Mechanical Properties of TiO_2 Reinforced Polystyrene- Modified Unsaturated Polyester

Prof. Dr. Adnan N. Abood Asst. Prof. Malia M. Fahan Mustafa M. Fadhil *
Engineering Technical college- Baghdad, Middle Technical University, Iraq
*E-mail of the corresponding auther : mustafamuhsin51@yahoo.com

Abstract

The aim of current research is carrying out some modifications on the properties of resin material Unsaturated Polyester (UP) by adding thermoplastic material Polystyrene (PS) in different weight ratios included 4%, 8%, 12%,14%,16%,20% and 24% was used to prepare binary polymer blend.

The best ratio was selected in terms of the homogeneity case between the two polymers and according to compression strength for all prepared specimens. The ratio 92/8 wt.% of UP/PS blend was selected and reinforced with different particle volume fractions of 1%, 3%, 5% and 7% using of TiO_2 particles.

The composite materials with unsaturated polyester-polystyrene matrix properties were evaluated by conducting the mechanical tests which included compression, hardness and impact resistance. Results of compression test showed that the compression strength decreases as polystyrene percentage (PS) increases. While the TiO_2 an addition has helped in balancing the original compression strength reduction up to 3% vol. of TiO_2 and then the strength decreases. The results confirmed that the best enhancement is of 3% vol. of TiO_2 considering compression strength and impact.

The SEM results indicate that the polystyrene particles have good distribution through UP, this distribution of smaller particles is responsible for lower crack growth. The SEM results of composites specimen show the TiO_2 particles have good distribution through the matrix up to 3% vol., the mechanical properties beyond 3% vol. decreased due to the presence of particle agglomerations.

Keywords: Unsaturated polyester, Polystyrene, Mechanical properties, SEM.

1. Introduction

Highly cross-linked thermosetting polymers, such as epoxy resins and unsaturated polyesters, are an important class of synthetic materials. Their main distinction from other types of polymers lies in their densely cross linked molecular structure. This cross-linking leads to a number of superior properties including high glass transition temperatures, high modulus and specific strength, high creep resistance, good dimensional stability at elevated temperature, and good solvent resistance. These properties in conjunction with ease of processing have led to the extensive use of thermosetting polymers as adhesives, potting and encapsulating materials, tooling compounds, electronic substrates and packaging, and perhaps most importantly as matrix materials for reinforced composites[1-3]. Unfortunately, the high degree of molecular crosslinking in thermosetting polymers also makes them poor resistance to crack initiation and propagation. This lack of toughness severely impacts the performance of highly cross-linked thermosets in almost all applications. For example, it is the lack of matrix toughness that governs two out of the three primary damage initiation modes in fiber reinforced laminated composites, viz. matrix cracking and delamination. Thus, improving the fracture toughness of thermosetting polymers will lead to significantly enhanced performance when used as is, and will also enhance the damage initiation threshold and long-term reliability of fiber-reinforced composites [4-7]. Improving the fracture toughness of thermosetting resins has been the subject of considerable research. Typically, these approaches have involved the addition of micron-sized soft (elastomeric or thermoplastic) or rigid (glass or ceramic) particles into the polymer matrix. These filler particles are then expected to provide extrinsic toughening mechanisms [8]. In the first approach, micron-sized rubber particles are dispersed in the polymer matrix to enhance the overall fracture toughness by triggering localized shear yielding of the polymer. However, highly cross-linked thermosetting polymers are incapable of extensive shear yielding. Thus, the effectiveness of rubber additions decreases rapidly with increasing cross-link density [9]. Moreover, the addition of rubber introduces other deleterious effects, such as a reduction in the elastic modulus and tensile strength, decreased creep resistance, poor hot/wet performance, and a lowering of the glass transition temperature [10]. Alternatively, ductile thermoplastic particles may be dispersed in the thermosetting polymer to provide extrinsic mechanisms for increasing the overall toughness. However, increases in the fracture toughness have been observed, especially for low volume fractions of added thermoplastic particles [11,12]. Other mechanical properties such as elastic modulus and high temperature performance are often compromised. Investigators have also explored the incorporation of high modulus ceramic or glass particles into the polymer matrix. These particles generally improve the elastic modulus and the glass transition temperature and also increase in fracture toughness, especially at low volume fractions of added particles [13,14].

This research addresses this issue and presents a systematic characterization of the fracture behavior of a highly cross-linked thermosetting polymer toughened with thermoplastic polymer and then reinforced with high-modulus inorganic particles, as a function of particle volume fraction. Such an understanding would then be essential for identifying parameters that will lead to the design and fabrication of optimally toughened thermosetting polymers.

2. Experimental

2.1 Materials

Unsaturated polyester resin was supplied by Saudi Industrial Resins (SIR) Company. The curing agent (hardener) was Methylethylketone Peroxide (MEKP); while the catalyst system was a solution of cobalt octoate in dibutyl phthalate as accelerator of reaction. The properties of Unsaturated polyester used in this study are listed in Table 1.

Table1. Properties of Unsaturated polyester

Properties	Density at 25 °C	Curing cycle	Compressive strength	Boiling point
Value	1160 kg/m^3	48 hrs at 25◦C	>100 MPa	> 250

Polystyrene PS125 was supplied by Sabic Company, Saudi Arabia; it is produced from styrene monomer by continuous mass polymerization. It is a crystal-like, brittle and hard polymer with high clearness and medium flow. It also has medium viscosity and heat deflection temperatures and makes it suitable for various applications. The properties of PS 125 used in this study are listed in Table 2.

Table2. Properties of PS 125

Properties	Melt flow rate at 200 °C	Density at 23 °C	Tensile strength	Tensile elongation	Rockwell hardness, L scale
Value	7.0 g/10 min	1050 Kg/m^3	43 MPa	2 %	95

Chloroform $CHCl_3$ is a solvent used to dissolve PS125. The properties of this solvent are given in Table 3.

Table 3.Properties of $CHCl_3$

Properties	Molecular weight	Boiling point	Density	Viscosity	Surface tension	Solubility in water	Solubility of water in chloroform	DOT Hazard Class
Value	119.38 gm/mole	61.15°C	1.4892 g/mL at 20°C	0.57 cP at 20°C	27.16 dyn/cm at 20°C	0.815% at 20°C	0.056% at 20°C	6.1, Toxic

A 1.3,5,7 %vol. of TiO_2 were added to the modified unsaturated polyester, titanium dioxide (TiO_2) is the most widely used as white pigment; it was manufacture by Riedel-de Haen (Germany). It has a specific gravity of 4.25 g⁄cm^3 with average particle size of 0.417 µm.

2.2Preparing unsaturated polyester – polystyrene blend and TiO_2 reinforced composite

UP/PS polymer blends with weight ratios included [(96/4), (92/8), (88/12), (86/14), (84/16), (80/20), (76/24)] % were prepared from mixing of Unsaturated Polyester resin (UP) with polystyrene (PS) by using magnetic stirrer with stirring speed of 500 rev/minute to allow better reaction and interlocking. After mixing the two liquid polymers (UP with PS), the hardener was added to the mixture with 2% weight ratio; while the ratio of the accelerator was 0.5%. It is vital to mention that (UP) is yellow liquid insoluble in cold water while (PS) is a clear, colorless polymer used extensively for low-cost applications. It is available commercially in both pellet and sheet form. White pellets of (PS) were used in this research. (PS) material was dissolved in chloroform into glass sealed containers for (24 hour). This binary polymer blend was poured in a mould prepared previously for this purpose at room temperature; then after solidification, the resulted cast was interred into an oven with a set temperature of 50°C for (1 hour); to ensure that full cure was achieved. Post-curing treatment reduces weight loss significantly while higher temperatures and relative humidity increases the weight loss rate [11]. The ratio (92/8)% of (UP/PS) polymer blends was selected for the reinforcement. An addition more than 8% of PS reduces the stiffness of resin (UP) and makes it behaves as ductile material, therefore the additional ratio of (8%) was selected. Same procedure was followed in fabrication of TiO_2 reinforced samples with adding TiO_2 to the blend at the stage before adding hardener.

2.3Characterization of prepared materials and composites

2.3.1 Compression test

The mechanical properties of composites were measured using a Universal Material Tester device, 20 KN. The samples with size of 12.5 x 25mm^2 according to ASTM D695 were compressed at a constant load speed (5mm/min) until the cracks were observed. From the stress-strain curve, the compression strength of the samples was determined and the modulus of elasticity was determined as well as elongation.

2.3.2 Impact test

The impact test was performed by using Charpy impact test instrument. Charpy impact tests were conducted on the specimens at room temperature; the measurements were made according to ASTM D256 method. The standard specimen was held as a horizontal cantilever beam, broken by a single swing of a pendulum and the energy to failure was measured.

The Impact Strength (I.S) was calculated as follows [15]:

$$I.S = Uc / A \qquad (J/m^2) \ \ldots\ldots\ldots (1)$$

Where (Uc): the required energy for breaking the specimen, (A) cross sectional area

$$A = b \times d \qquad (m^2) \ \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

2.3.3 Hardness test

This test was performed on the three specimens with dimensions 10 x 10 mm and thickness 4 mm, according to ASTM D2240 by using the Landtek tester.

2.3.4 Scanning electron microscopy

Philips XL40 Scanning Electron Microscope was used to investigate the dispersion behavior and the fracture surface topography characterization. Which shows the SEM system type (X-MAX) used in this work, it exists in UK/ Sheffield Hallam University/Materials and Engineering Research Institute (MERI). Institute (MERI) in Sheffield, UK. A thin section of fracture surface was cut and cleaned with cleaning solution followed by sonication, nitrogen blow, then mounted on an aluminum stub using conducting (Carbon) paint and was sputter coater with 12 nm thick gold to reduce any charge build up on the surface. The images were analyzed at an acceleration voltage of 10KV.

3. Results and Discussion

3.1 Influence of polystyrene and TiO_2 addition on the Compression Stress-Strain Behavior of Unsaturated Polyester

3.1.1 Effect of Polystyrene Addition

Compression of unsaturated polyester-PS with different percentages of PS was investigated (Figure 1). Compression test of unsaturated polyester showed that behavior like that of brittle polymers and recorded the compression strength of 103 MPa. The addition of PS caused a decrease in compression strength of UP and changed the stress-strain behavior from brittle to ductile to elastomer depending upon the PS percentage in UP.

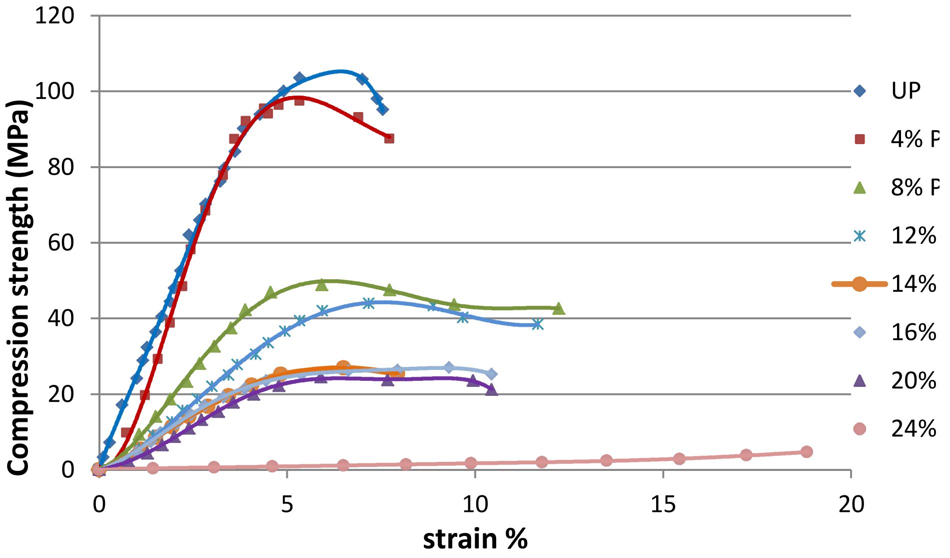
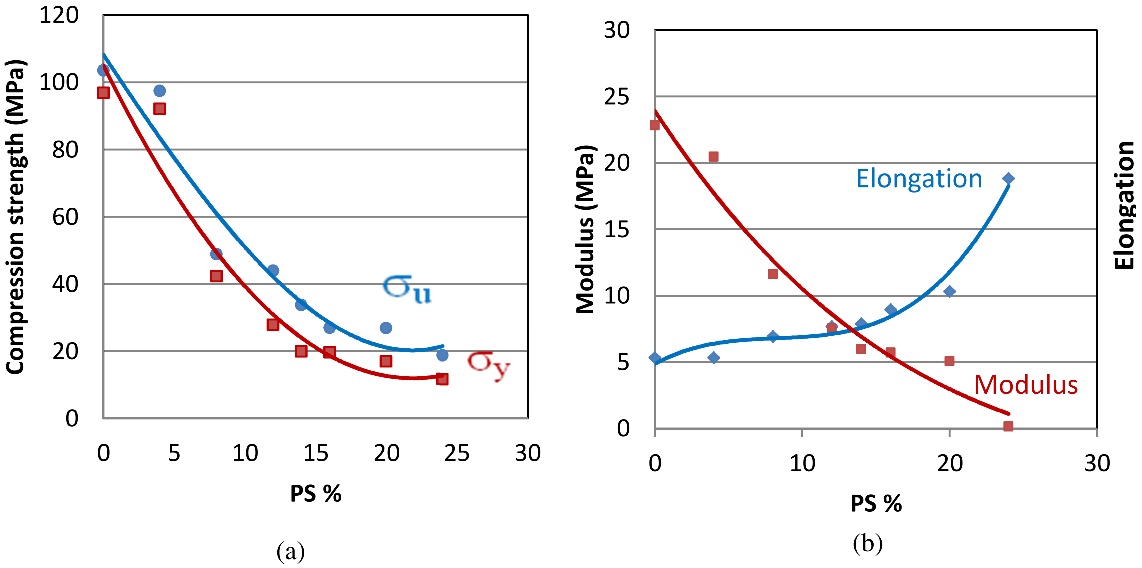


Figure 1. Compression stress – strain curves of blends UP– polystyrene

On the other hand the yield strength and ultimate strength (Figure 2a) decrease with increase in the PS percent. The modulus of elasticity of blend (Figure 2b) is lower by 8%, 49%, 65%, 70%, 76%, 77% and 99% than that of the UP, while the elongation of blend (Figure 2b) increases with increase in PS percent .



(a)

(b)

Figure 2. Effect of PS% on the (a) Yield and ultimate strength (b) Elongation and modulus

From the results, the ratio 4% PS showed the same behavior of UP without addition, therefore any fillers addition to this blend don’t give any sensible change in the properties, while the ratio 8 % of PS polymer blends was selected for the reinforcement because it achieved acceptable reduction in stiffness with suitable increase in elongation. An addition of more than 8% of PS reduces the stiffness of resin UP and makes it behave as a ductile material. When the PS content is increased above the selected ratio, the mechanical properties decrease. This behavior may be due to the fact that as the fraction of thermoplastic in thermoset increases, the dispersing phase of thermoplastic in the thermoset rich matrix increases, which hinders the cross linking of the thermoset with hardener by there decreasing the total strength of the system [16].

3.1.2 Effect of TiO_2 Addition

Pure unsaturated polyester shows compression strength of 103 MPa and the blend UP-8% PS shows compression strength of 48 MPa (Figure 2). The goal of addition of TiO_2 is to increase the mechanical properties of blend such as compression strength and modulus, while on the other hand it keeps acceptable ductility.

The compression strength of TiO_2 powder filled blend is 88, 86, 81and 77 MPa for 1, 3, 5 and 7 vol. % TiO_2 (Figure 3), while the elongation is lower by 3%, 8%, 17%, 23% than that of the blend. The compression strength of blend composites increases up to 1% and on further addition of TiO_2 powder the compression strength decreases. The specimen containing 1 vol. % TiO_2 particles possess an optimum level of dispersion, and, hence, the improvement in compression strength is caused by limited cross linked network structure and the restriction of mechanical restraint and the filler particle size [16].

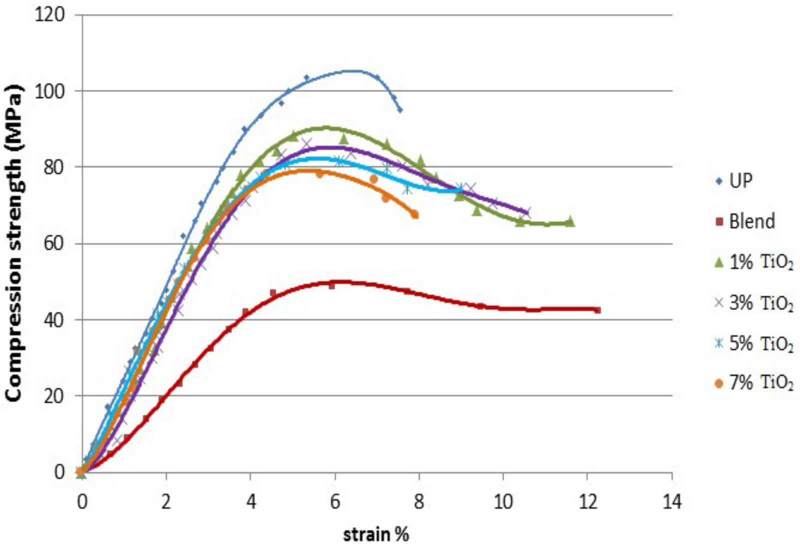


Figure 3. Compression stress – strain curve of blend / TiO_2 composite

3.2 Impact Resistance

Pure unsaturated polyester shows impact strength of 2.5 kJ/m^2 (Figure 4). The impact strength is 5.3kJ/m^2 for 8 % polystyrene blended with unsaturated polyester. The impact strength of TiO_2 filled blend [UP-8% PS] composites increases gradually up to 3% vol. powder content and then is found to decrease.

Incorporation of rigid filler may enhance or deteriorate the impact properties of composites. Impact strength is an indication of tolerability for a sudden impact. When a composite is subjected to an impact, rapid crack propagation is initiated through the material. Improvement in impact strength is due to the limited cross linked network structure of the cured resin [17]. The particles are tracer to move within the matrix and correspondingly, the matrix is free to stretch around particles. The stress transfer rate becomes very low, which leads to a lowest impact strength. In the filled composites, as filler loading increases the tendency for agglomerates also increases, interfacial adhesion becomes weaker leading to weaker interfacial region. These agglomerates then act as strength concentration points or crack initiation sites. Therefore reduction in the impact strength with increasing filler content is expected [18].

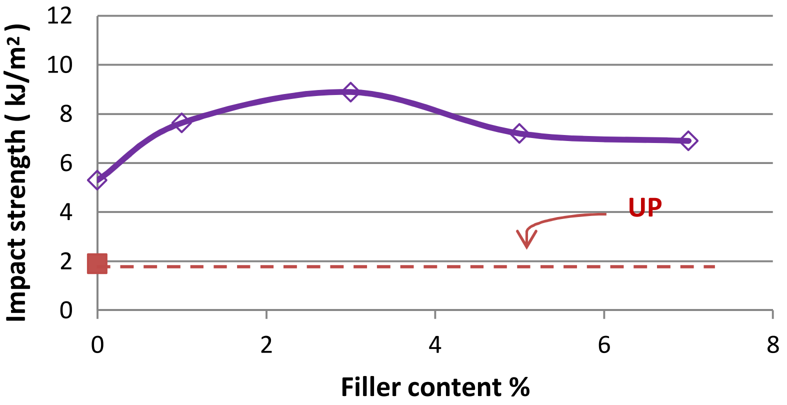


Figure 4. Effect of TiO_2 content on the impact strength of blend

3.3 Hardness Test

Composite material supported by particulate does not depend only on the properties of components, but also depends on the nature of the interface between the components and the weight fraction [19]. The reinforcement of blend UP-8% PS with TiO_2 particles has a great role in obtaining a higher hardness. Figure 5 illustrates that the hardness increases with increasing volume fraction. Adding the filler particles will raise the materials hardness due to the increasing in material resistance against the plastic deformation. Results reveal that the hardness of blended polymers alone is 60 shore D compared to the maximum value of 74 shore D when particles at volume fraction of 7% have been added. The main reason for increase in hardness of composites with increasing filler content is the fact that particles as an element are harder than the matrix. In general, the addition of TiO_2 particles to polymer matrix significantly increases the mechanical properties, particularly modulus and hardness, of the composites if the particles are strongly bonded to the polymer matrix [20].

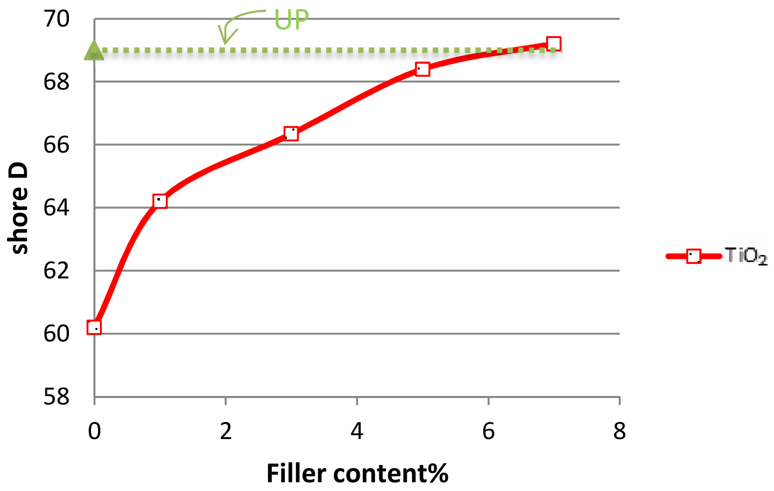


Figure 5. Effect of the filler content on the hardness of composites

3.4 Morphology of fracture surfaces

The fractured surfaces of impact specimens were examined using scanning electron microscope (SEM). The UP shows smooth, glassy fractured surfaces with ripples (Figure 6). The relative smoothness of the fractured surface, irrespective of the presence of few shear deformation lines, indicates that no significant plastic deformation had occurred. The morphological development during cure can be correlated with the impact behavior. The ripples are due to the brittle fracture of the network, which accounts for its poor impact strength, as there is no energy dissipation mechanism operating here, as mentioned by Ramakrishna H. V. [21].

But the fractured surface of the modified UP, (Figure 7) clearly shows two distinct phases a continuous UP matrix and the dispersed PS phase. This heterogeneous morphology results opacity in samples. The particles are uniformly distributed throughout the matrix. This distribution of smaller particles is responsible for lower crack growth in these specimens which is indicated by the presence of relatively large number of deformation lines. Also, the fracture surfaces, unlike that of UP, are not very smooth, indicative of a ductile manner of fracture.

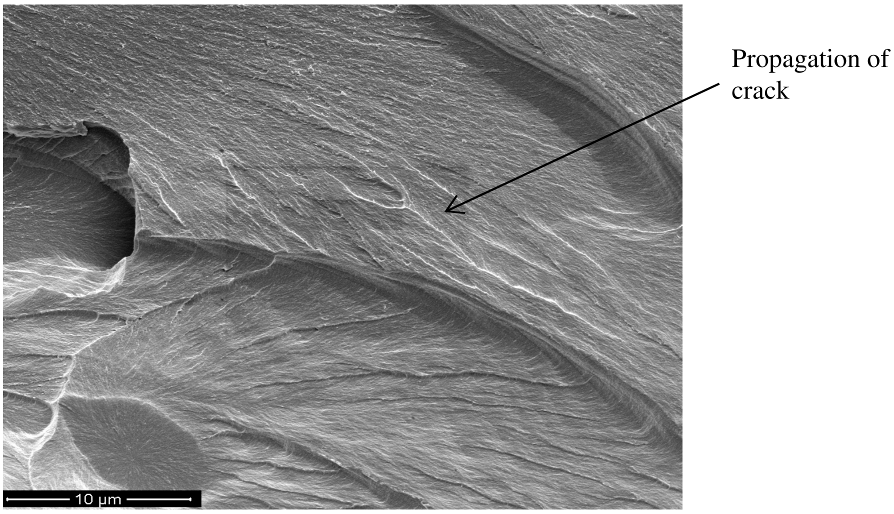


Figure 6. SEM micrograph of the fracture surface of the UP

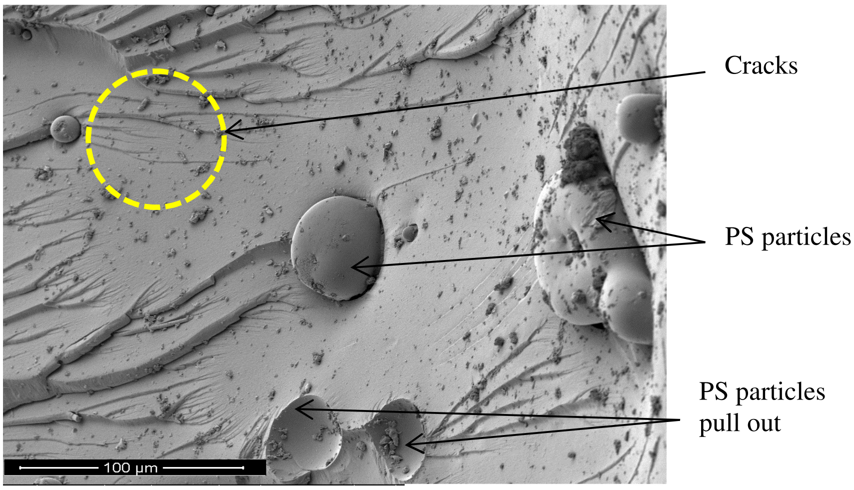


Figure 7. SEM micrographs of the fracture surface of the blend

According to Albdiry M. T. and Harry Ku [22], the amount of deformation lines is proportional to the increase in toughness of the material. Relatively distorted shape of PS domains in these cured resin matrices is supposed to be attributed to higher amount of plastic deformation. The deformation lines are propagated through PS domains, promoting stress transfer between the particles and UP matrix.

In order to operate the yielding process throughout the matrix, a homogenous distribution of smaller particles is necessary. This morphological structure is believed to be responsible for the highest impact performance of modified UP. Thus distributed PS particles act as stress concentrators and exhibit highest impact strength than unmodified UP. The presence of dark voids indicates the filler pullout from the blend matrix.

However, the introduction of TiO_2 particles into the blend is associated with better absorbing of energy, leading to localized shear yielding. Similarly, the appearance of isolated shear bands is referred to as an energy absorption mechanism accompanied by better plastic deformation in the failure mode of polymer having a second phase [23]. Furthermore, the addition of filler into the blend results in particle pinning of the crack (Figure 8) leaving behind tail-like structure.

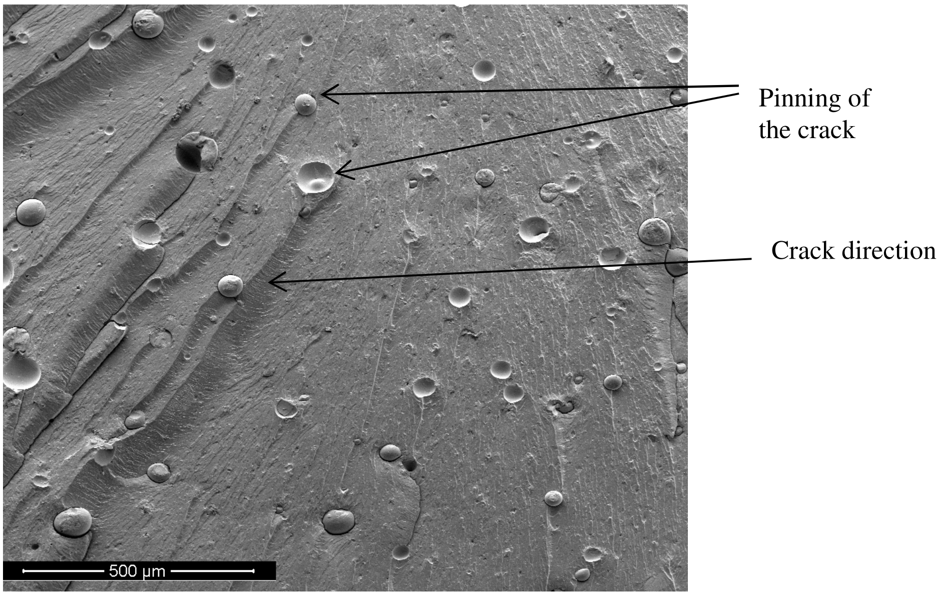


Figure 8. Scanning electron microscope examination of 1% TiO_2 composite

The impact fracture surface shows the differences between the fracture surfaces of the blend in Figure 7 and the fracture surface of the composite in Figure 8. The blend surface exhibits relatively smooth behavior with directional fracture propagation, while the composite surface shows various directions of crack propagation due to the interruption of fillers which cause the surface to be rough.

Qualitative investigation of Figure 9 shows that the presence of the particles reflects itself with significant increase in the roughness of the impact fracture surface surrounding the fillers, as previously noted by Ramakrishna H. V. [16], further increase in surface roughness occurs as filler volume fraction increases.

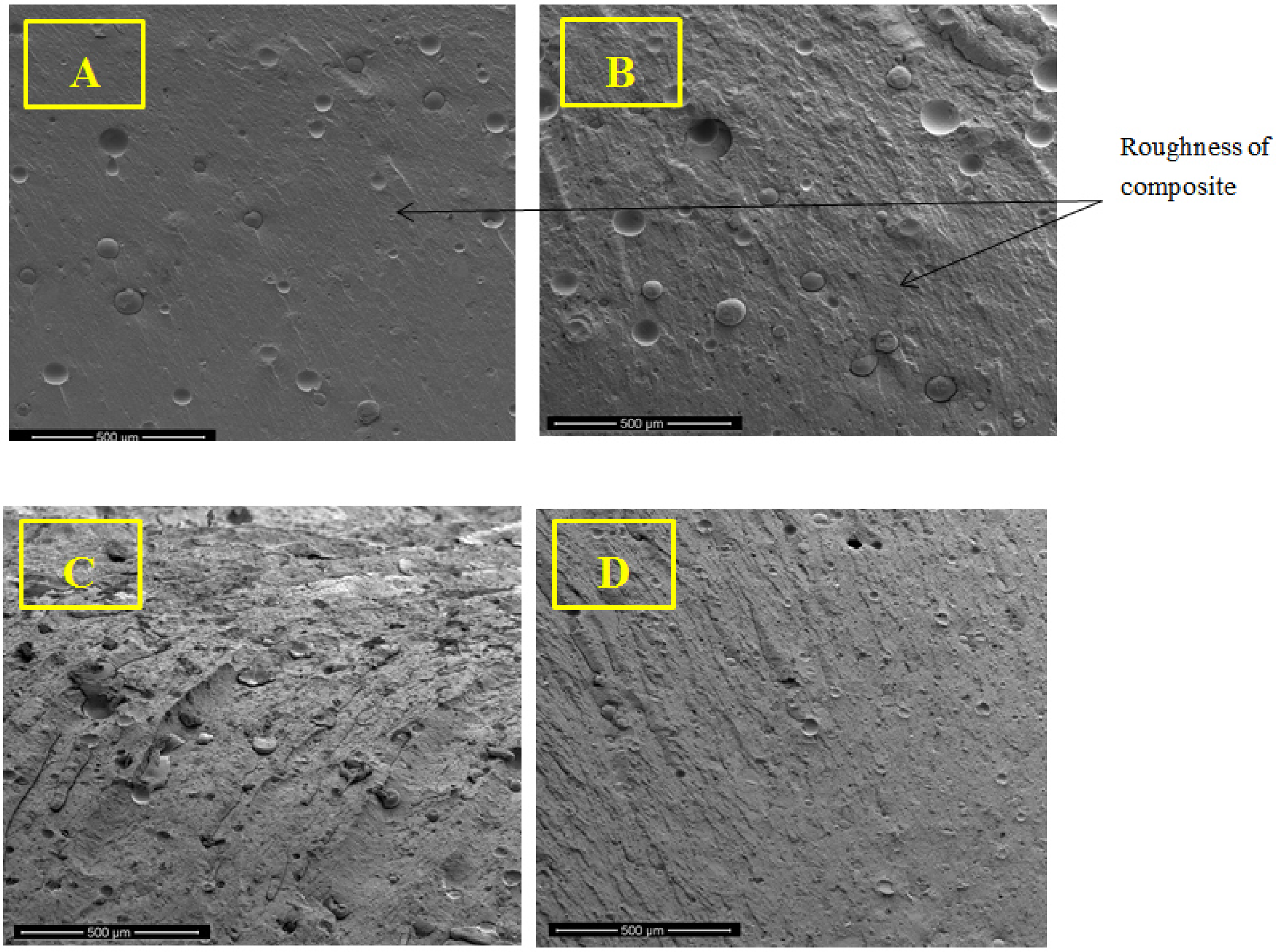


Figure 9.SEM image of composite reinforced with (a) 1%TiO_2 (b) 3%TiO_2 (c) 5%TiO_2 and (d) 7%TiO_2

4. Conclusions

Based on the results obtained and discussed previously, the following conclusions can be drawn

1. Modifying unsaturated polyester with PS decreases the compression strength and hardness while improving elongation and impact resistance. The best mechanical results are obtained when 8% percentage of PS is blended with unsaturated polyester.
2. Reinforcing the blend with TiO_2 improves the compression strength, impact resistance and hardness. The best mechanical results are obtained when 1% and 3% percentage of TiO_2 reinforce blend. They have balancing effect to compensate the PS reduction in mechanical properties.
3. SEM observation of the fracture surface show a noticeable roughness when TiO_2 was added. SEM images show that particles disperse well when their percentage ranges from 1% to 3%, while increasing their percentage causes agglomeration.

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