

Comparative Study of Some Properties of Two Groups' Binary Polymer Blends Prepared By a Twin-Screw Extruder

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Abstract:

In this paper, the preparation and compare of some mechanical and physical properties of two groups of polymer blends consisting of polyvinyl chloride with polypropylene (PP-PVC) and poly-vinyl chloride with high-density polyethylene (HDPE-PVC). Using a twin-screw extruder, three weight percentages of PP and HDPE (5, 10 and 15%) were used to prepare the polymer blends. Experimental investigation was carried out for analyzing the mechanical properties like tensile strength, flexural strength, compression, impact, and hardness and physical properties (thermal characteristics and melt flow index) for the polymer blend samples. The results show that the polymer blend (HDPE-PVC) get higher values than polymer blend (PP-PVC) in fracture strength, young's modulus, elongation, flexural strength, creep resistant and maximum shear stress and thermal characteristics, whereas the polymer blends (PP-PVC) get higher values in impact strength, fracture toughness, hardness and compression and melt flow index. Besides, the increment in PP or HDPE content weak the properties of the polymer blends and the samples with (5%PP:95%PVC) and (5%HDPE:95%PVC) were the best among the other polymer blends samples.

Keywords: Mechanical Properties, PVC, PP, HDPE, Extruding and polymer blend

دراسة مقارنة لبعض الخصائص لمجموعتين من الخلائط البوليمرية الثنائية المحضرة بواسطة باثقة ثنائية اللولب

الخلاصة

تم في هذا البحث تحضير ومقارنة بعض الخواص الميكانيكية والفيزيائية لمجموعتين من الخلائط بوليمرية المتكون من البولي فاينيل كلورايد مع البولي بروبيلين (PP-PVC) والبولي فاينيل كلورايد مع البولي اثيلين عالي الكثافة (HDPE-PVC). وباستخدام الباثقة ثنائية اللولب , حضرت الخلائط بوليمرية باستخدام ثلاثة نسب وزنية لكل من البولي بروبيلين و البولي اثيلين عالي الكثافة (5 و 10 و 15). وقد تم اجراء التحري التجريبي لتحليل الخواص الميكانيكية مثل مقاومة الشد ومقاومة الانحناء والانضغاط والصدمة والصلادة والخواص الفيزيائية لنماذج الخلائط البوليمرية. وقد بينت النتائج ان الخليط البوليميري (HDPE-PVC) حصل على اعلى

النتائج في مقاومة الكسر، معامل يونك، الاستطالة، متانة الالتواء، مقاومة الزحف واقصى إجهاد للقص و الخصائص الحرارية مقارنة مع الخليط البوليميري (PP-PVC). بينما الخليط البوليميري (PP-PVC) حصل على اعلى النتائج في مقاومة الصدمة، متانة الكسر، الصلابة، والانضغاط ومؤشر التدفق. وقد بينت النتائج ايضا ان زيادة محتوى PP او HDPE في الخليط البوليميري تؤدي الى اضعاف الخصائص الميكانيكية للخليط وان نسبة (5% PP:95% PVC) و (5% PVC:95% PVC) كانت الافضل بين العينات الاخرى للخليط البوليميري.

INTRODUCTION

Considerable research interest is focused on new polymeric materials obtained by blending two or more polymers [1]. The major feature of such a process is that the intermediate properties are in some cases better than those exhibited by either of the single components. In addition, some modification in terms of processing characteristics, durability, and cost can be achieved via polymer blending [2].

Poly (vinyl chloride) (PVC) is one of the most common commodity plastics, which has been widely used in the automobile, building construction, biomedical material, packaging fields, etc., because of its low cost, easy method of preparation, and the broadening of the properties range [3-4]. PVC is thermoplastic and due to its low thermal stability the use of PVC polymer is limited in industry. Several attempts have been made to enhance the thermal stability and mechanical properties of PVC in recent years [5-6]. Unmodified PVC polymer is a brittle, inflexible material with rather limited commercial possibilities. The processing of PVC in the raw form using heat and pressure resulted in severe degradation of the polymer [7-8].

Sombatsompop and Sungsanit [9] investigated the structural changes of polyvinyl chloride (PVC) in melt blends of a low-density polyethylene (LDPE) and polyvinyl chloride (PVC), the effects of (LDPE) content and number of extrusion passes. These effects were examined in terms of changes in weight average molecular weight (M_w) and number average molecular weight (M_n), polyene and carbonyl indices, color changes of the blend, and the variations in glass transition and decomposition temperatures. It was found that loading LDPE into PVC led to the formation of short-chain LDPE grafted PVC (*s*-LDPE-*g*-PVC) copolymers, via a macro-radical cross-recombination reaction, which had greater (M_w) with unchanged (M_n), increased decomposition temperature, lower glass transition temperature, as compared to the pure PVC sample.

Khang and Trung [10] prepared quaternary-polymer blends based on polyvinyl chloride (PVC), nitrile-butadiene rubber (NBR), natural rubber (NR) and polyethylene (PE). The mechanical properties of these blends in dependence of mixing time and temperature were characterized. The results showed that the two-step blending method, where PVC and NBR were first mixed together and then blended with NR and PE, is the best one to prepare blends with high mechanical properties.

Unar et.al, [11] studied the compounding of Polyvinylchloride (PVC) with some additives for the enhancement of physical and mechanical properties. Two categories of formulations (unplasticized and plasticized PVC) were prepared with PVC (K value - criteria of the chains polymer average length - ranging from 60 to 70) taking as base polymer. Different additives generally categorized as plasticizers, fillers, stabilizers, pigments and processing aids, were mixed in the standard concentration.

In this work, the mechanical properties of polyvinyl chloride-polypropylene (PVC-PP) blends were compared with that of poly(vinyl chloride)- high density

polyethylene (PVC-HDPE) blends prepared by a twin-screw extruder. The mechanical properties like tensile strength, flexural strength, compression, impact, hardness and physical properties i.e. thermal conductivity, thermal diffusivity and specific heat for the polymer blend samples were investigated.

Experimental

Materials

PVC, PP and HDPE used in this study were commercial products. PVC was the product of Bandar E mam Center (suspension type, K value = 70 Iran) and it is supplied by the General Company of Chemical Industries in Zafarania (Baghdad). Viscosity index and apparent density of PVC are 120 and $(0.44 - 0.48 \text{ g/cm}^3)$ respectively. The corresponding processing agents of PVC: dibasic lead phosphate (DLP) as stabilizer (1.5 phr) and stearic acid (SA) as lubricant (0.5 phr). Polypropylene (PP) was supplied from Sabic Company, Saudi Arabia, and has a trade name of "520 LPP", has melt flow rate of $(10\text{g}/10\text{min})$ and E-modulus (1600 N/mm^2) . High density polyethylene was produced from the General Company of Chemical Industries in Zafarania/ Baghdad. The trade name of the HDPE is "2200J/MITSUI" has melt flow rate of $(6 \text{ g}/10\text{min})$, density (0.968 g/cm^3) and tensile strength (41 MPa) .

Blend Preparation

The experiment was commenced by melt-blending PVC with PP and PVC with HDPE using a twin-screw extruder machine with a screw L/D of 30:1. The blending temperature profiles on the extruder for three zones (feed zone, compression zone and melting zone) are $175 \text{ }^\circ\text{C}$, $165 \text{ }^\circ\text{C}$ and $160 \text{ }^\circ\text{C}$ respectively with the screw speed 50 r.p.m.

The samples of polymer blends (PP-PVC) and (HDPE-PVC) were prepared according to the formula $(X\% \text{ PP} : Y\% \text{ PVC})$ and $(X\% \text{ HDPE} : Y\% \text{ PVC})$ with weight ratios selected for (X, Y) values $[(5, 95\%), (10, 90\%) \text{ and } (15, 85\%)]$. The prepared samples were going in four steps

- 1- Weighing: - particles of polymer materials were weighed according to the selected ratios to prepare the batches for extrusion.
- 2- Mixing: - for optimum distribution, the polymer in pellet and particle form respectively, were mixed together in dry condition at room temperature for 20 minutes by mill made of porcelain material.
- 3- Extrusion: - forming process was carried out using a (Twin screw extruder which is available in Materials Engineering Department / University of Technology. The mixed plastic component usually in form of granules was fed from a hopper on the screw. It's then conveyed along the barrel where it is heated by conduction from the barrel heaters and shear due to its movement along the screw flight. The depth of the screw channel is reduced along the length of the screw so as to compact the material.
- 4- Cutting: - plates with dimensions are $(500 \times 35 \times 4 \text{ mm})$ produced and have been prepared for cutting and mechanical machining by using electrical saw with very soft teeth to ensure that samples would not vibrate, deformed through processing, cutting was done according to international standard specifications for each test used.

Test Methods

Tensile tests: samples were cut according to ASTM D 638 [12]. The machine used for the testing of tensile properties is micro computer controlled electronic universal testing machine (model WDW 200 E) made in China. The test was conducted at velocity of (5 mm/min) at ambient temperature, tensile stress was applied till the failure of the sample and stress-strain curve was obtained. Each sample was tested 3 times and average results have been reported.

The modulus of elasticity was evaluated using the following equation:

$$\varepsilon = \frac{\sigma_y}{(L - L_o) / L_o} \quad \dots(1)$$

Where,

L is the length of sample at yield, L_o is the initial length. And σ_y is the stress at yield.

Flexural strength: bending behavior of the prepared sample was tested using a three point test instrument, (model WDW 200 E) made in China, this test is performed according to ASTM D-790-78 [12 and 13] at room temperature and after fixing the ends of the sample on the supports of the instrument, the load were increased gradually on at the middle of the sample with velocity (5mm/min) until the failure of the specimen occurred. Each sample was tested 3 times and average results have been reported. the value of fracture load (F) is read from the gage. The flexural strength (σ_{bend}) and flexural modulus and maximum shear stress (τ) are valued from the relationships (1-3) respectively.

$$\text{Flexural strength for three - point bend test} = \sigma_{\text{bend}} = \frac{3FL}{2wh^2} \quad \dots (2)$$

where F is the fracture load, L is the distance between the two outer points, w is the width of the specimen, and h is the thickness of the specimen.

$$\text{Flexural modulus} (E_f) = \frac{FL^3}{4\delta wh^3} = \frac{mL^3}{4wh^3} \quad \dots(3)$$

Where δ is the deflection of the beam when a force F is applied, m is the slope of the load (F) /deflection curve.

$$\text{Maximum shear stress} (\tau) = \frac{3F}{4wh} \quad \dots(4)$$

Compression test: the samples were prepared according to ASTM- D 695[13], depending on thickness of the sample. The test was conducted at velocity of (5mm/min) at ambient temperature. The machine for the testing of compression was made in China and it is model (WDW200E). The load was applied gradually to the

longitudinally fixed sample, the increasing of the load continued until the failure of the specimen occurred. Each sample was tested 3 times and average results have been reported.

Impact test: is performed at room temperature according to ASTM ISO 179[12], the impact test instrument model XJU-22, supplied from Time group Inc was used. Samples were used without notched point. Using izod method the sample was placed vertically, the testing method of this instrument includes lifting of pendulum to its maximums height and fixing it firmly where its potential energy would be changed to kinetic energy. Each sample was tested 3 times and average results have been reported. Impact strength: - can be calculated from the following relationship:-

$$G_c = \frac{U_c}{A} \quad \dots (5)$$

Where:-

G_c :- The impact strength of the material (J/m^2).

U_c :- The required energy for sample fracture (J).

A :- the cross sectional area of the sample (m^2).

Fracture toughness: - can be calculated as follows:-

$$K_c = \sqrt{G_c E_b} \quad \dots (6)$$

Where:-

K_c :- Fracture toughness of the sample (N/mm^2).

G_c :- Impact strength of the material (J/m^2).

E_b :- Young Modulus of the material (MPa).

Hardness test, it has been used (Shore D) hardness test to measure the hardness of the samples, and the used ones must have smooth, plain surface with thickness at least more than (3mm) and must not be exposed to mechanical vibrations so that the prepared sample has (10×10×4) mm. These dimensions were taken according to ASTM- D-2240[13]. Each sample was tested 5 times and average results have been reported.

Thermal properties test, thermal conductivity, thermal diffusivity as well as specific heat per unit volume were measured using Hot Disk Thermal Constants Analyzer. Each sample was tested 3 times and average results have been reported.

Morphology test, analytical Scanning Electron Microscope (SEM), model (Tescan VEGA-SB) made in Belgium available in Nanotechnology and Advanced Materials Research Center/ University of Technology is used to examine the morphology of polymer blends composites.

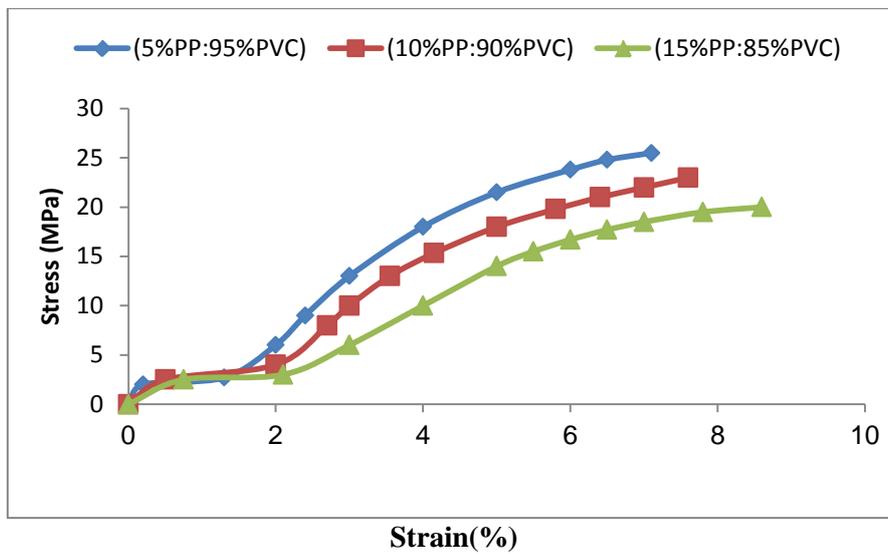
Results and Discussion

Mechanical properties

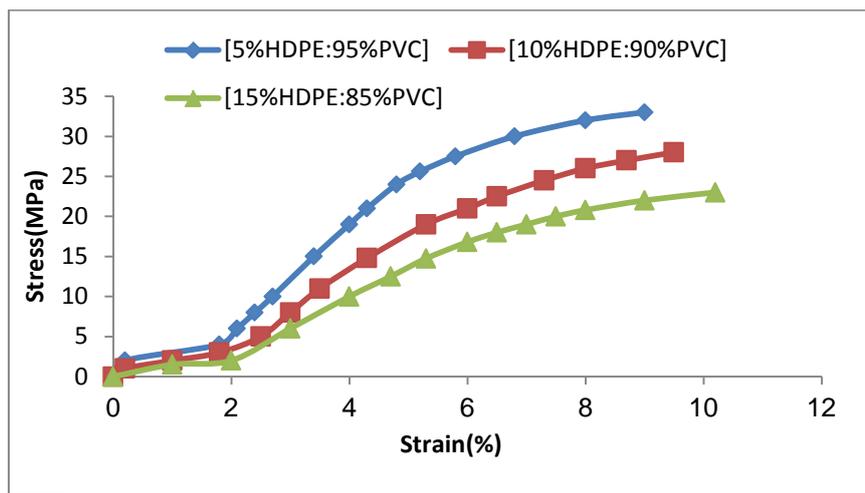
Figures (1) and (2) show the (stress –strain) curves of the first and second groups of polymers blends of (PP-PVC) and (HDPE-PVC) respectively which consists with different ratios by increasing the weight percentage of PP or HDPE (5%, 10% and 15%) in the blends. It has been observed from these figures nonsignificant difference in the behavior of (stress-strain) curves as ratios of PP or HDPE increased in the

prepared polymers blends. As well as it was shown from these curves at the beginning the behavior show elastic deformation then was changed into plastic deformation until to fracture. Also from Figure (1) shows that the sample of ratio (5%PP:95%PVC) of the first group bear maximum stress at fracture and less elongation as compared to samples of other ratios. This ratio could bear stress (25.5MPa) with an elongation (7.1%). On the other hand, samples of other ratios for this group bear low stresses.

As well as from Figure (2) show the sample of ratio (5%HDPE: 95%PVC) of the second group bear maximum stress and less elongation as compared to samples of other ratios. This ratio could bear stress (33MPa) with an elongation (9%).

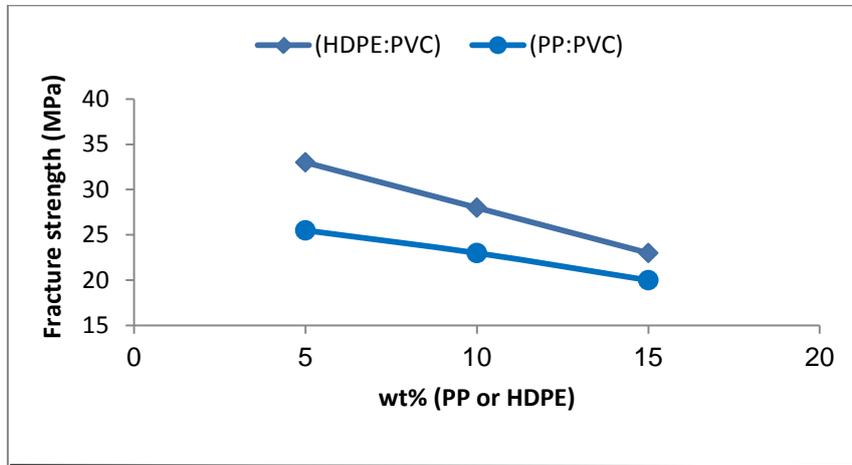


Figure(1): Stress-strain curve of the polymer blend (PP-PVC).

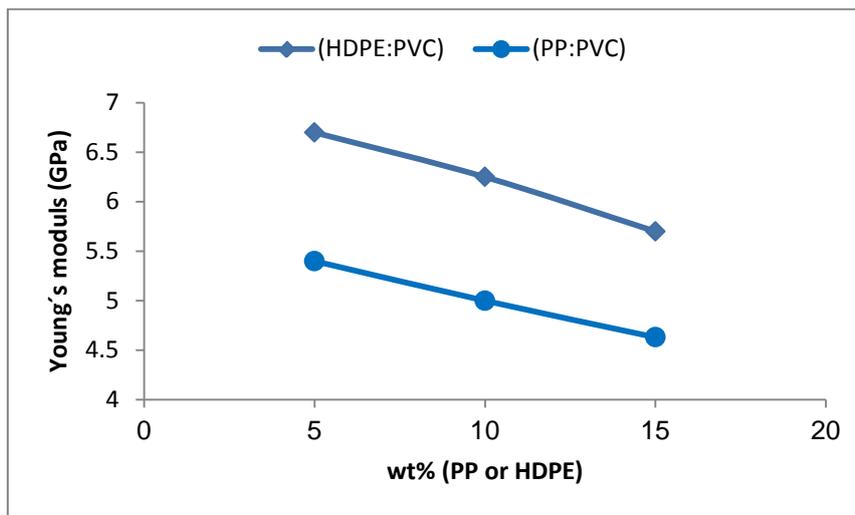


Figure(2): Stress-strain curve of the polymer blend (HDPE-PVC).

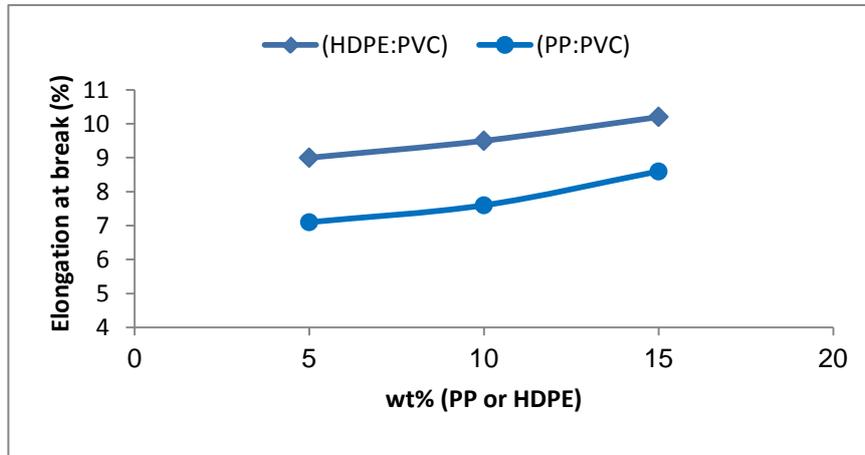
The fracture strength, young's modulus and elongation at break for these samples are shown in Figures (3, 4 and 5) respectively. It was noticed from these figures that the polymer blend (HDPE-PVC) get higher values for the above properties as compared with the polymer blend (PP-PVC) due to HDPE having higher crystallinity than PP and can be observed the addition of PP or HDPE to PVC of polymers blends reduction the fracture strength and young's modulus values whereas the elongation at break increase with increased ratios of PP or HDPE in the blend for both groups, that is refer to the nature of microstructure for PVC due to the presence of the large negative chlorine atom on every other carbon atom of the main chain of polyvinyl chloride cause some steric hindrance and electrostatic repulsion, which reduces the flexibility of the polymer chains as compared to the methyl group on every second carbon atoms of the polymer main chain, whereas high density polyethylene, in contrast has the chains can pack more closely together to increase strength^[12].



Figure(3): Fracture strength for the polymer blends (PP-PVC) and (HDPE-PVC) as a function of (PP) or (HDPE) content in blend.

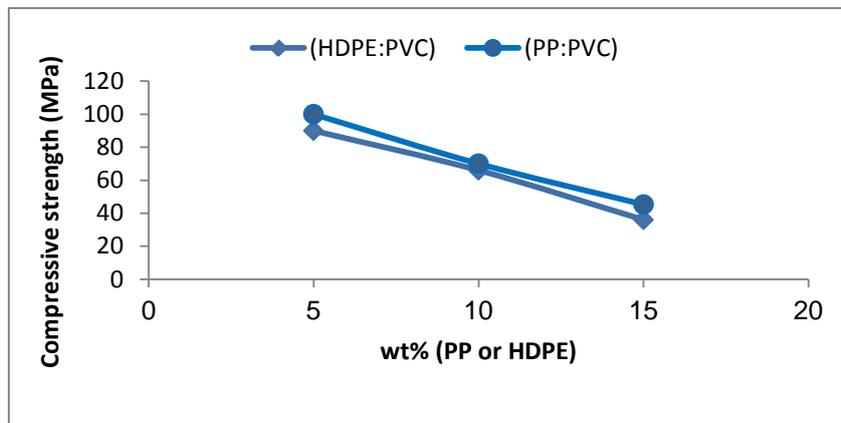


Figure(4): Young's modulus for the polymer blends (PP-PVC) and (HDPE-PVC) as a function of (PP) or (HDPE) content in blend.



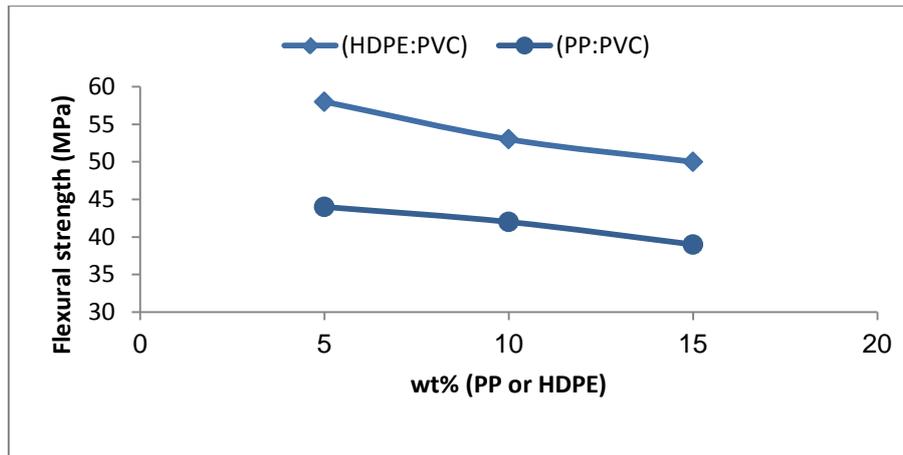
Figure(5): Elongation at break for the polymer blends (PP-PVC) and (HDPE-PVC) as a function of (PP) or (HDPE) content in blend.

From the results of stress-strain curves for compression test of the two main groups of prepared polymers blend (PP-PVC) and (HDPE-PVC), it was noticed from figure (6) that the compressive strength of the two groups of polymers blend decreases with increasing of PP or HDPE content in blend, and the compressive strength of the polymers blend (PP-PVC) samples were higher as compared with their counterparts of the other group (HDPE-PVC) polymer blend samples and this is related to the chemical structure of PVC chain, the presence of the large chlorine atom on every other carbon atom of the main chain, and this is cause of PVC is a fairly rigid polymer, so the addition of another polymer having less flexible structure like PP and HDPE, so the producer polymer blend have less flexible strength compare to PVC alone. As well as the samples of polymer blends (PP-PVC) have the higher values compressive strength as compared with their counterparts of (HDPE-PVC) polymer blend samples. That is referring to the high crystallinity and molecular weight of HDPE as compare to the chemical structure of PP which have a methyl group on every second carbon atom of the polymer main chain producing less flexible material [12,14].

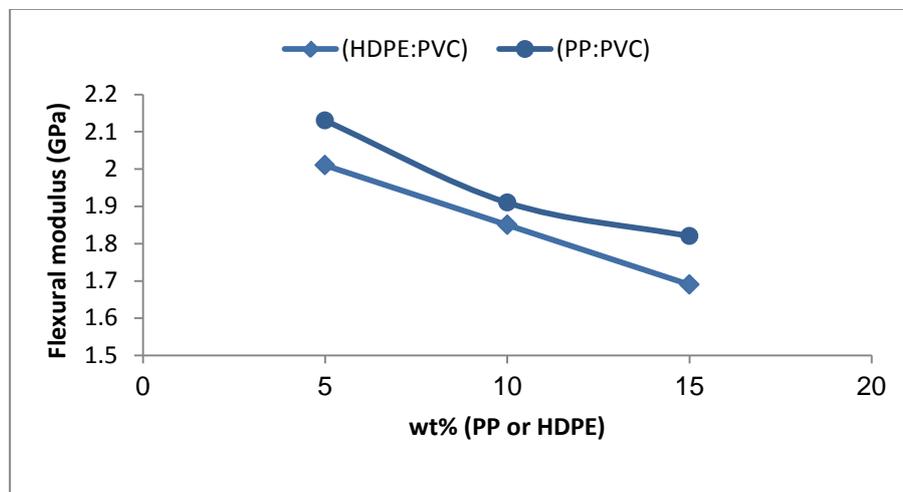


Figure(6): Compressive strength for the polymers blends (PP-PVC) and (HDPE-PVC) as a function of PP or HDPE content in blends.

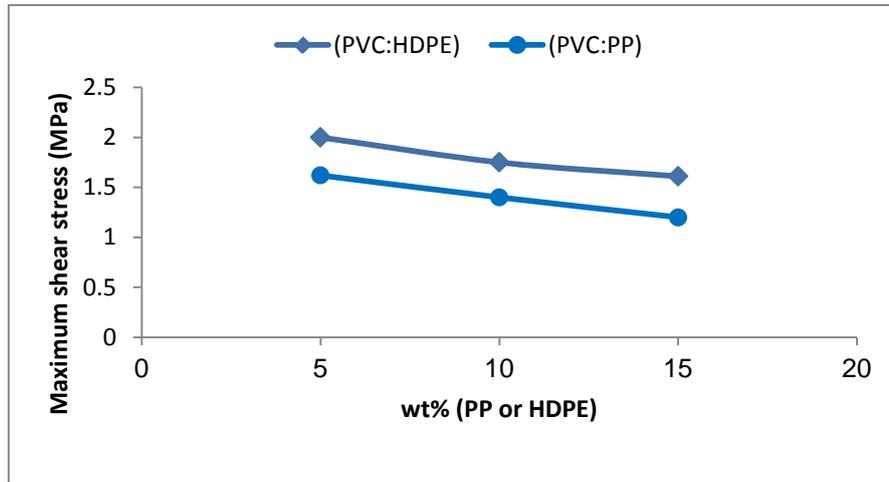
From figures (7, 8 and 9) it was noticed that the addition of PP or HDPE to the base polymers blend (PP-PVC and HDPE-PVC) decrease the flexural strength (σ_{bend}), flexible modulus (E_f) and maximum shear stress respectively, and this it is related to the chemical structure of PVC, PP and HDPE as mentioned earlier in compression test.



Figure(7): Flexural strength for the polymer blends (PP-PVC) and (HDPE-PVC) as a function of (PP) or (HDPE) content in blend.

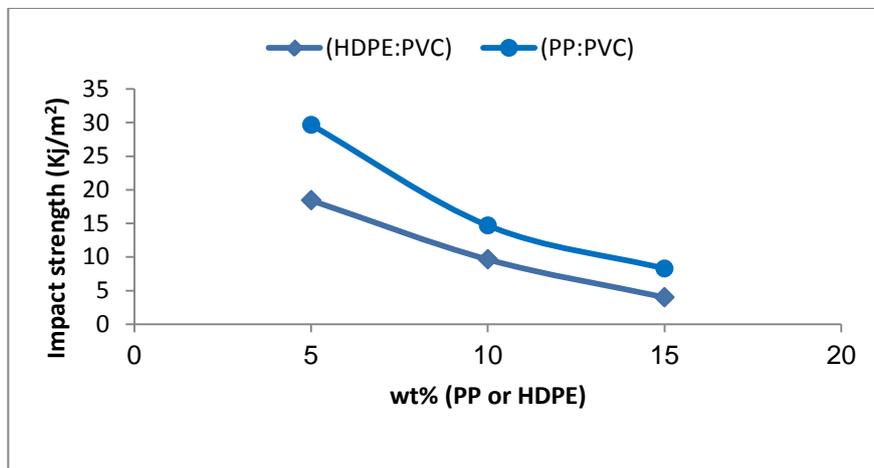


Figure(8): Flexural modulus for the polymer blends (PP-PVC) and (HDPE-PVC) as a function of (PP) or (HDPE) content in blend.

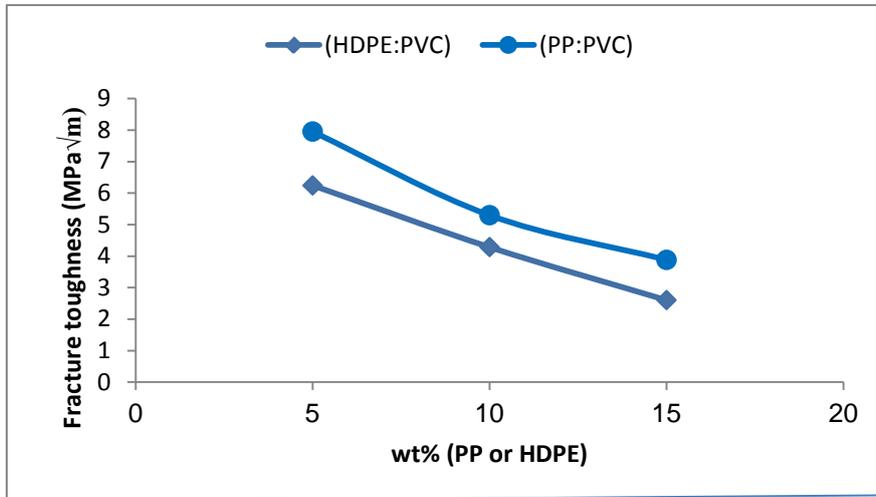


Figure(9): Maximum shear stress for the polymer blends (PP-PVC) and (HDPE-PVC) as a function of (PP) or (HDPE) content in blend.

From figures (10 and 11) it was noticed that the impact strength and fracture toughness respectively of the base polymers blends (PP-PVC) and (HDPE-PVC) decrease with the increasing of PP or HDPE content in blends, as well as the impact strength and fracture toughness of the polymer blend (PP-PVC) is higher than the polymer blend (HDPE-PVC) this is refer to the flexibility of polymer blend (PP-PVC) (figure 8) making it more shock absorption and In addition to the reasons that mentioned earlier in the tensile test results.

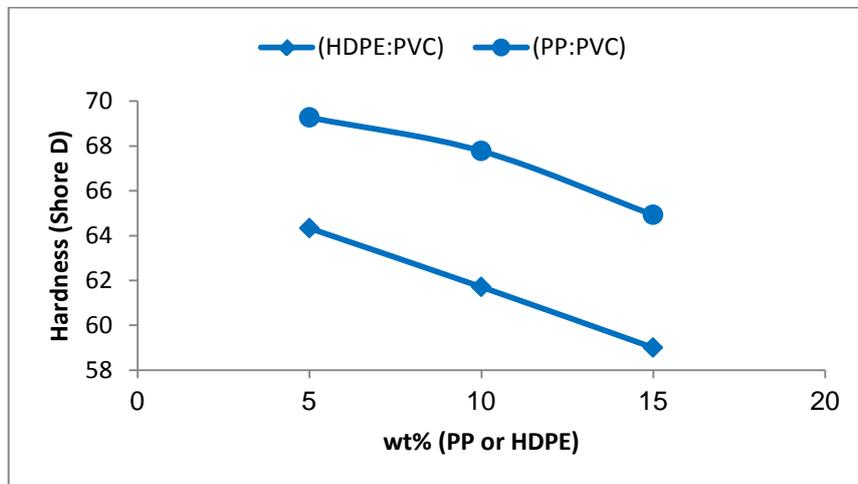


Figure(10): Impact strength for the polymer blends (PP-PVC) and (HDPE-PVC) as a function of (PP) or (HDPE) content in blend.



Figure(11): Fracture toughness for the polymer blends (PP-PVC) and (HDPE-PVC) as a function of (PP) or (HDPE) content in blend.

Hardness (Shore D) was taken for the base polymers blends (PP-PVC) and (HDPE-PVC), the results are shown in figure (12) it was noticed from this figure that the hardness for the both groups polymers blends was decreased with the increasing of PP or HDPE content in blends, as well as the values for the polymer blend samples (PP-PVC) were higher than its counterparts of the samples polymer blend (HDPE-PVC).



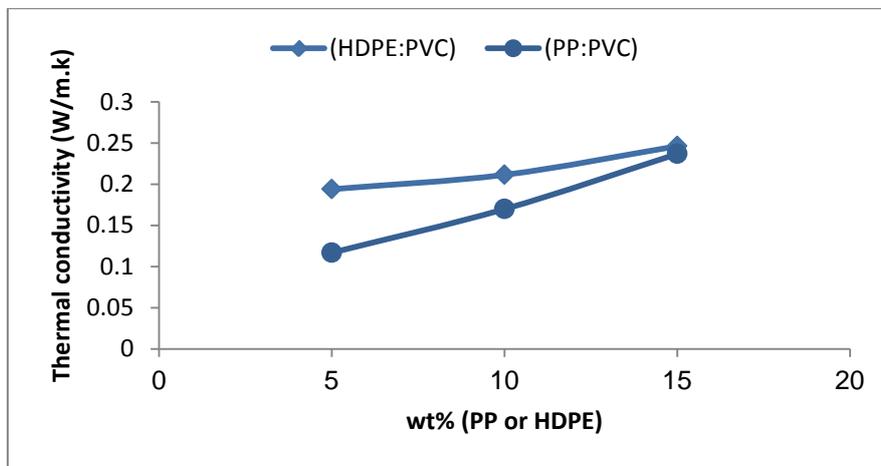
Figure(12): Hardness for the polymer blends (PP-PVC) and (HDPE-PVC) as a function of (PP) or (HDPE) content in blend.

Thermal Properties

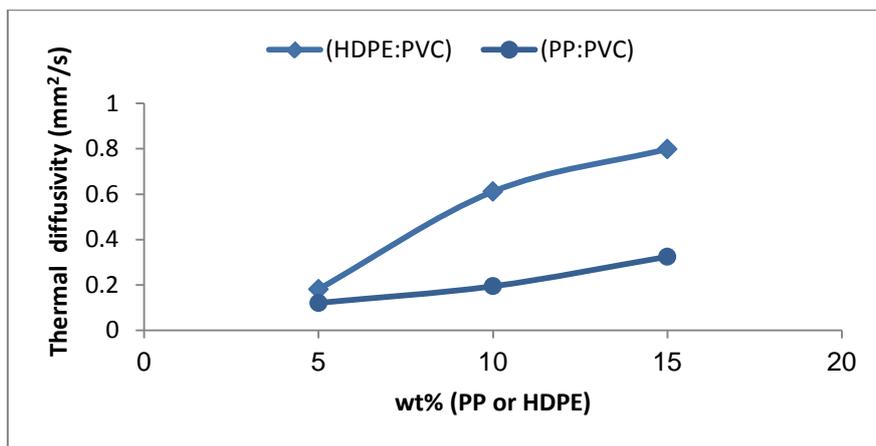
Thermal conductivity, thermal diffusivity and specific heat characteristics for polymer blends (PP-PVC) and (HDPE-PVC) are shown in Figures (13, 14 and 15) respectively. It was noticed that the thermal characteristics increased with increasing PP or HDPE content in blends.

This increasing in thermal conductivity, specific heat and thermal diffusivity with the increasing of PP or HDPE content in blends return to the susceptibility of thermal conductivity of PP and HDPE material in comparison with the other rest of ingredients in the polymer blend [15]

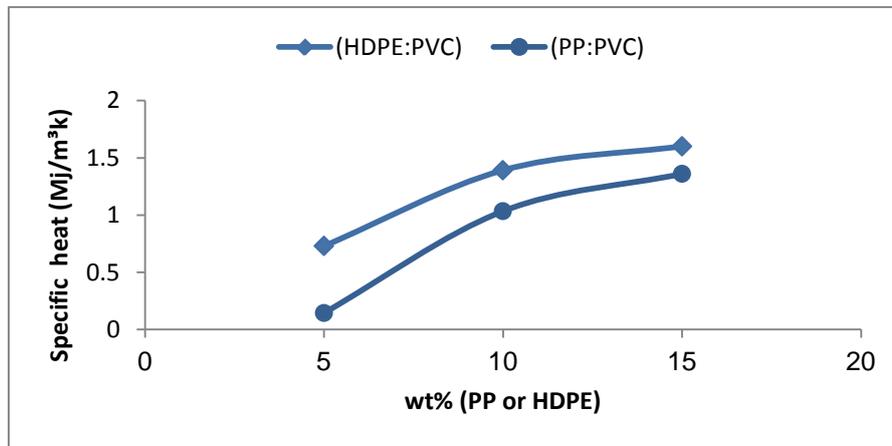
As well as it was noticed that the polymer blend (HDPE-PVC) has greater values of thermal properties than its counterparts of the polymer blend samples (PP-PVC), this is return to molecular structure of HDPE which have linear structure and high degree of crystallinity compared with molecular structure of PP having methyl group (CH₃) and this lead to decrease in crystallinity and then decrement in thermal conductivity.



Figure(13): Thermal conductivity for the polymer blends (PP-PVC) and (HDPE-PVC) as a function of (PP) or (HDPE) content in blend.



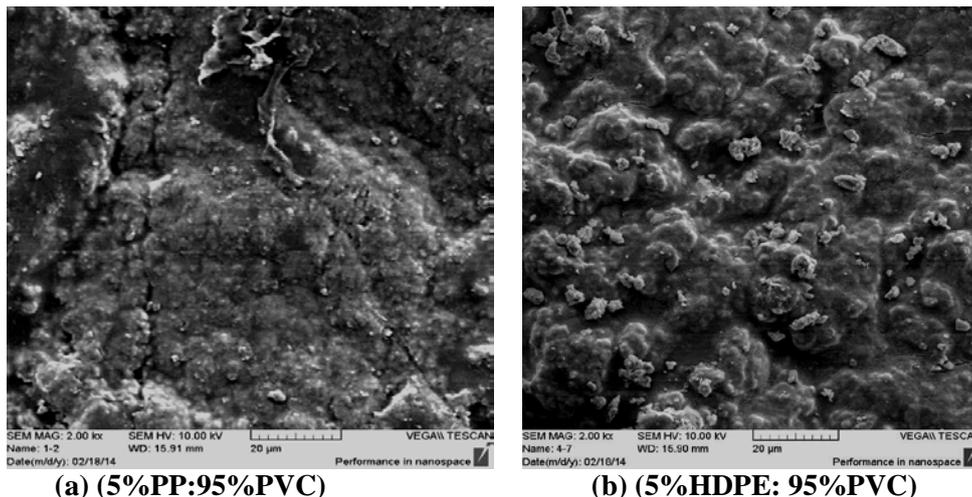
Figure(14): Thermal diffusivity for the polymer blends (PP-PVC) and (HDPE-PVC) as a function of (PP) or (HDPE) content in blend.



Figure(15): Specific heat for the polymer blends (PP-PVC) and (HDPE-PVC) as a function of (PP) or (HDPE) content in blend.

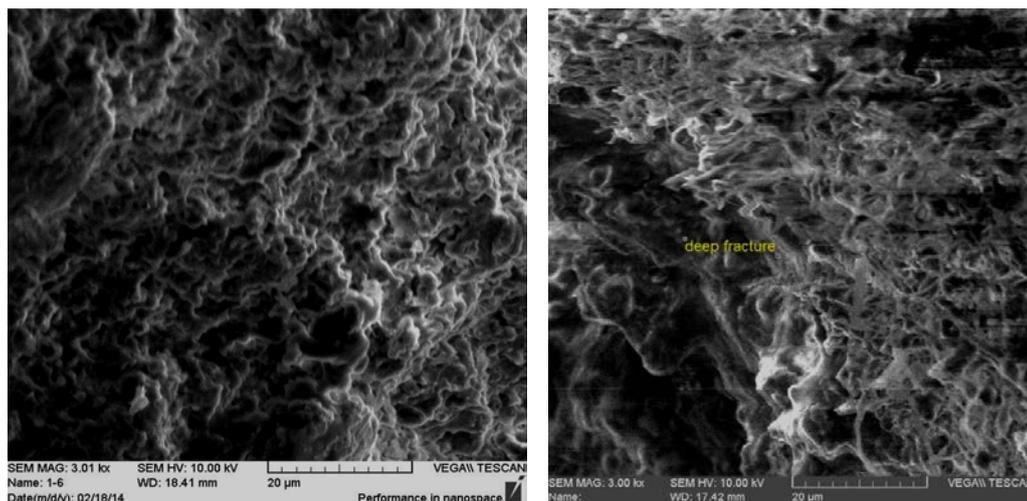
SEM test

the SEM photography of the surface of the polymers blends (5%PP: 95%PVC) and of the polymers blends (5%HDPE: 95%PVC), was shown in figures (20 a and b) respectively, from this figure (20 a) it was shown that the separate phase appearing as small white zone embedded in semi-continuous phase polymer blends (5%PP: 95%PVC). Figure (20 b) shows the surface morphology of the polymer blend (5%HDPE: 95%PVC), these photograph images show a homogenous distribution of HDPE phase as spherical drops, which are embedded in to PVC phase. As well as from photographs it can be seen some micro cracks may take an interphase path as shown in figure (20 b), and that may be related to the addition of HDPE to the polymer base PVC, make the polymer blend (HDPE-PVC) behave as brittle and strength material comparison with the polymer blend (PP-PVC), and this conform to the results obtained from mechanical tests.



Figure(20): SEM images showing the surface morphology of polymer blends, (a) (5%PP:95%PVC) and (b) (5%HDPE: 95%PVC), at magnification (X=2000)

As well as the SEM photographs were taken to the fracture surface morphology of the polymers blends (5%PP: 95%PVC) and (5%HDPE: 95%PVC), images are shown in Figure (21a and b) respectively. The morphological results of the fracture surface figure (21 a) clearly show that the fracture surface behavior as a ductile fracture since the fracture surface shows a plastic deformation. As well as from fracture surface morphology of the polymers blends (5%HDPE: 95%PVC), figure (21-b) show semi-brittle fracture with deep fracture as shown in this figure.



(a) (5%PP:95%PVC)

(b) (5%HDPE: 95%PVC)

Figure(21): SEM images showing the fracture surface morphology of polymer blend, (a) (5%PP:95%PVC) and (b) (5%HDPE: 95%PVC), at magnification (X=3000).

Conclusion

The polymer blend (HDPE- PVC) get higher values than polymer blend (PP-PVC) in fracture strength, young's modulus, flexural strength and maximum shear stress, whereas the polymer blends (PP- PVC) get higher values in impact strength, fracture toughness, elongation, hardness and compression. Besides, the increment in PP or HDPE content weak the properties of the polymer blends and the samples with (5%PP:95%PVC) and (5%HDPE:95%PVC) were the best among the other polymer blends samples.

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