dB diameter of the cylinder(cm) , and V_{XH} is the cross head speed (cm/min) .

3) The apparent viscosity ήa (Poise) was calculated from equation:

$$\acute{\eta}_a = \tau_w / \gamma_w$$

4) The activation energy of viscous flow was derived from of Arrhenius equation:

$$\acute{\eta} = A.e^{Ea/RT}$$

Where $\acute{\eta}$, viscosity; A, constant; E_a, activation energy; T, absolute temperature; and R, Universal gas constant.

Figures (2), (3), (4) and (5) refers to curves of shear stress against shear rate (fig.2 and 3) with several weights ratio PAA and against %PAA with various shear rate (fig.4and 5) at temperature 210 and 230 °C. In this figures we can see the shear stress increasing with increased shear rate at the same percentage of PAA, while increases slightly with %PAA constituent at shear rate (6.15, 20.5, 61.58, 205.2 and 615.8). which may be the polarity nature of maleic anhydride group grafting on LDPE produce a better interfacial adhesion of the PAA to the LDPE matrix this interaction among polar –nonpolar chains as well as hydrogen bonding formed between functional groups in both polymers provided strong chains in blend prevent or reduce from flowing.

Another way, at the low percentage of PAA the interaction between functional groups is low that lead to free chain movement, thus decrease the shear stress.

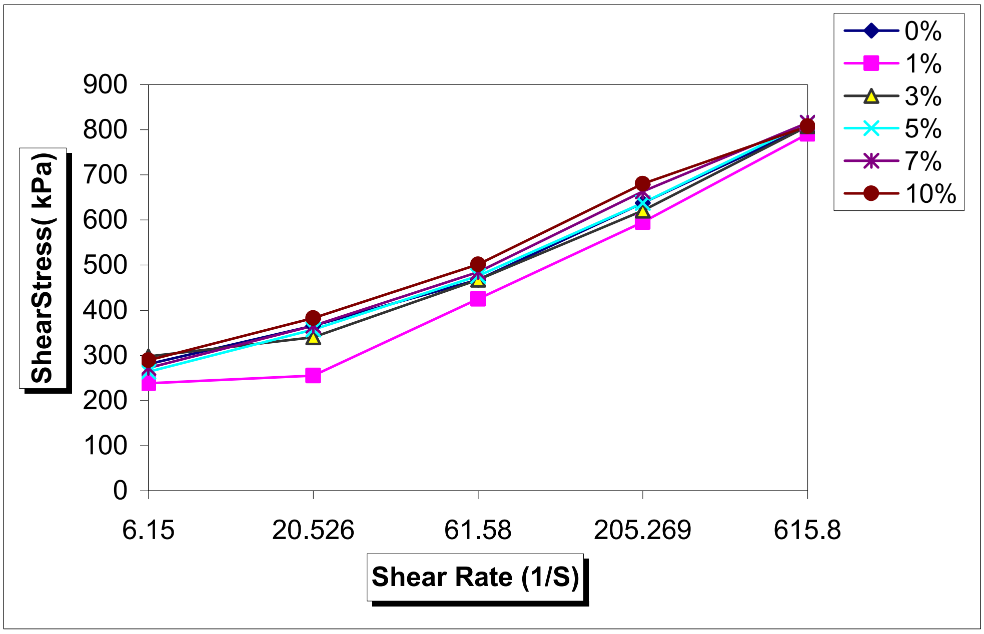


Fig.(2) Curves shear stress with shear rate for LDPE-g-MAH/PAA blends at 210 °C

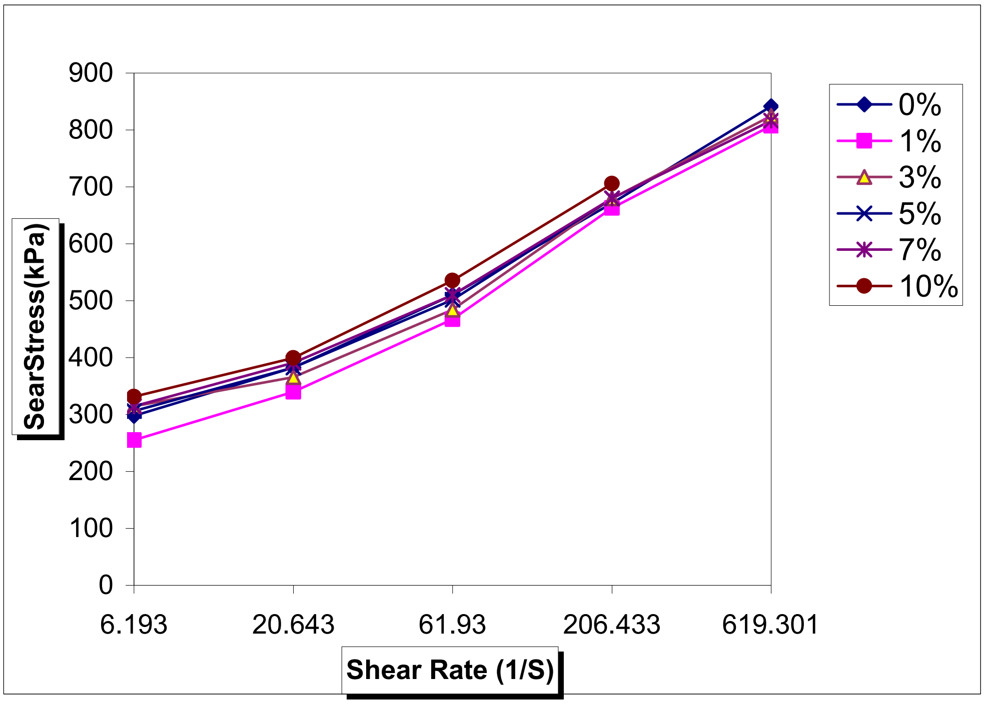


Fig.(3) Curves shear stress with shear rate for LDPE-g-MAH/PAA blends at 230 °C

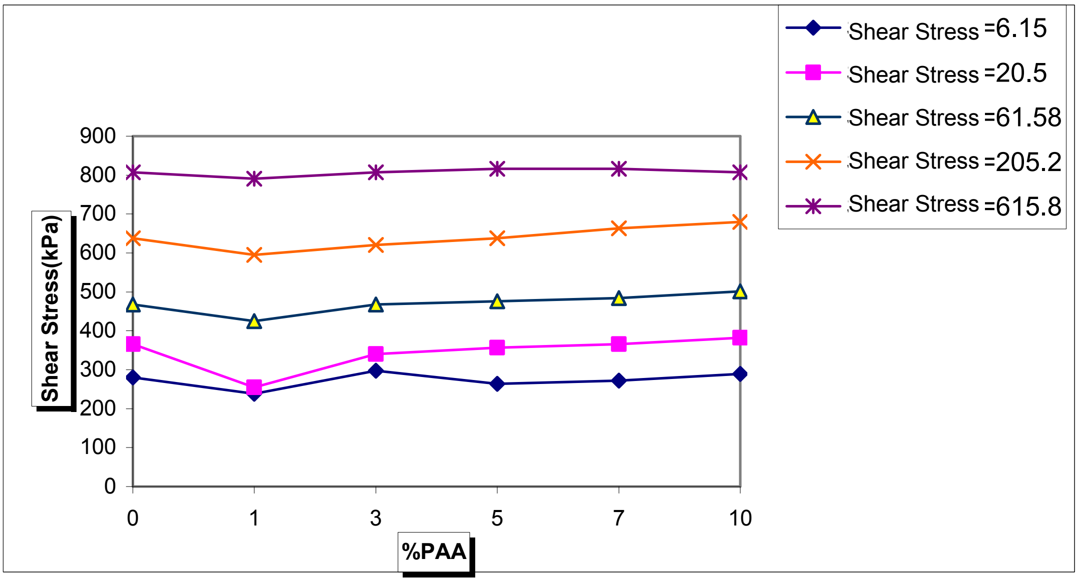


Fig.(4) Effect %PAA constituent on the shear stress of LDPE-g-MAH/PAA blends at various shear rate and temperature 210°C

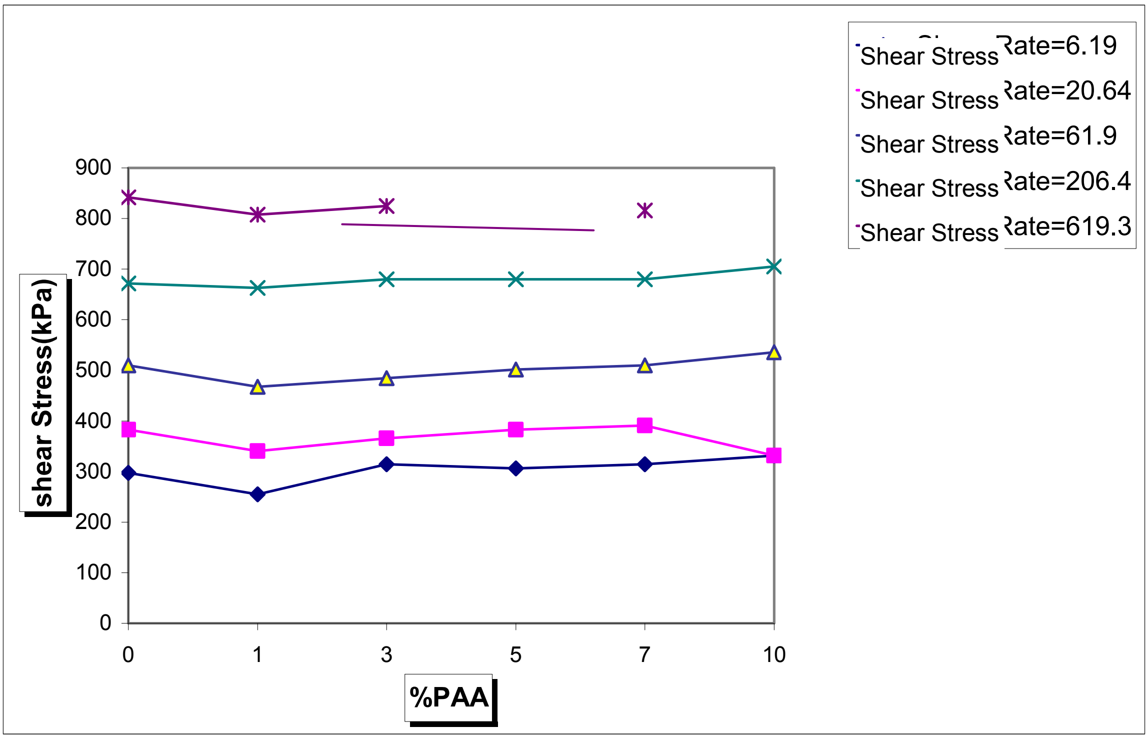


Fig. (5) Effect %PAA constituent on the shear stress of LDPE-g-MAH/PAA blends at various shear rate and temperature 230°C

Figures (6) and (7) show the apparent viscosity at various shear rates and temperature 210 and 230 °C for LDPE-g-MAH and its blends. The pseudoplastic behavior in the flow of all types of blends was observed. That is, the viscosity decreased with an increase in the share rate the same results was published at 190 and 170 °C[11.12] .

The viscosity in the polymer blends depends on the interface adhesion in other side the blends characteristics a summed properties polymers in this blends[12] .Figures (8) and (9) refers to increase of viscosity with increased percentage ratio of PAA in the blends at 210 and 230 °C in the same shear rate, in this case , for low content the PAA bonding and chemical interaction(dipole–dipole and/or hydrogen bonding interactions between the pendant functional groups) takes place in some LDPE-g-MAH chains (small number of grafted molecules of MAH on LDPE here) that lead to limited chemical bond formed in the interface LDPE-g-MAH/PAA properties. For higher PAA contents, the bonding and interaction occurs along the polymer chains .While all blends revealed increase of viscosity with increase the PAA content.

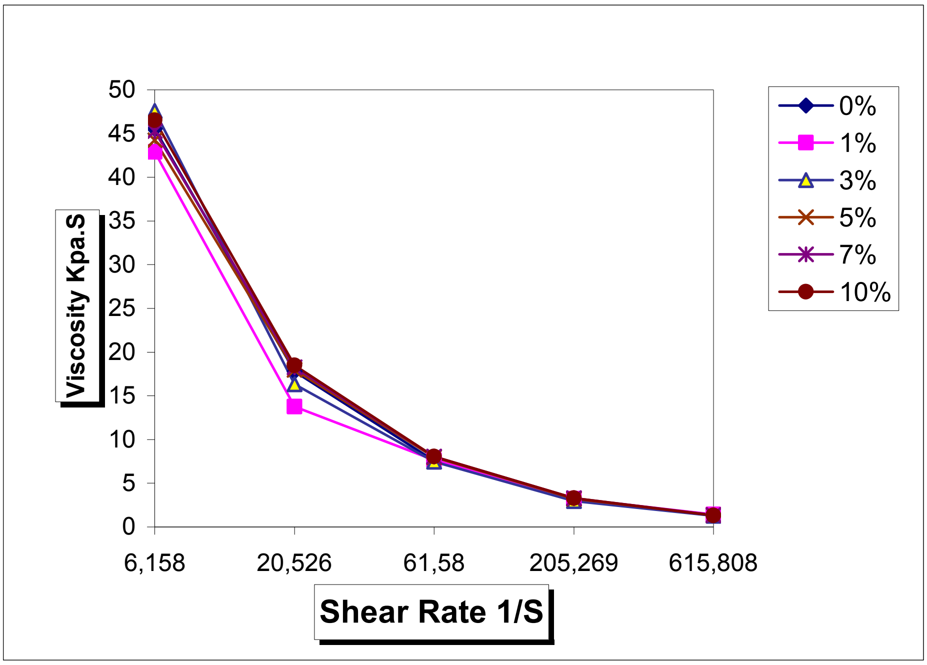


Fig. (6) Effect of shear rate on the viscosity of LDPE-g-MAH/PAA Blends at 210 °C.

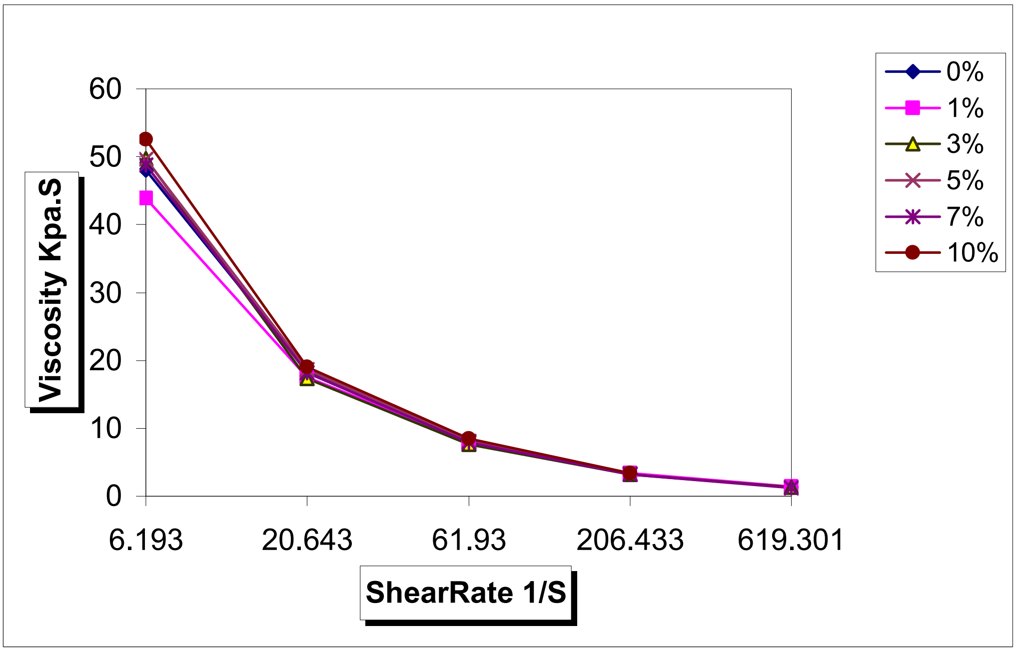


Fig.(7) Effect of shear rate on the viscosity of LDPE-g-MAH/PAA blends at 230 °C

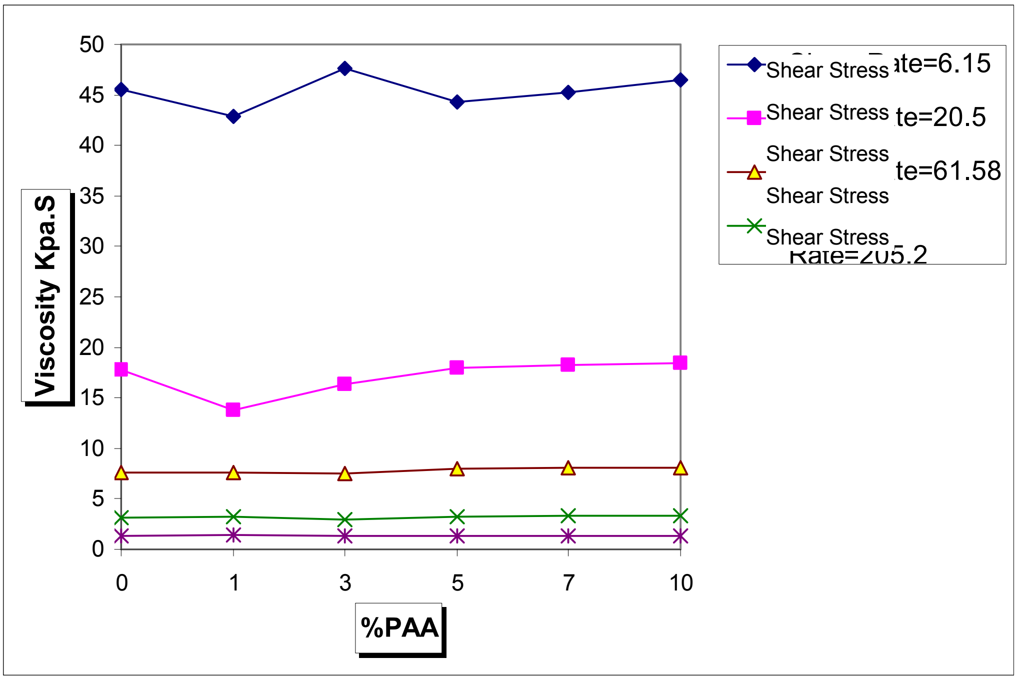


Fig. (8) Effect of PAA percent on the viscosity of LDPE-g-MAH/PAA blends at various shear rate and 210 °C

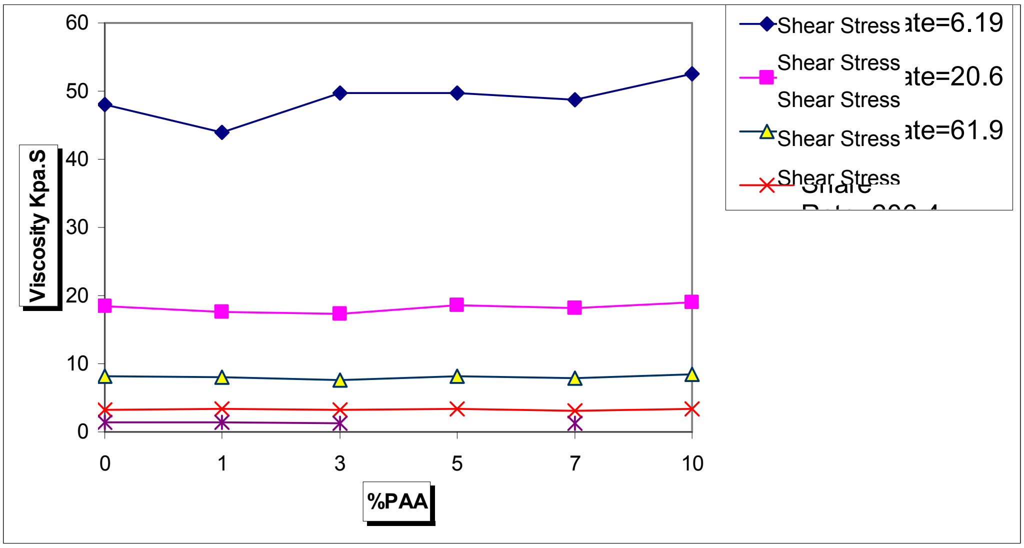


Fig. (9) Effect of PAA percent on the viscosity of LDPE-g-MAH/PAA blends at various shear rate and 230 °C

Arrhenius equation permits the calculation of activation energies of viscous flow for LDPE-g-MAH/PAA blends in order to the influence of temperature. In Figures (10), (11) and (12), logarithm of viscosity is plotted as a function of reciprocal temperature. The activation energy (E_a) of flow, calculated from the slope of these lines.

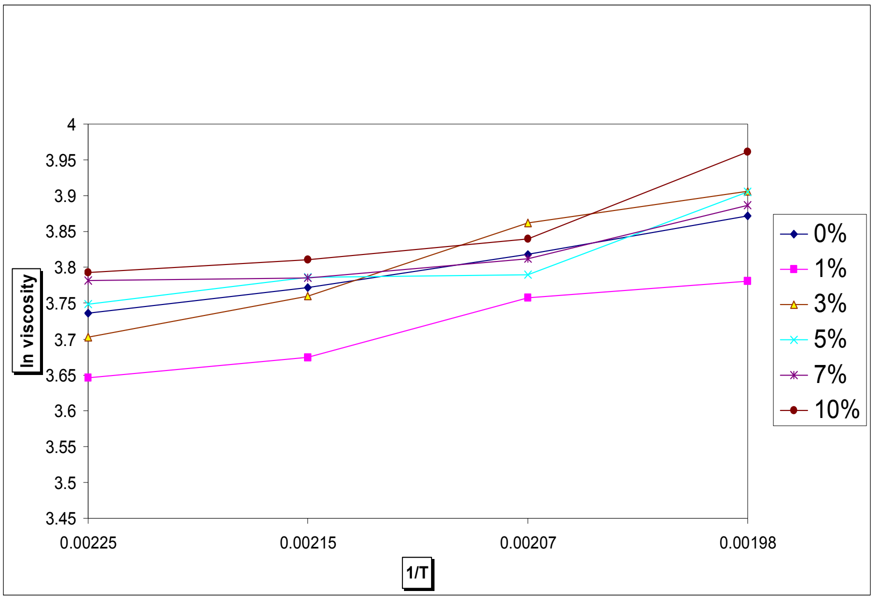


Fig. (10) The effect of absolute reciprocal temperature (170,190,210 and 230 ^{o}C) on the viscosity of LDPE-g-MAH/PAA blends at various percent of PAA when shear rate=6.19 s^{-1}

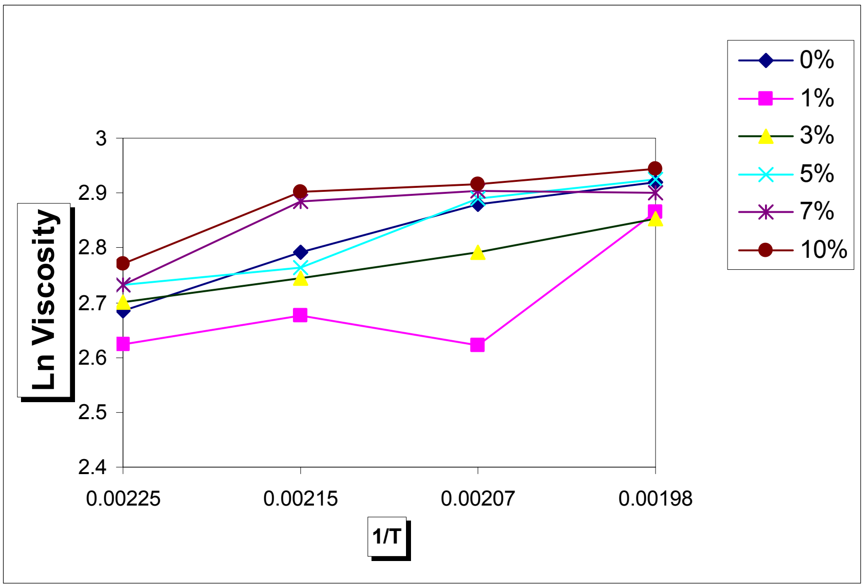


Fig. (11) The effect of absolute reciprocal temperature (170,190,210 and 230 ^{o}C) on the viscosity of LDPE-g-MAH/PAA blends at various percent of PAA when shear rate=20.6 s^{-1}

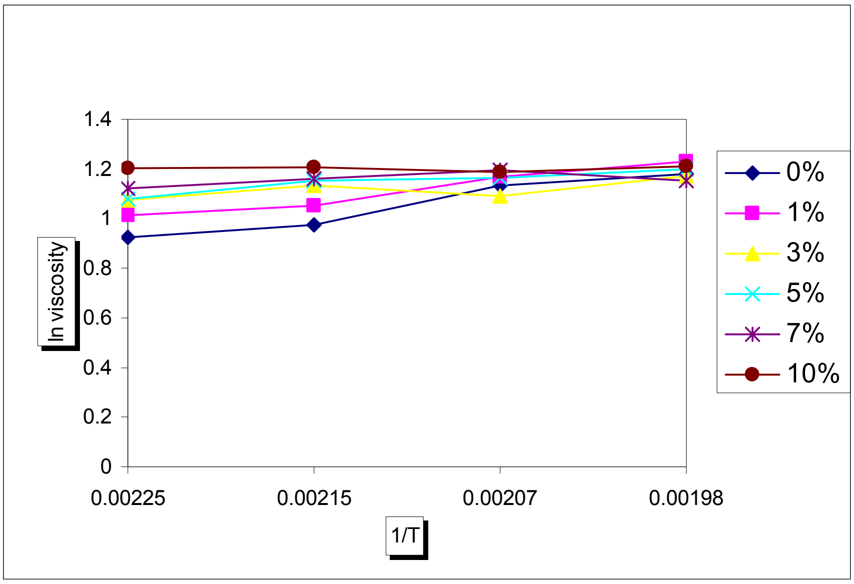


Fig. (12) The effect of absolute reciprocal temperature (170,190,210 and 230 °C) on the viscosity of LDPE-g-MAH/PAA blends at various percent of PAA when shear rate=206.4 s^{-1}

From fig. (13) we can see that the increase in PAA content decreases the activation energy of the LDPE-g-MAH/PAA formulation at shear rate(6.19, 20.6 and 206.4 s^{-1}) and cross head speed 0.06, 0.2 and 2 cm/min), the same results was reported by Mousa [13] for PVC/NBR and also George and Joseph [14] when studied blend of SBR/NR .

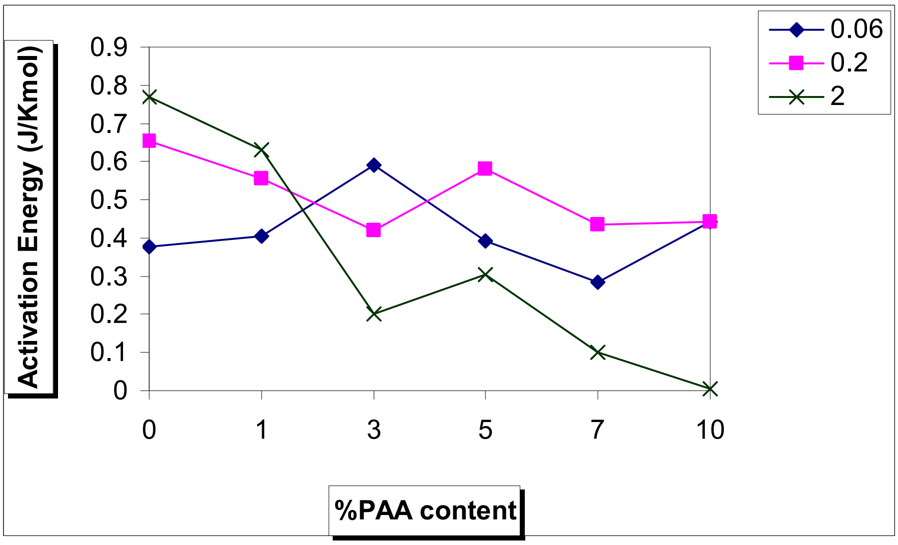


Fig. (13) The effect PAA content on the activation energy of LDPE-g-MAH/PAA blends at 0.06, 0.2 and 2 cm/min cross head speed and shear rate 6.19, 20.6 and 206.4 s^{-1}.

Dieswell:

The die swell is an important parameter for determining the size of extrudate polymer product that lead to measurement of this behavior become widely recognized in the plastics industries as an important indication of polymer process ability [15]. Fig. (14) and (15) shown the effect of wt% PAA on the die swell of LDPE-g-MAH/PAA blends at cross head speed (0.06,0.2,0.6,2,6 and 20 cm/min) at 210 and 230 °C ,all curves appears increases in %PAA was few affective on the die swell for blends, also we can see decreasing in die swell slightly specially at temperature 230 °C, may be the increase of network produces a restraint of the both polymer chains movement due to hydrogen and chemical bonding occur ,and in this case , the chains polymers of the blends orientation increase that lead to decreasing in swelling ratio of blends.

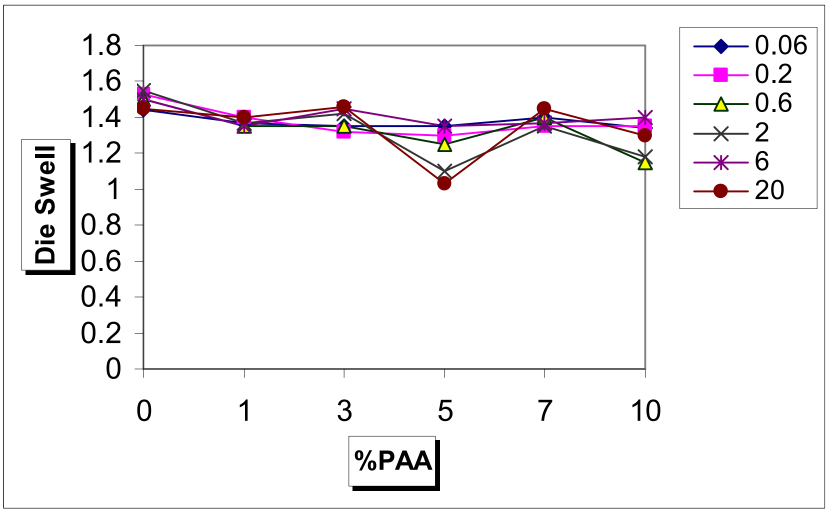


Fig.(14) show effect percentage weight of PAA on die swell at cross head speed (0.06,0.2,0.6,2.0,6.0 and 20.0 cm/min) and 210 °C

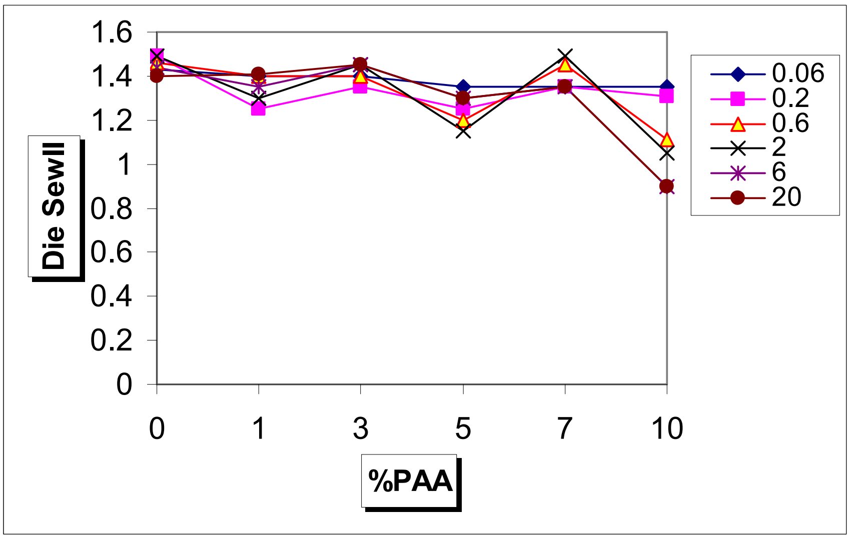


Fig.(15) show effect percentage weight of PAA on die swell at cross head speed (0.06,0.2,0.6,2.0,6.0 and 20.0 cm/min) and 230 °C

Conclution:

From this study, the maleic anhydride grafted on LDPE promoted interaction and enhancement of compatibility between LDPE and PAA in spite of different polymers in polarity the FTIR shown interface the functional group peaks in both polymers in the blends (LDPE-g-MAH/PAA). All curves that drew among rheological data, shear stress, shear rate and melt viscosity exhibited pseudoplastic behavior. When increasing the weight ratio of PAA in the blends increased the shear stress, viscosity and reduce the die swell besides activation energy.

Increasing PAA content in the blend caused restrict chain mobility or movement due to interaction maleic anhydride on LDPE and PAA groups, that lead to increase the activation energy at lower shear rate especially at 3% PAA, but by increasing shear rate that interaction will be disjointed that causes decreasing in activation energy.

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