Rheological Study of MALDPE/PAA Blend

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Abstract

The effect of polyacryclic acid (PAA) on rheological properties of maleated low density polyethylene (MALDPE) was studied. The presence of maleic anhydride (MAH) on the LDPE backbone increase the interface interaction via chemical or physical interactions between the polymers in the blend.FTIR spectroscopy of the MALDPE, PAA and MALDPE/PAA shows new peak shifted to lower frequency. The shear stress, shear rate, apparent viscosity and swelling ratio were evaluated using Instron capillary Rheometer. For all samples the rhological properties measured at 170°C and various cross head speed. The results showed increasing shear stress and decreasing apparent viscosity when shear rate increase. At higher PAA weight content the die swell for all blends reduced.

الخلاصة

%7 %5 %3 %0)

(%10   .

170   . (   )

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Introduction

Few polymer pairs form miscible blends.. Most polymers, however, are immiscible. But immiscibility is not always a bad thing. Blends do not have to be miscible to be useful. The key to make successful blends of this kind is the use of compatibilization or functional group to control morphology. A required reactive group can be incorporated into a polymer by incorporation into the backbone, side chain, and at chain ends as a usual result of polymerization; and chemical modification of a preformed polymer through a variety of chemical reactions[1].The chemical modification of polymers may be carried out in solution[2], in the melt[3], or even in the solid state[4]. However, the modification of polymers during a melt processing step has several advantages and is increasing rapidly. First of all, a solution process is eliminated, thus reducing costs associated with solvent removal, recovery, and losses. Secondly, melt processing reduces the likelihood of contamination of final products. Various chemical reactions have been used in chemically modifying preformed polymers, like free radical catalyzed grafting of maleic anhydride (MAH)[5], acrylic acid (AA)[6]...etc, onto a variety of polymers, It has been found that the addition functional group to non-polar polymer can improve the properties of immiscible polymer blends (polar/nonpolar polymer), because these modifiers are able to enhance the interaction between the material components[7]. Attention has been given to the influence of the dispersion state on the reological properties of blends produced by reactive extrusion, using compatibilizers or functional chemical groups grafted onto one of the components of the blend. A different approach to compatibilization of polymer blends is through ionic bonding instead of covalent bonding hence, polymers contain potentially reactive groups inherent in their side chains and improve blend properties.e.g. Carboxylic acid in poly (acrylic acid) and succinic group in maleated polyolefin.

In this paper, blend of MALDPE with low molecular weight polyacrylic acid PAA was prepared, the weight ratio of PAA was (0%,3%,5%,7% and 10%) on MALDPE . the effect of this ratio on the rheological properties of MALDPE (Shear Stress, Shear Rate, Viscosity and Die Swell) was studied .

Experimental

1- Materials :

Maleated low density polyethylene (MALDPE)prepared in the melt[8] with the following specifications, maleic anhydride(%MAH)=9.8, MFI=1.578 gm/10min , Density=0.9237 gm/cm^3.Acrylic acid was supplied by BDH company and polymerized to Low molecular weight polyacrylic acid(viscosity average molecular weight (M_v)=11370-11376) g/mol .

2- Preparation of Blends:

The blends were prepared in mixer-600 attached to Haake Rheocord Torque Rheometer with a speed of 32 rpm at temp. 165 ^{o}C .MALDPE was melted for 3 min.(0%,3%,5%,7% and 10%) PAA was added in four portion in total time of 10 min.. The blends compressed by compression molding in a hydraulic press at 175 ^{o}C under 5 ton for 3 min , then the pressure raise to 15 for 9 min. . The blends were cut into a small pellets (average length 2x2cm) by a cutter. Thin film with thickness 0.5mm was prepared

by compressed molded pellets for Fourier transform infrared (FT-IR) characterization .

3- Rheology measurements:

Melt rheological properties of the prepared blends were evaluated using an Instron capillary Rheometer machine at constant plunger speeds 0.06 , 0.2 , 0.6 , 2.0 , 6.0 cm/min according to ASTM D3835.The capillary barrel diameter was 1.257mm , capillary length to diameter L/D ratio 80/9 , load weighing was constant 1000 Kg .Shear Stress τ_w , Shear Rate γ_w and apparent Viscosity $\acute{\eta}_a$ were calculated using the standard methods[9a,b] .

The wall shear stress was calculated using the following equations:

$$\text{Wall shear stress } (\tau_w) = \frac{\Delta P}{2L} \times r \qquad \ldots (1)$$

Where ΔP = pressure applied along the capillary tube

L = length of the capillary tube

$r = \dfrac{dc}{22}$, where dc = radius of the cylinder

$$\tau_w = \frac{\Delta P}{2L} \times \frac{dc}{2}$$

$$\tau_w = \frac{\Delta P}{4} \frac{dc}{L} \qquad \ldots (2)$$

The force applied on the piston F is :

$$F = Ap . \Delta P \qquad \ldots (3)$$

Where Ap is the area of the piston = 0.7126 cm^2

$$\Delta P = \frac{F}{0.7126} \qquad \ldots (4)$$

substitution of equation (4) in equation (2) get

$$\tau_w = 0..351 \text{ x F x } \frac{dc}{L} \qquad \ldots (5)$$

For force in Kg

$$\tau_w = 0.351 \text{ x } 9.806 \text{ x } 10^5 . \text{ F x } \frac{dc}{L}$$

$$\tau_w = 3.44 \text{ x } 10^5 \text{ x F x } \frac{dc}{L} \qquad \ldots (6)$$

equation (6) was used to calculate the wall shear stress (τ_w).

The shear rate (γ) for Newtonian fluid was calculated from the equations :

$$\gamma = \frac{8V}{dc} \qquad \ldots (7)$$

where v is the speed of flowed fluid through the capillary tube :

$$v = \frac{V_{XH}}{60}\left(\frac{d_b}{d_c}\right)^2 \qquad \ldots (8)$$

where V_{XH} is the speed of the piston in cm min^{-1}, db = diameter of the cylinder.

$$\gamma_w = \frac{2}{15}V_{XH}\frac{d_b^2}{d_c^3} \qquad \ldots (9)$$

In the case of non Newtonians fluid the Rabinowich correction was used :

$$\gamma_w = \frac{3\eta^- + 1}{4\eta^-}\left(\frac{8V}{dc}\right) \qquad \ldots (10)$$

where η^- was the slope of line plotted between ln τ_w against ln $(\frac{8V}{dc})$.

From equation (7) and (9), substitution in equation (10) we get :

$$\gamma_w = \frac{2}{15}\frac{3\eta^- + 1}{4\eta^-}V_{XH}\frac{d_b^2}{d_c^3} \qquad \ldots (11)$$

equation (11) was used to calculate the wall shear rate.

The apparent viscosity (η_a) was calculated from the equation :

$$\eta_a = \frac{\tau_w}{\gamma_w} \qquad \ldots (12)$$

Results and Discussion

1- Characterization :

FTIR spectroscopy for the grafted LDPE samples after removing of non-reacted monomer, initiator and homopolymer (poly maleic anhydride) spectra were recorded on a Shimadzu FTIR-8400S spectrophotometer , from 4000 to 500 cm^{-1} and PAA and MALDPE/PAA blends .The FTIR spectrum of the grafted MALDPE (Fig 1) showed two absorption bands in the carbonyl region(1899and1787 cm^{-1}) for asymmetrical and symmetrical, respectively, which correspond to stretching of C=O in maleic anhydride

group on MALDPE[10]. The bands at 1712 cm^{-1} belong to the C=O of maleic acid .The FTIR spectrum for PAA (Fig 2) shows tow assignment types of vibrations , the first one at about 1728 cm^{-1} due to carbonyl group while the second one at about 1288 cm^{-1} due to C-O vibration .in addition small band at 1629 cm^{-1} may be correspond to unsaturated double bond in polymer chains. Chemical reaction and physical interaction takes place between the two polymers, the chemical reaction including the breaking of C-O-C (in cyclic group) bond and forming of new bonds as suggested in scheme 1.
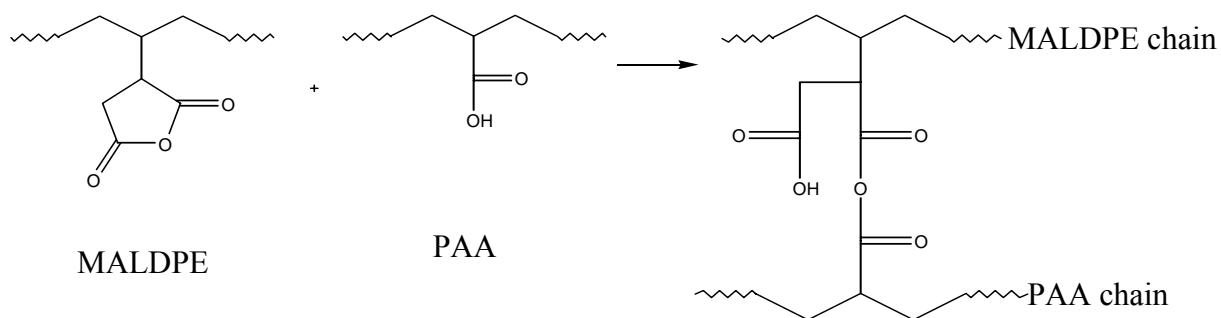
Scheme (1)

That is shown clearly in spectrum of blend product (Fig 3) , the absence of symmetrical vibration of carbonyl group in succinic group at 1787 cm^{-1} in addition of the formation of a new C-CO-O-CO-C bond at a lower frequencies (less rigidity from C-CO-O-CO-C in cyclic anhydride). At 1078 cm^{-1} and 1299 cm^{-1} bands.

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The FTIR spectrum give an evidence that the physical interaction between the polymers MALDPE and PAA, the Vander waals forces in the blend product caused very small shifts to low frequencies the vibrations of assignment bond carbonyl bond and C-O bonds see scheme 2(A and B)
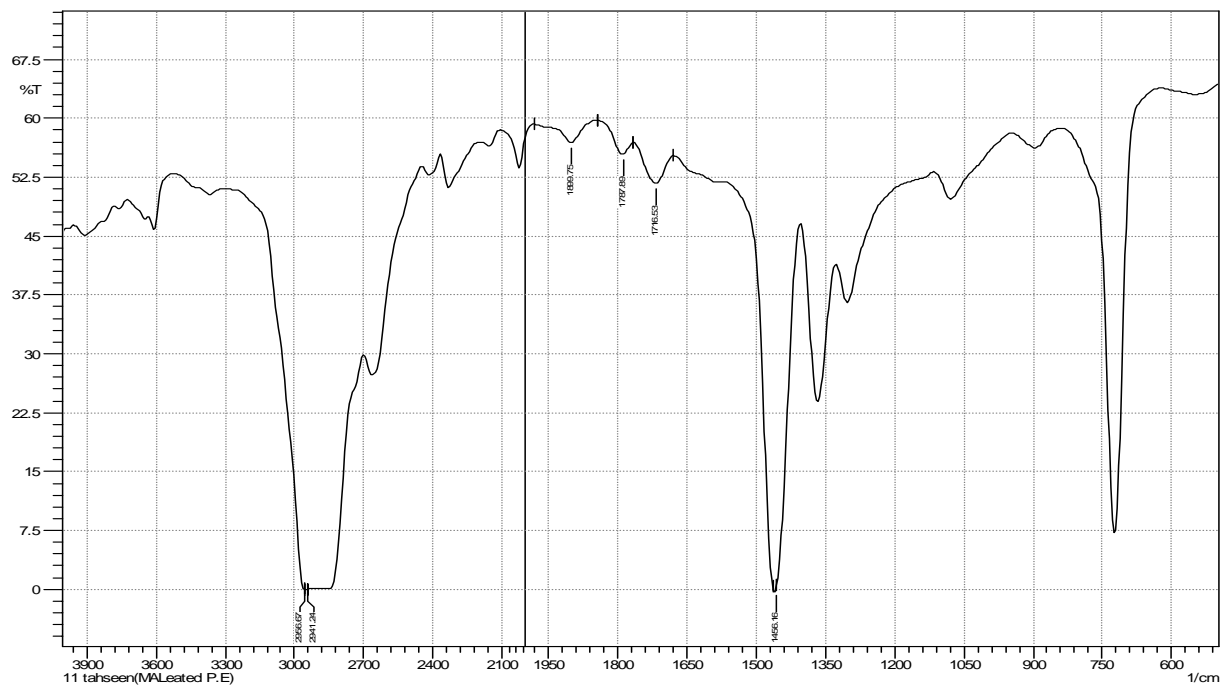
(A)   (B)
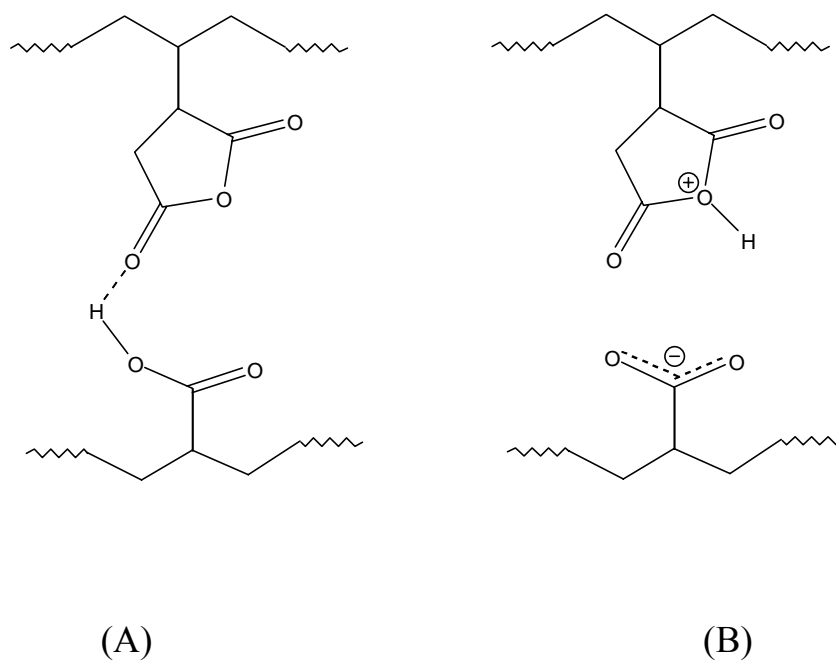
Scheme(2)

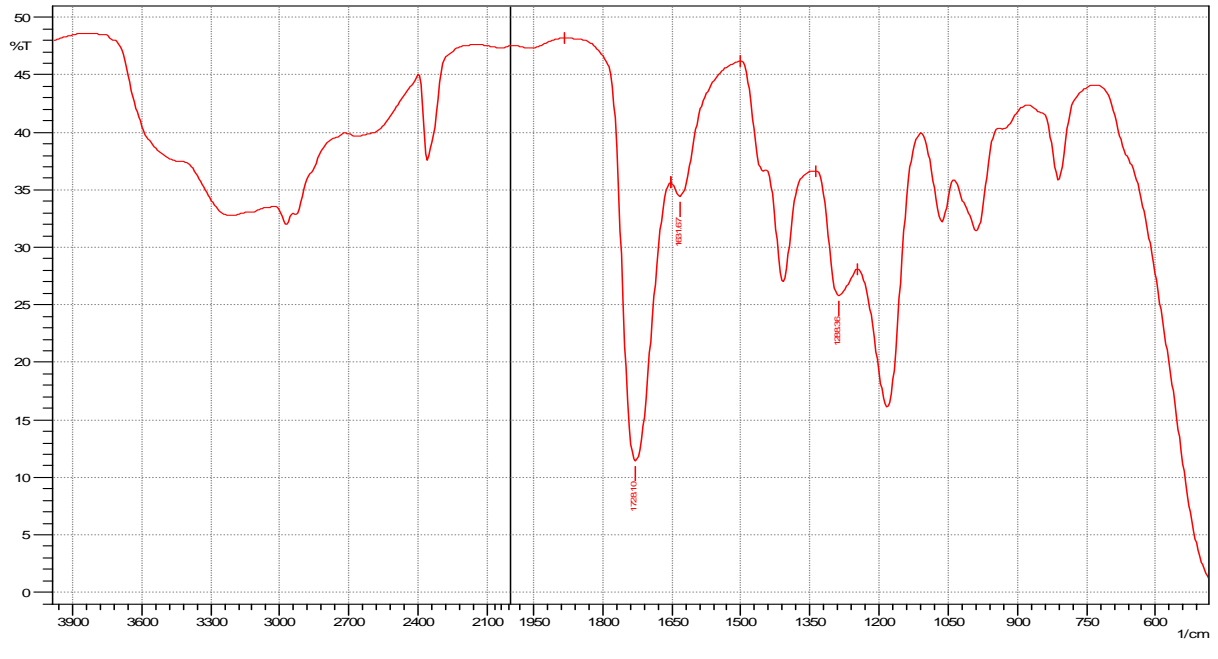**Fig (1) The FT-IR for maleated LDPE (MALDPE)**

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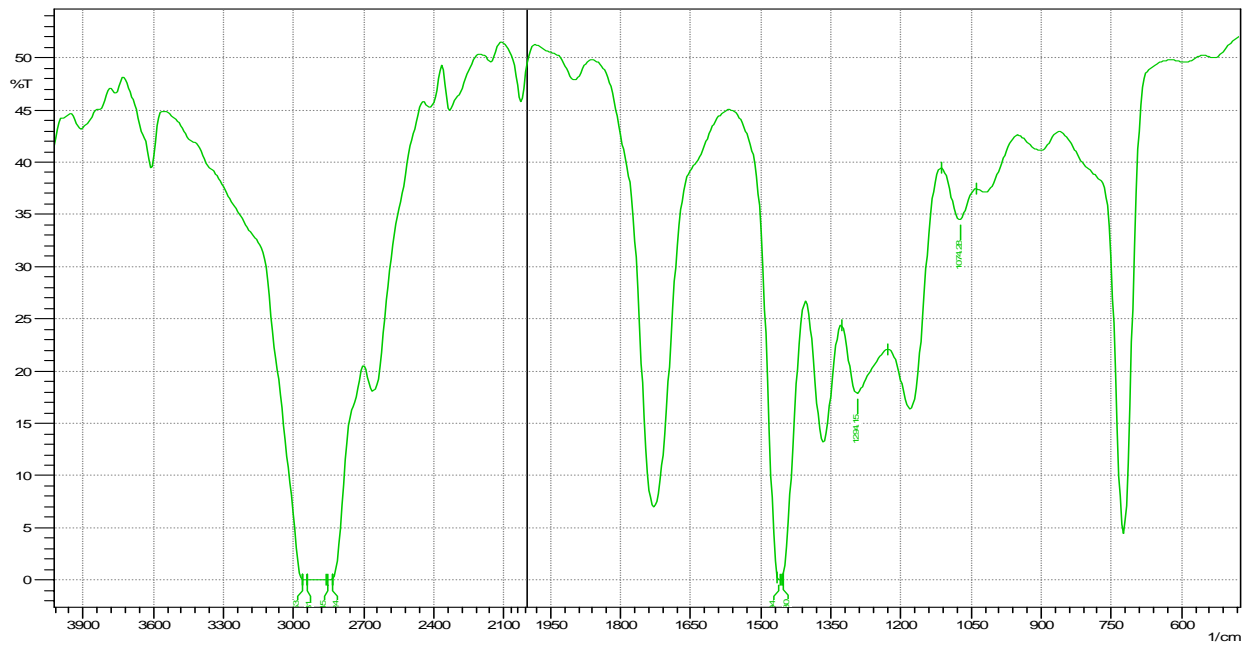Fig (2) The FT-IR for polyacrylic acid (PAA)

Fig (3) The FT-IR for MALDPE/PAA (90/10)blend

2-Rheology Results:

The morphology of an immiscible polymer blend is closely related to its rheology .Therefore , the rheological properties of the blend components have been studied here .

The data for the shear stress and the apparent viscosity as a function of shear rate are shown in Figures (4)and (5), respectively. As observed from Figures (4)and (5), with increasing shear rate, the apparent viscosity of the blends evidenced a declining trend, which indicated that the force required to flow the blends melt was increased due to the chemical reaction and intermolecular bonds (hydrogen bonding) 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.
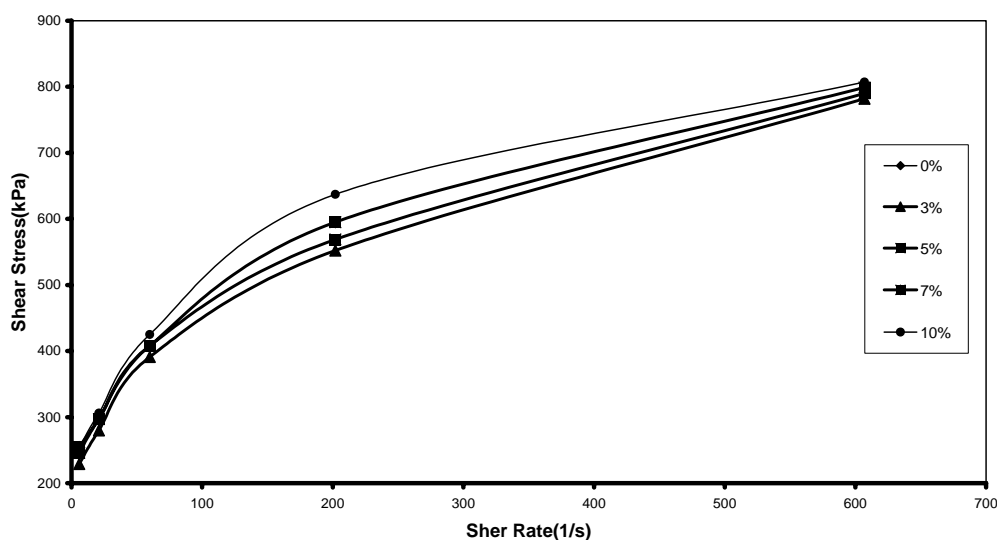
Fig(4) Shear Stress and Shear Rate curves of MALDPE/PAA blends measured at 170°C
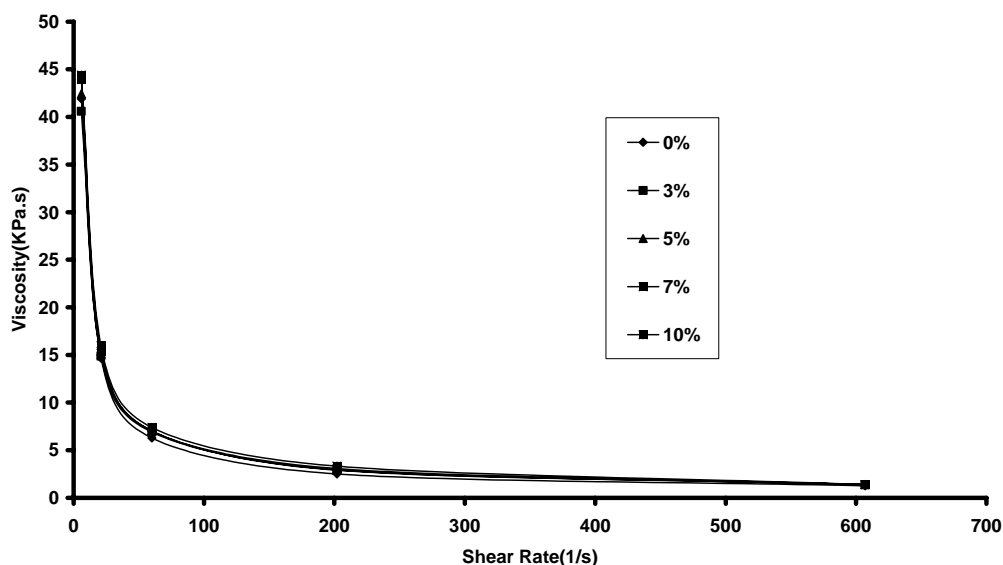
Fig(5) Plots of apparent viscosity versus shear rate for blends at 170°C

From Table (1) for 3%PAA in MALDPE the viscosity at speed 0.06 cm/min decreased firstly indicating that the PAA act as processing aid due to insufficient interaction between the two polymers , then increasing for all ratio PAA(>3%), the interaction between the two polymers take place and the force needed to flow the polymers will be high as shown in increasing the viscosities and reach its maximum (10% of PAA) and cross head speed (0.06). Increasing the cross head speed will compress higher force on the polymer blend that can reduce the effect of polymers interaction and causes the polymers to flow with reducing the viscosity of the blend.

Table (1) The relation between Viscosity of MALDPE/PAA blends and PAA % content at crosshead speed (0.06,0.2,0.6,2.0 and 6.0 cm/min) at 170°C

ή at 6.0	ή at 2.0	ή at 0.6	ή at 0.2	ή at 0.06	PAA % content
1.258	2.517	6.294	14.687	41.969	0
1.382	2.930	6.913	14.880	40.584	3
1.362	2.944	7.030	15.379	42.479	5
1.376	3.074	7.028	15.374	43.928	7
1.405	3.329	7.399	15.982	44.4031	10

The tendency of thermoplastic polymer to enlarge when emerging from an extruder die is called *Die Swell* [11]. Die swell normally refers to the ratio of extruded size to die size.

This behavior is a measure of the relative elasticity in the flowing polymer stream. Fig(6) shows the relationship between Die Swell with weight ratio content of PAA . All curves revealed reduced in the die swell with increasing the percentage ratio of PAA .the interaction between the two polymers will increase the chain entanglement which resist the polymers chain to returned its past shape.
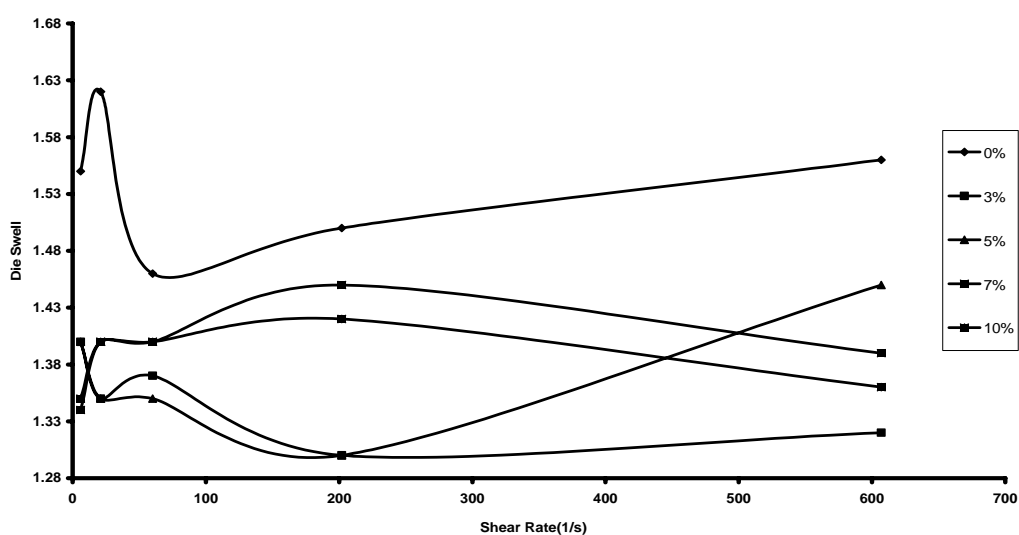
Fig(6)The effect of PAA content (wt%) on the Die Swell of the MALDPE/PAA blends at 170°C

Conclusion

Rheological measurement was carried out using a capillary rheometer. From the apparent viscosity data of the blend (MALDPE/PAA) with shear rates. The blend characterized a pseudoplastic behavior in the flow for all % ranges of PAA in the blends was observed . That is, the apparent viscosity decreased and shear stress increased with increased shear rate, while increasing % PAA the Die Swell for all blends decrease. From FT-IR figures the maleic anhydride bands shifted to lower wave length and disappear absorption peak at 1778 cm^{-1} for symmetrical C=O anhydride .

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