

Mechanical and Morphological Properties of HDPE: PP and LDPE: PP Polymer Blend Composites Reinforced with TiO₂ particles

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ABSTRACT

In this research two groups of polymer blends have been prepared *First group* included (High density polyethylene (HDPE): Polypropylene (PP)) While the *Second group* (included Low density polyethylene (LDPE): Polypropylene (PP)) both groups prepared with polypropylene of (20% and 80%). From the results of tensile test for the prepared blends it has been showed that the optimum blending ratio was (20%LDPE:80%PP and 20%HDPE:80%PP) which then reinforced with (2, 5 and 8wt %) of titanium dioxide (TiO₂), particle size (0.421μm). Titania particles were mechanically mixed with the polymers prior to melt mixing for better dispersion. Polymer blend composites were obtained by using single screw extruder. Results showed that mechanical properties increased as titania content increased except elongation. Furthermore the result recorded highest values of impact strength and fracture toughness at 2% wt TiO₂ which is 312 Mpa and 572.8Mpa respectively, for the polymer blend (20%HDPE: 80%PP) composite and for the polymer blend (20%LDPE: 80%PP) composites the impact strength and fracture toughness are 262.5Mpa and 468 Mpa respectively. The mechanical properties values of 20%HDPE: 80%PP is higher than 20%LDPE: 80%PP polymer blend composites. Scanning electron microscopy (SEM) images showed that there is bonding developed between TiO₂ and polymer blends in some regions.

Keywords: Polymer blend, TiO₂, HDPE, PP, composite, Mechanical properties.

الخواص الميكانيكية و المجهرية لمتراكبات الخلائط البوليمرية HDPE: PP و LDPE: PP المقواة بدقائق اوكسيد التيتانيوم

الخلاصة:

في هذا البحث تم تحضير مجموعتين من الخلائط البوليمرية المجموعة الاولى تضمنت (بولي بروبيلين PP وبولي اثيلين عالي الكثافة HDPE) وبينما المجموعة الثانية تضمنت (بولي بروبيلين PP وبولي اثيلينواطي الكثافة LDPE) كلا المجموعتين حضرت بنسب من البولي بروبيلين (80% and 20%). ومن نتائج اختبار الخواص الميكانيكية للخلائط البوليمرية المحضرة حددت القيمة المثلى لنسب

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الخلط والمتمثلة في (20% HDPE : 80% PP) و (20% LDPE:80% PP) والتي بعد ذلك تم تقويتها بدقائق ثنائي اوكسيد التيتانيوم (TiO₂) بنسب وزنية (2% , 5% and 8 wt%) وحجم حبيبي (0.421 μm). ولغرض تجانس الخلط تم مزج دقائق TiO₂ مع الحبيبات البوليمرية ميكانيكيا قبل اجراء عملية البثق باستخدام باثقة احادية المحور . واطهرت النتائج زيادة في الخصائص الميكانيكية مع زيادة محتوى دقائق التقوية بأستثناء المطيلية. وعلاوة على ذلك سجلت النتائج اعلى القيم لمقاومة الصدمة ومتانة الكسر عند 2 wt% TiO₂ وبلغت (312.5 Mpa و 572.8 Mpa) على التوالي لمتراكبات الخليط البوليمرية (20% HDPE:80% PP) ولمتراكبات الخليط البوليمرية (20% LDPE:80% PP) بلغت قيم مقاومة الصدمة و متانة الكسر (262.5 Mpa و 468 Mpa) على التوالي. الخصائص الميكانيكية للمتراكبات المحضرة ذات اساس (20% HDPE+80% PP) هي اعلى من مثيلاتها ذات اساس (20% LDPE+80% PP). صور المجهر الالكتروني الماسحاطهرت ان هنالك ترابط جيد في بعض المناطق ما بين مادة التقوية ومادة الاساس .

Introduction

During the past several decades, polymer material has had a marked very direct practical impact on the way of life people in nearly every region of the earth. A new approach to the science and technology [1]. Blending of two polymers in a possible way to tailor their individual properties in a single material. The properties of polymer blends strongly depend on their morphology which is determined by the size distribution and shape of distributed particles [2, 3].

Some studies showed that uncompatibilized immiscible polymer blends provide synergy of mechanical properties when the processing and compositional parameters are near optimum values [4-6].

The incorporation of fillers into thermoplastics is another method widely used to enhance certain properties. The degree of property enhancement depends on the filler type, filler particle size and shape, the content of filler (Albano et al. [7] analyzed the effect of CaCO₃ on blend of PP/HDPE found that the addition of this blend at 30wt% did not improve the mechanical properties of the blend) and most importantly the filler origin [8-10]. Studies dealing with polymer blend reinforced with rigid filler to give three-phase polymer composites have been increased considerably during the last few years [11-13]. Michel A. H., and Hongbo Li investigated the structure development in the starch gelatinization and thermoplastic starch mixing with PE, PP, PS and showed the tensile strength, tensile modulus and elongation at break of the blend were decreased by addition of the thermoplastic starch [13].

The objective of this study was to investigate the effect of titania particles content on the mechanical and morphological properties of the two types of polymer blends-based composites.

Materials and Experimental Methods

In this research three types of polymer materials used which were provided from the National Company for Plastic and Chemical Industries / Zaffrania - Baghdad. The polymer materials are High density polyethylene (HDPE), Low density polyethylene (LDPE) and Polypropylene (PP). Physical properties data for each polymer is given in Table (1). All polymers were supplied from the supplier (Sabic Company / Saudi Arabia) in a pellet form. (20% HDPE: 80% PP) and (20% LDPE:

80%PP) blends were mixed with (2,5 and 8%)TiO₂ particles were supplied from (Nabond Company/ China).

Table (1) Polymer materials information

<i>Material</i>	<i>supplier</i>	<i>Melt flow index (gm/10 min)</i>	<i>Density(g/cm³)</i>
HDPE	sabic	8	0.964
LDPE	sabic	7	0.922
PP	sabic	8	0.905
TiO ₂	Nabond	-	4.23

Particle Size Distribution of TiO₂ Powder

Particle size distribution of TiO₂ was carried out using laser diffraction particle size analyzer type (SHIMADZU SAID-2101) in Science and Technology ministry/Baghdad. The result of particle size distribution is shown in Fig. (1). the mean diameter was (0.421 μm) and the median value was (0.417 μm). SEM (Model VEGATS SI136XM) was used at Bicocca University, Milano/Italy, Fig. (2) shows SEM micrographs of titania particles used in this study.

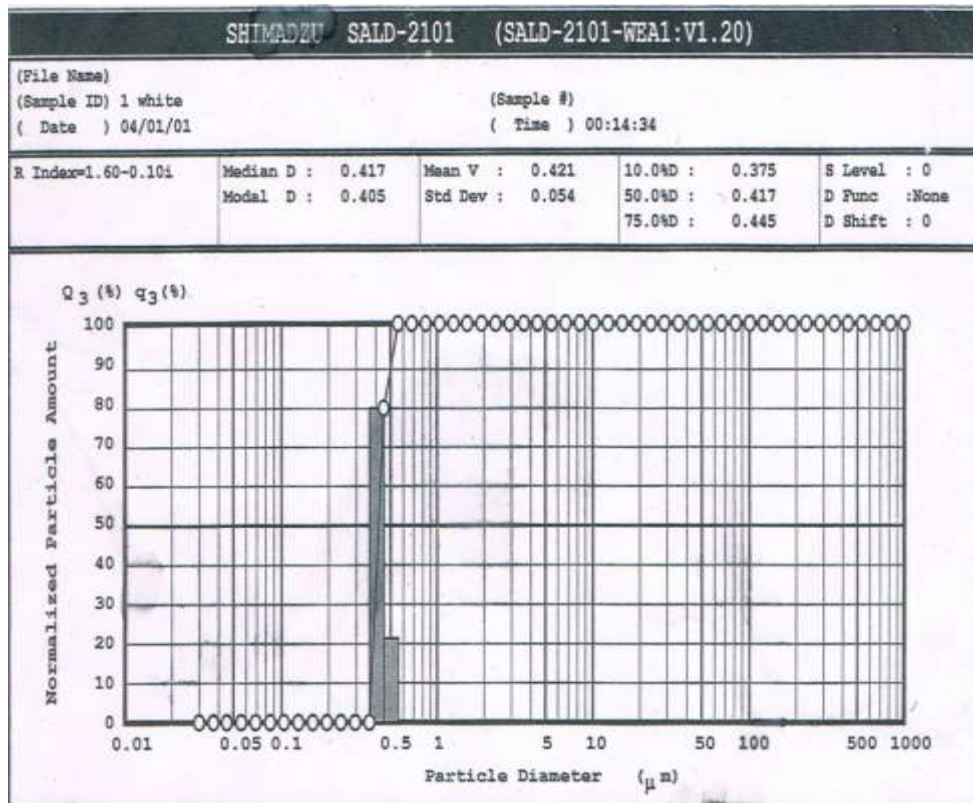


Figure. (1) Particle size analysis of TiO₂.

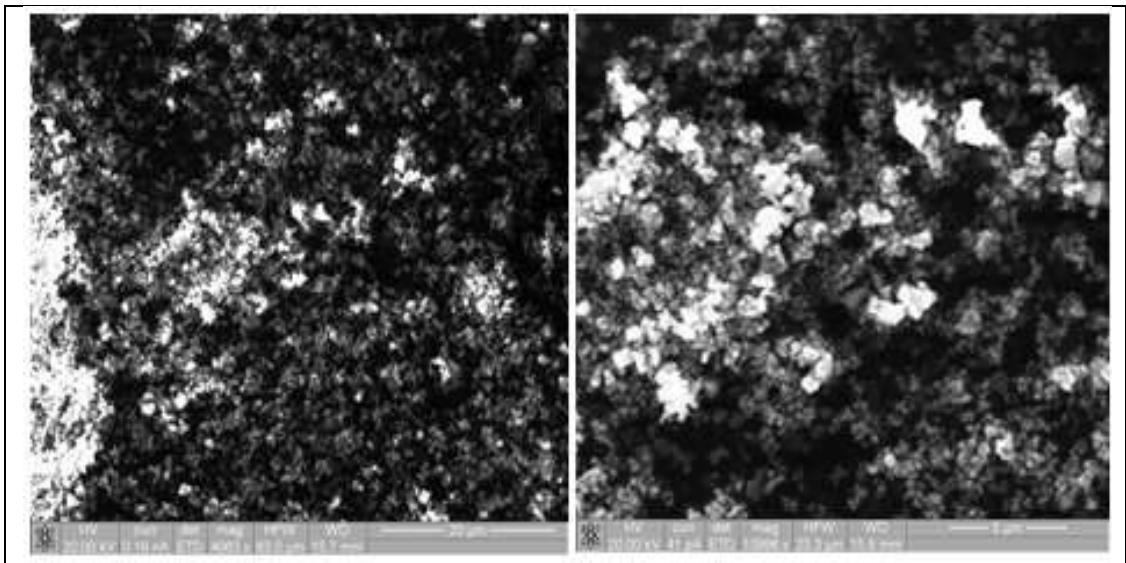


Figure. (2) SEM images of TiO₂ powder.

Blending

Polymer blends of (HDPE:PP) and (LDPE:PP) both groups prepared with polypropylene of (20% and 80%) were melted in a single screw extruder machine with a screw L/D of 30:1 (Iraqi Al-Forat Company 2004 Extruder) to make strips of polymer blends with 1.5mm thickness. Tables 2 and 3 show the compositions and the extrusion parameter respectively for both polymer blends and composite prepared.

Table (2) compositions of polymer Blend and composite.

No.		%HDPE	%LDPE	%PP	%TiO ₂	
1	Group 1	blend	80	zero	20	0
2			20	zero	80	0
3		composite	20	zero	80	2
4			20	zero	80	5
5			20	zero	80	8
6	Group 2	blend	zero	80	20	0
7			zero	20	80	0
8		composite	zero	20	80	2
9			zero	20	80	5
10			zero	20	80	8

Table (3) Extrusion parameters.

No.	Blend System	Temperature(°C)			Screw speed (r.p.m)
		Zone1	Zone2	Zone3	
1	HDPE:PP	150	160	160	20
2	LDPE:PP	140	150	150	20
3	HDPE:PP:TiO ₂	160	170	170	20
4	LDPE:PP:TiO ₂	150	160	160	20

Samples prepared by compression moulding technique including locating previous extrudate blendstrips in a mold made of steel to have the suitable thickness for inspections which is previously heated at 160°C for one hour, compression technique carried out at pressure (300 kgf/cm²) for (5 -10) minutes depending on the type of the blend.

Mechanical test

Samples were prepared for the tensile test in accordance with ASTM D638-87[14]. A computerized universal testing machine model (WDW-200D Jinan Shijin Group company-china) was used to conduct a test at a constant cross head speed of the order 10 mm/min at room temperature. Tensile load was applied till the failure of the sample and stress -strain curve was obtained. Each sample was tested for 3 times and average results have been reported. Impact test is performed at room temperature according to ASTM ISO 179[15]. Izod Charpy tension impact (measurement test machines Inc, Amityville-New York). Bending modulus measured from three point test, this test is performed according to ASTM D-790-78 [14] at room temperature. Hardness test carried out on a Durometer shore D scale according to ASTM D-570[15]. A creep test is performed under a constant applied load (40N) at room temperature according to BS 1178 [15].

Results and discussion:-

Tensile test of HDPE: PP and LDPE: PP blend and its composite.

Polymer blends with different weight percentages of polypropylene (20% and 80%) in both blends (HDPE: PP) and (LDPE: PP) have been studied. The results of ultimate tensile strength and young modulus are shown in Fig.(3 a,b) respectively these figures showed that 80%wt of PP is the best ratio in the two types of blends (HDPE: PP) and (LDPE: PP). According to these results, polymer blends which are (20%HDPE: 80%PP) and (20%LDPE: 80%PP) are selected as the optimum polymer blend ratio and reinforced with chosen ratios (2, 5 and 8%) of titania particles. The stress -strain behavior of the neat blends (20%HDPE: 80%PP) and (20%LDPE: 80%PP) and its composites are shown in Fig. (4a, b) respectively. It can be noticed that as TiO₂ content increased in the blend there will be change in the behavior from hard and tough for neat blends to hard and strong for polymer blends (20%HDPE:80%PP) which reinforced with 8%wt of titania particles.

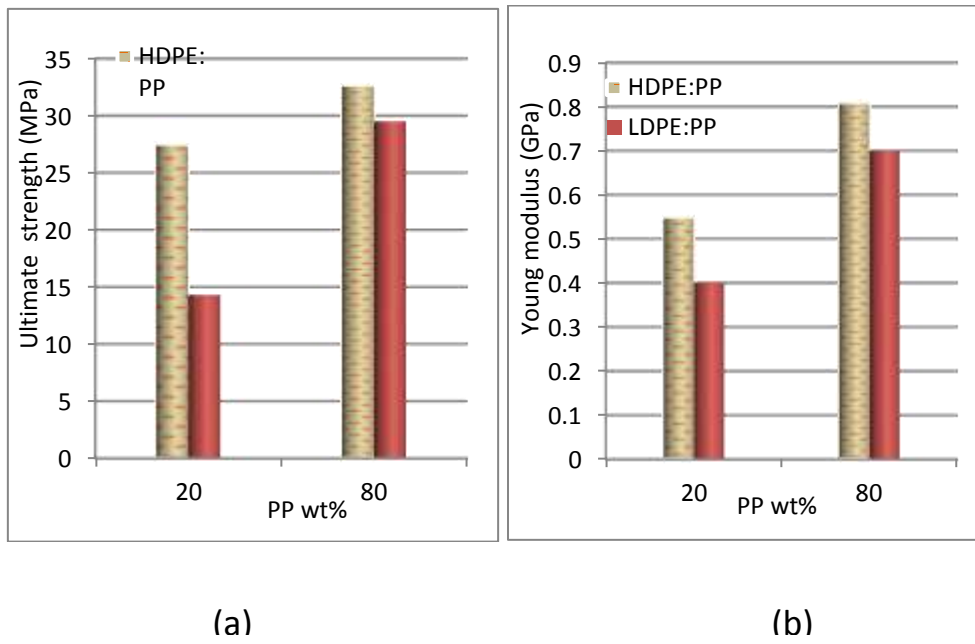


Figure. (3) (a) Ultimate tensile strength and (b) Young modulus of (HDPE: PP and LDPE: PP) blends.

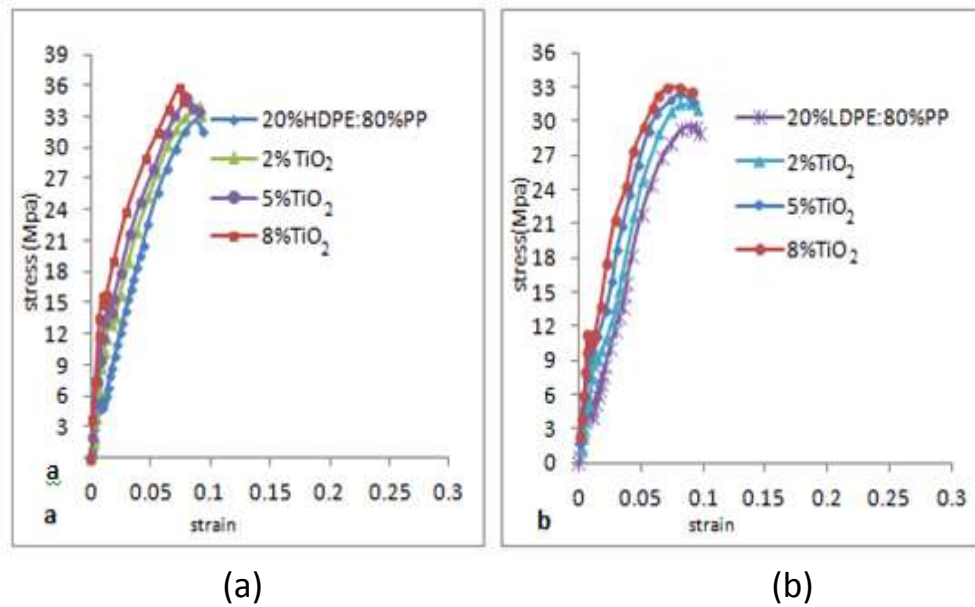


Figure. (4) Stress-Strain curves of (a) 20%HDPE: 80%PP and (b) 20%LDPE: 80%PP blend composites.

It can be seen from Fig.(5 a,b,c and d) an increase in ultimate strength values with the addition of TiO₂ particles for the two groups of blends and similar result is observed in each of fracture strength and young modulus, but differs in elongation and this related to the nature of TiO₂ particles which are stiffer and stronger than the continuous polymer blend matrix [10]. And it is noted from these figures that the ultimate strength, fracture strength and young modulus values for the (20%HDPE: 80%PP) blend composite is higher than the (20%LDPE: 80%PP) blend composite that may be related to the difference between both types of PE in molecular chain structure, HDPE has very little branching on the main chains, and so the chains can pack more closely together to increase crystallinity and strength [14].

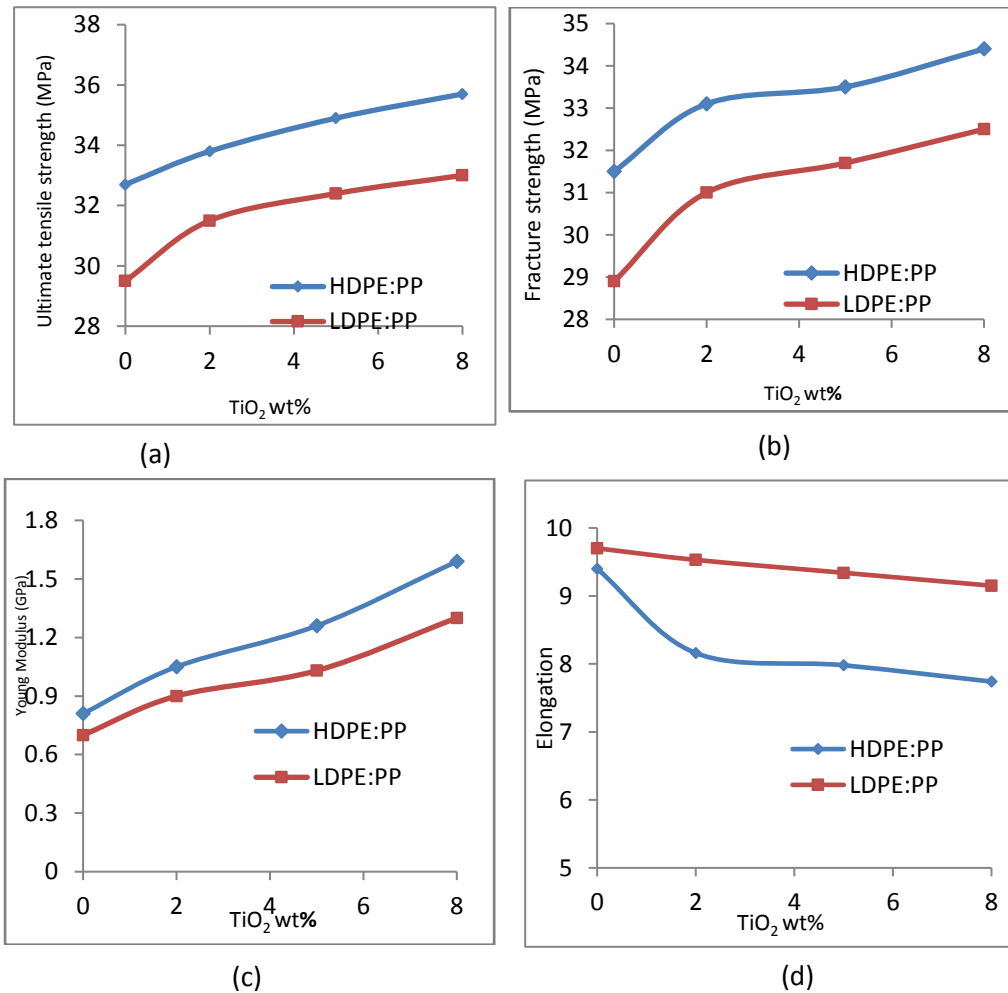


Figure. (5)(a) tensile strength (b) fracture strength (c) Young modulus and (d) elongation of (20%HDPE:80%PP and 20%LDPE:80%PP) blend composites. as a function of TiO₂ content in the blends.

Bending test of polymer blend composites

The results of three –point bending test show that the elasticity modulus of bending (E_{bend}) values for the composites increased as TiO₂ particles content increased for both types of blends (20%HDPE: 80%PP) and (20%LDPE: 80%PP) as shown in the Fig. (6) The incorporation of TiO₂ with the polymer blend leads to higher bending modulus due to the interfacial reaction between polymer blend and TiO₂ particles, and these values for the (HDPE: PP) blend composites is more than (LDPE: PP) blend composites.

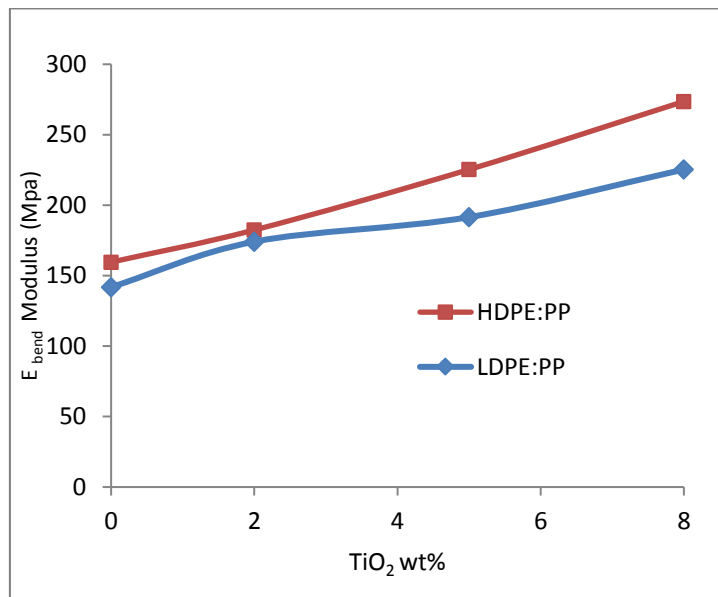


Figure. (6) Bending modulus of (20%HDPE: 80%PP) and (20%LDPE: 80%PP) blend composites as a function of TiO₂ content in the blends.

Impact test of polymer blend composites

It has been realized from Fig. (7 a) that there is a high increment of impact strength at 2% TiO₂ particles when it is compared with the neat blends in both polymer blends, but this increment has decreased gradually as TiO₂ ratio increased to higher than 2% ratio, this is due to the fact that TiO₂ particles are ceramic particles have a high hardness compared with the polymer materials, so that the impact strength decrease when it is added in a high ratio [10].

So the best ratio that increased the impact was at 2% TiO₂ and the rate of increment were 125% and 150% for both 20%LDPE: 80%PP and 20%HDPE: 80%PP blend composite respectively as shown in the Fig. (7a), while Fig. (7 b) shows fracture toughness values of blends were increased as TiO₂ particles added to the blends and

reach to high values at 2%TiO₂ ratio, then the rate of increment were decreased, but fracture toughness values for two group of polymer blend composites are larger than their matrix (net polymer blends). Incorporation of TiO₂ particles into polymer blends leads to higher fracture toughness values due to the interfacial reaction especially when it is added in slight ratio, and provides an effective barrier for the advancing cracks [17].Also it has been noted from both Fig. (7 a and b) that impact strength and fracture toughness values of composite materials for (20%HDPE: 80%PP)blend are higher than the other blend (20%LDPE: 80%PP).

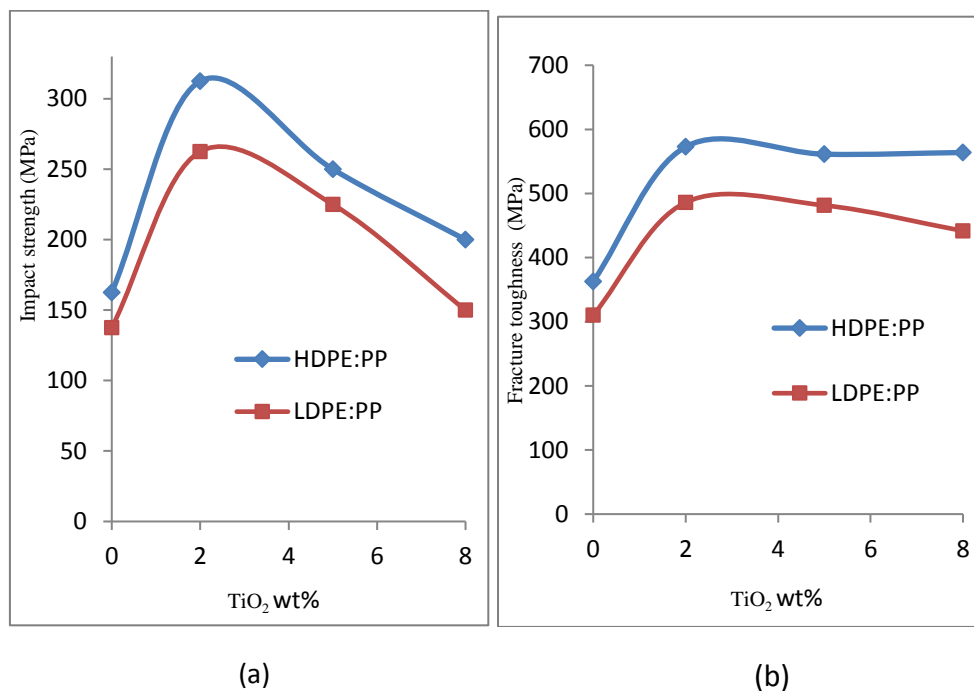


Figure. (7) The effect of TiO₂ content on (a) Impact strength (b) fracture toughness of (20%HDPE:80%PP) and (20%LDPE:80%PP) blend composites.

Shore D Hardness of polymer blend composites

The hardness values of Shore D increases with the increasing of TiO₂ particles content in the blends as shown in the Fig. (8). This is related to the titania particles which are ceramic particles have a high hardness compared to polymer blends. Furthermore hardness values of (20%HDPE: 80%PP: TiO₂) slightly higher than hardness values of (20%LDPE: 80%PP: TiO₂) composites due to the difference in the chain structure for two type of PE [16].

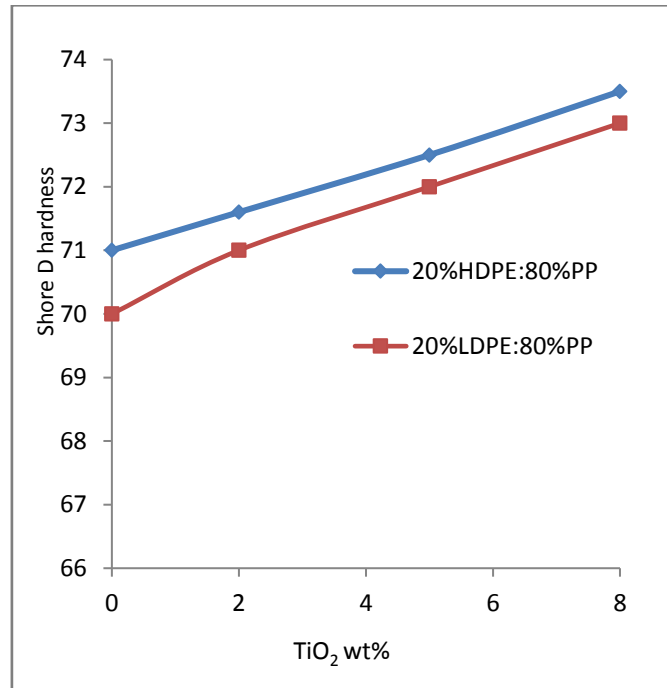
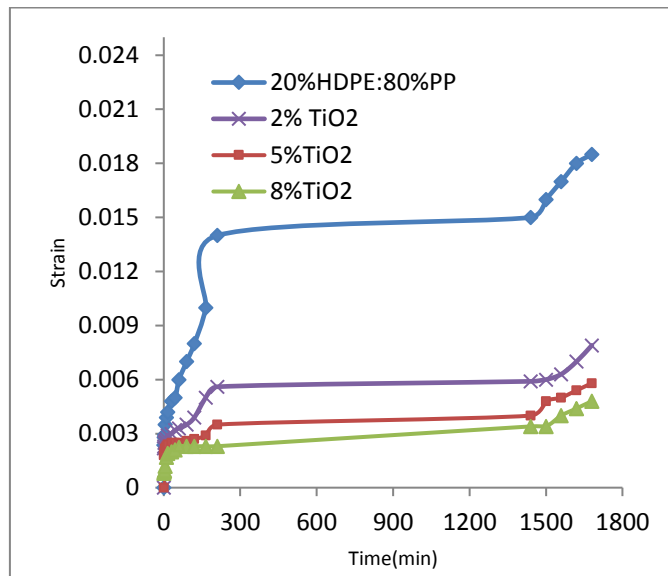


Figure. (8) Shore D hardness for (20%HDPE: 80%PP and 20%LDPE: 80%PP) blend composites as a function of TiO₂ content in the blends.

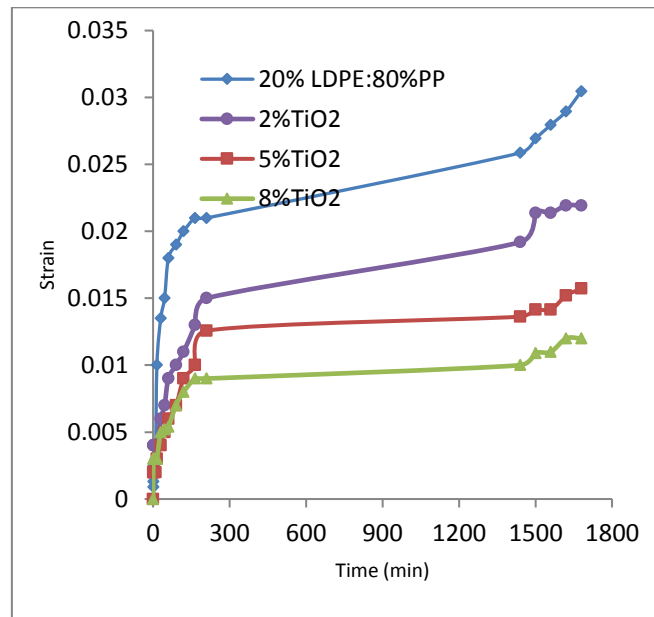
Creep behavior of blend composites

Strain-time curve of (20%HDPE:80%PP) and (20%LDPE:80%PP) blend composites are shown in Fig. (9 a,b) respectively. This figure shows that the creep rate at room temperature and at constant applied load (40 N) decreased with increased TiO₂ particles amount in the polymer blend composites due to restricted molecular chain mobility by reinforcing particles.

creep rate at room temperature and at constant applied load (40 N) decreased with increased TiO₂ particles amount in the polymer blend composites due to restricted molecular chain mobility by reinforcing particles.



(a)



(b)

Figure. (9) Creep behavior of (a) (20%HDPE:80%PP) and (b) (20%LDPE:80%PP) blend composites as a function of TiO₂ content in the blends.

Also as shown in Fig. (10) creep modulus (the ratio of the initial applied stress to the creep strain $\epsilon_{(t)}$ after a particular time and at a constant temperature of testing [16]) of blend composites increases as reinforcement titaniaparticles increased. Furthermore, it has been also realized from Fig. (10) That creep modulus of (20%HDPE:80%PP) blend composites is higher than (20%LDPE:80%PP) blend composite this related to the difference in the molecular chain of both types of PE.

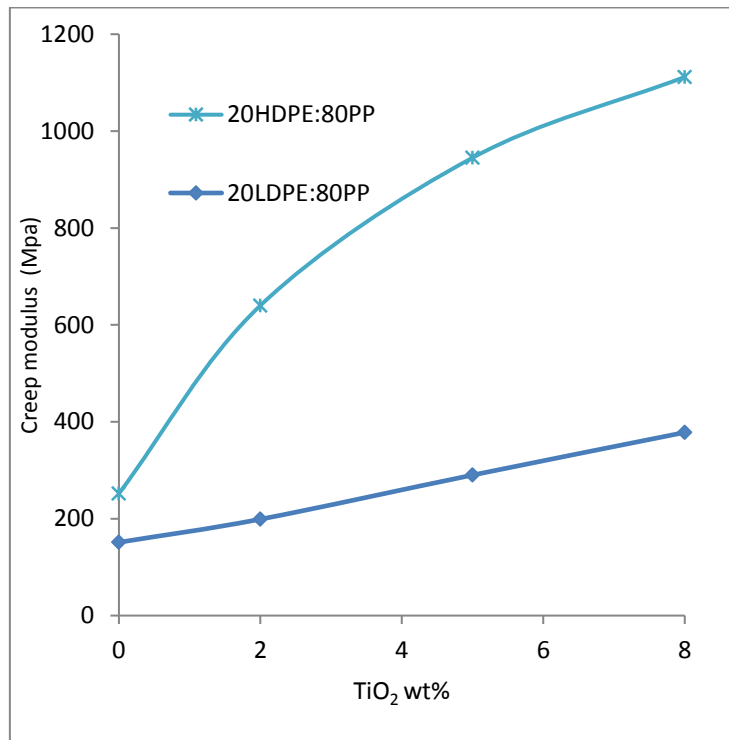


Figure. (10) Creep modulus of (20%HDPE:80%PP) and (20%LDPE:80%PP) blend composites after 1500 min as a function of TiO₂ content in the blend.

Morphological Test

In order to evaluate the changes in surface morphology of the prepared samples (polymer blends and polymer blend composites). Scanning electron microscope (Model VEGATS S1136XM) in Bicocca University, Milano/Italy was used to examine the samples.

To achieve good electrical conductivity, all samples were first coated with graphite and line of silver. SEM micrographs clearly show the difference in the morphology of the polymer blends (20%HDPE: 80%PP) and (20%LDPE: 80%PP) Fig. (11a and b) respectively. Also Fig. (12 a, b and c) and Fig. (12 d, e and f) show the difference in the morphology of the prepared composites for the two groups of blends when compared with the morphology of the polymer matrix separately. There are more of

TiO₂ particles are dispersed in the matrix. The interaction between TiO₂ and polymer blends matrix is limited because TiO₂ has polar surface and polymer blends is non-polar [11]. So the SEM photographs of the polymer blend composites shown in Fig. (12 a, b, c, d, e and f) indicates that there are different regions having different morphology, some of these regions show there are strong bonding developed between TiO₂ and polymer blends (as shown in Fig. (12f) for (20%LDPE: 80%PP):8%TiO₂ composite) and they behave like one phase which shown good compatibility between composite content. Whereas in another regions SEM micrographs show that there are some of individual TiO₂ particles are presented in the matrix due to the poor adhesion between the incompatible particles and polymer blend matrix. Fig. (13 a, b, c and d) shows SEM micrographs of fractured surfaces of polymer blend composite specimens. The SEM micrographs indicate that there are many regions having sufficient interfacial adhesion between TiO₂ particles and polymer blend matrix, it can be readily seen that many particles were not pulled out from thermoplastics blend matrix and their surfaces were covered by polymer blend. Although there is some of particles pulled out from blend matrix (the light very small areas reflect Titania particles and the dark large areas show polymer blends based composites).

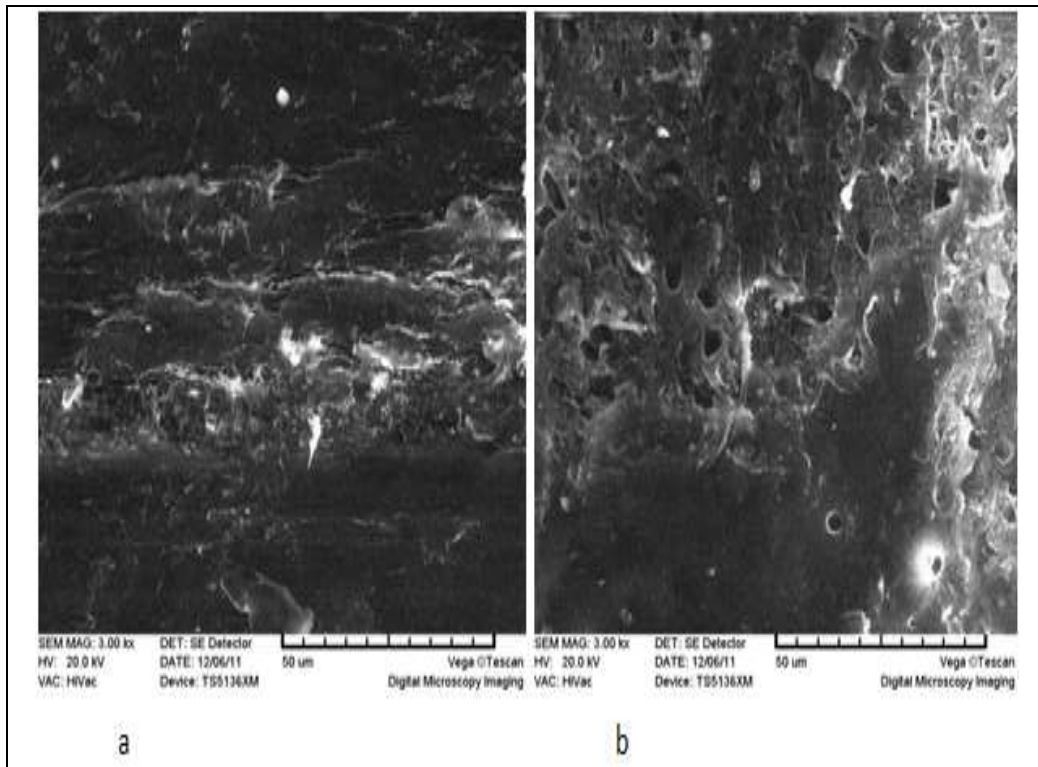


Figure. (11) SEM micrographs of (a) 20%HDPE: 80%PP polymer blends (b) 20%LDPE: 80%PP polymer blends.

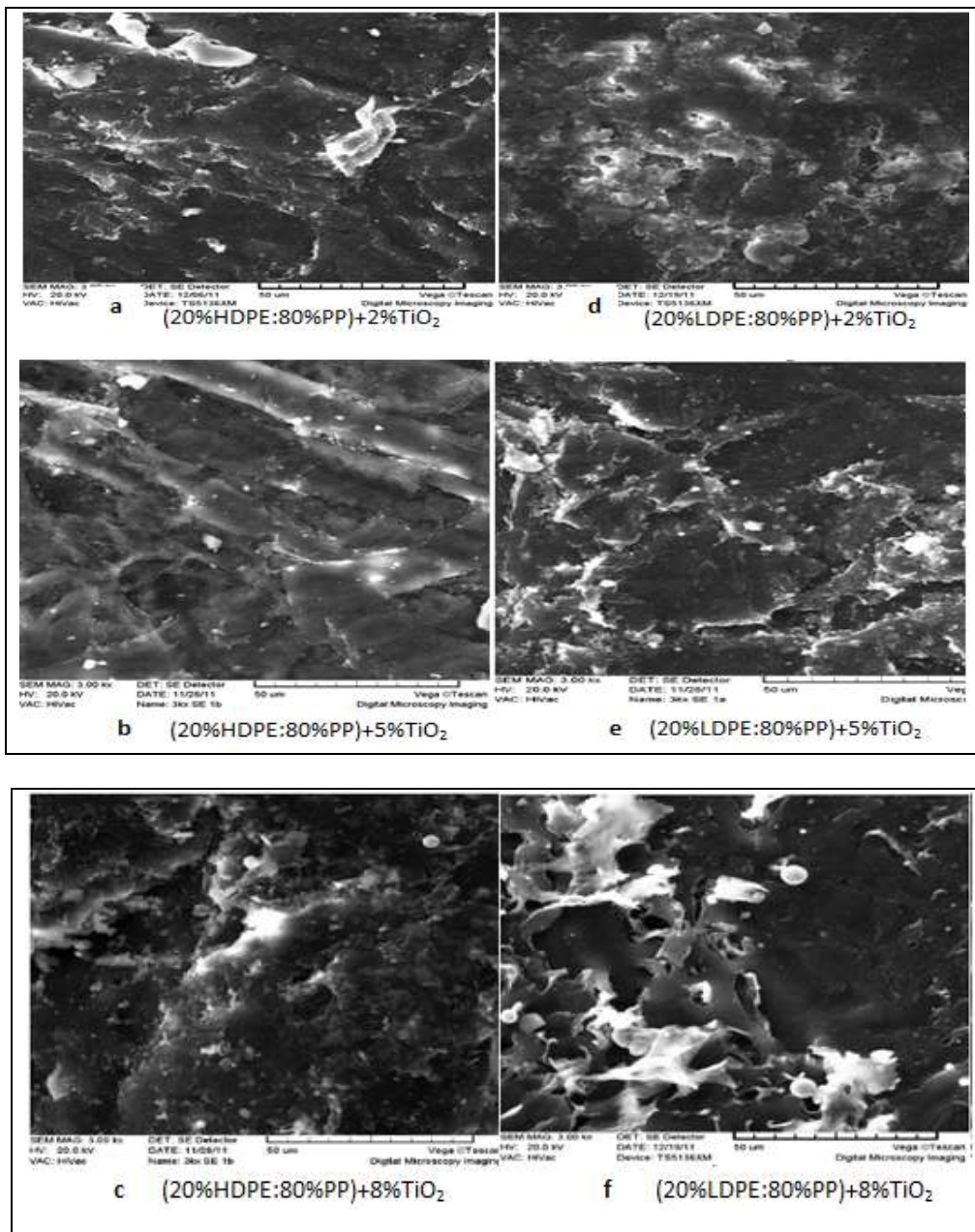


Figure. (12)SEM micrographs of (20%HDPE:80%PP) composites (a, b and c) and (20%LDPE:80%PP) composites (d, e and f) as function of Titania content.

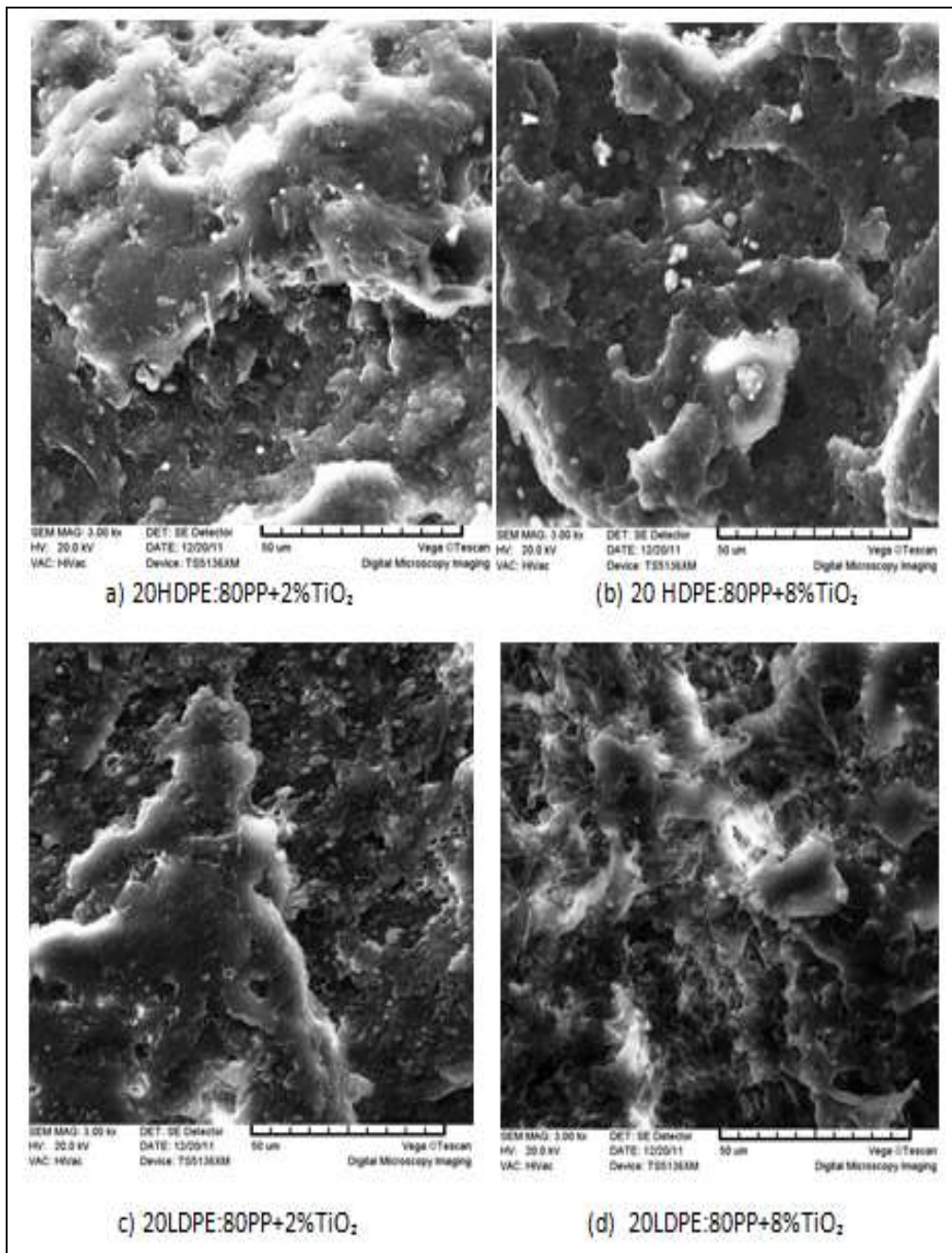


Figure. (13) SEM micrographs of fracture surfaces for (20%HDPE:80%PP) and (20%LDPE:80%PP) blend composites as function of TiO₂ content.

Conclusions

Tensile strength and Young modulus of two polymer blends (HDPE: PP) and (LDPE: PP) were studied under tensile loading. It was concluded that polymer blends ratios (20%HDPE: 80%PP) and (20%LDPE: 80%PP) exhibited optimum properties as compared to other ratios. The mechanical properties for these polymer blend composites were investigated as a function of TiO₂ particles content in the blends. The following conclusions were drawn from this study:

1. The mechanical properties of polymer blend composites were found to be higher than the polymer blend matrix (without TiO₂).
2. Increasing the weight percentage of TiO₂ particles into polymer blend composites, leads to improved mechanical properties of prepared composites.
3. 20HDPE:80PP polymer blend composites were found to be higher than 20LDPE:80PP polymer blend composites.

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