



## Properties of Oil Shale Ash Filled Polypropylene Composite Material: Mechanical and Physical Characterization

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Received: 21 May 2021;

Accepted: 16 July 2021;

Published online: 20 August 2021;

AJC-20481

The outcome of oil shale ash (OSA) filler addition on the mechanical, morphological, thermal and water uptake properties of the polypropylene (PP) matrix was investigated. The test specimens were prepared with various ratios of the mixtures that contain OSA and polypropylene in the following weight percentages: 0%, 10%, 20%, 30% and 40% OSA in polymer matrix. Composites specimens were produced by using a co-rotating twin screw extruder and a thermal press machine. The properties of the polymer composite specimens were characterized by using a universal testing machine (WDW-5) and izod impact testing machine (FI-68). The morphology of the composite samples was also characterized by using the scanning electron microscopy (SEM). Impact strength and Young's modulus of the OSA/PP composite formulations were consistently improved on OSA inclusion. On the other hand, addition of OSA to pure polypropylene had consistently reduced the tensile stress at yield, tensile stress at rupture, tensile strain at yield and tensile strain at break. Adding OSA to polypropylene decreased the maximum flexural stress and flexural strain of maximum force. The observed SEM confirmed that the addition of OSA to pure polypropylene resulted in a significant increase in its agglomerates and filler pullout. Differential scanning calorimetry (DSC) results confirmed the addition of the OSA to pure polypropylene resulted in a significant decrease in normalized heat of crystallization, normalized enthalpy of melting. Where the degree of the crystallinity ( $X_c$ ) of polymer composite decreased from 59% to 34% for 0% and 40% OSA addition, respectively. While melting temperature ( $T_m$ ) of the composite did not change (167 °C) the crystallization temperature ( $T_c$ ) increased from 116.6 °C to 127.1 °C for 0% to 40% OSA addition, respectively. Water uptake, however, demonstrated different behaviour. The initial addition of OSA to polypropylene increased the water uptake property up to 4% for the 40% filler addition. The results of this study demonstrated that the OSA could be used as reinforcement material for polypropylene, as long as good mechanical properties and homogeneous morphology obtained.

**Keywords:** Oil shale ash, Polypropylene, Composite material.

### INTRODUCTION

Polypropylene (PP) is a partially crystalline, non-polar thermoplastic polymer and considered the second most produced plastic commodity after polyethylene [1,2]. Polypropylene has good mechanical, high thermal and dimensional stability, relatively low cost and excellent recycling property. These attributes have given polypropylene its utility in many long-life commercial applications [3]. However, due to low biodegradability of polypropylene creates a serious environmental problem. A wide variety of morphological structures of polypropylene can be achieved with the use of fillers or reinforcing agents leading to more desirable properties. Among the reinforced types of polypropylene are elastomers modified filled polypropylene and filled polypropylene [4].

Oil shale is a sedimentary rock contains great quantities of kerogen. Kerogen is a forerunner for the formation of petroleum, oil shale yields considerable quantities of oil and combustible gas upon distillation. Oil shale may hold between 60 and 90% mineral matter [5] and also serves for oil production, power generation [6,7], cement production and widely use in chemical industries at Estonia, Germany, Brazil and China [8,9]. Oil shale is a promising source of energy in Jordan where more than 50 billion tons of deposits have been discovered [10]. By the end of 2020, it is anticipated to generate energy from oil shale burning in Jordan [11].

Oil shale ash (OSA) is produced after the process of burning oil shale. This ash is composed of inorganic (minerals) and organic compounds (char), which classified as coke-ash residue. This ash is classified as a harmful and hazardous waste to the

environment [12-14]. Ahmad & Mahanwar [15] studied the mechanical properties of fly ash filled high density polyethylene. They observed that the mechanical properties were improved with fly ash addition. Liu *et al.* [16] investigated the rheological and mechanical properties of the blends of the polyethylene and the modified oil shale ash (MOSA). While the yield strength of the blends increased, its elongation at break decreased. Gummadi *et al.* [17] evaluated the flexural properties of the fly ash filled polypropylene composites and found that fly ash as a good filler for polypropylene matrix composites, which improved both flexural strength and flexural modulus. VinayKumar [18] investigated the effect of some organic and inorganic filler on the physical properties of low density polyethylene (LDPE) composites and found that the tensile strength of LDPE significantly increased with the addition of fly ash.

The aim of this study was to reduce the consumption of the neat synthetic polypropylene and to decrease the impact of oil shale waste on the environment by compounding of both components into a useful composite material. The variations of the tensile, flexural and impact strength and water absorption as a function of oil shale ash (OSA) content of OSA/PP polymer composite were investigated. Moreover, the morphological and the thermal properties and water uptake were also reported in this study.

## EXPERIMENTAL

The composites were prepared using polypropylene, which was purchased from TASNEE PP (H4120 PM2371202) as the polymer matrix. This polypropylene has a density (0.9 g/cm<sup>3</sup>) with a melt flow rate 12 g/10 min. Local oil shale was obtained from the mining station in the central part of Jordan.

**Preparation of oil shale ash :** The OSA used in this research was obtained by burning oil shale at 600 °C for 2 h on the laboratory scale. No additional processing was performed on the OSA other than grinding into a fine powder; the grinding was performed with a Pulverisette 9 vibrating cub mill (Fristch, Germany). In order to reduce moisture content of the powder particles to 1.5% or below, OSA was oven dried for 24 h at 103 °C. The average particle size obtained by dry sieving was in the range of 63-106 µm. Dried OSA was then kept for further processing.

**Composite sample preparation:** The OSA was mixed with polypropylene using a co-rotating twin screw extruder (TSE 20, L/D: 40:1, diameter 22 mm) having temperature range of 195-220 °C. The screw speed was 60 rpm. The weight percentages of the input formulations of polypropylene and OSA are given in Table-1. By using an aluminum mold with (L: 63.5 × W: 6.4 × T: 12.7 mm) the impact strength test samples were prepared. Multiple sheets having surface area of 30 mm × 20 mm × 2 mm were prepared by using a stainless steel mold in a compression-molding machine (XH-406B). With an ASTM D-638 type IV specimen die, the tensile test samples of standard dumbbell shape were cut out from the composite sheets. The flexural test samples were prepared by using an iron mold of 200 mm × 10 mm × 4 mm dimensions.

**Mechanical characterization:** The composite samples to be analyzed were stored at 25 °C and 25% relative humidity

TABLE-1  
FORMULATION OF THE OSA/PP COMPOSITES

Composite (OSA/PP)	0%	10%	20%	30%	40%
PP (wt.%)	100	90	80	70	60
OSA (wt.%)	0	10	20	30	40

for 15-20 days. Samples were then examined using a universal testing machine (WDW-5). It was operated at the rate 1 mm/min. Tensile strength and Young's modulus were analyzed using dog-bone specimens according to ISO 257. The flexural test samples were measured according to BS EN ISO 178:2003. Unnotched IZOD impact strength was measured according to ASTM: D256 using impact testing machine (FI-68) at an impact speed of 3.5 m/s. The results were obtained from the average of at least 5 samples.

**Water absorption test:** The water absorption of the composite disk samples (50 mm diameter and 3.4 mm thickness) were conducted according to the standard ASTM D570. Samples were immersed in distilled water at 25 °C then removed, wiped with tissue paper and weighed on daily basis for 30 days after which the water absorption percent was calculated accordingly to eqn. 1:

$$\text{Water absorption (\%)} = \left( \frac{M_t - M}{M} \right) \times 100 \quad (1)$$

where M and M<sub>t</sub> stand for dry weight of the sample and the weight of the immersed sample at specific time, respectively.

**Scanning electron microscopy (SEM):** SEM was used to study the distribution of OSA in OSA/PP composite material. The prepared sample was examined by (FEI Quanta 600) at an acceleration voltage of 25 kV.

**Differential scanning calorimetry (DSC):** DSC analysis was performed according to (ASTM E 473-85) in a NETZCH DSC 204 Phoenix® ASC. The test specimens weighing about 11-15 mg in an aluminum crucible were heated up to 200 °C with the heating rate of 10 °C/min and kept at this temperature for 3 min. Then the specimens were cooled down to -50 °C with the cooling rate of 10 °C/min and kept for 3 min. Subsequently, the non-isothermally crystallized specimens were reheated up to 200 °C with the heating rate of 10 °C/min. All heating-cooling runs were carried out under nitrogen atmosphere at a flow rate of 50 mL/min to prevent oxidation of the specimens. The degree of the crystallinity (X<sub>c</sub>) was determined from the melting enthalpy values using eqn. 2:

$$X_c = \left( \frac{\Delta H_m}{\Delta H_o} \right) \times 100\% \quad (2)$$

where, ΔH<sub>m</sub> is melting enthalpy of the specimens (J/g), ΔH<sub>o</sub> is the enthalpy value of melting of a 100% crystalline form of polypropylene (209 J/g).

## RESULTS AND DISCUSSION

**Impact and tensile properties:** The impact strength is the resistance of a material to sudden stress such as a hammer blow. The impact strength of a given material is determined by several characteristics including the filler nature, composite matrix, bonding strength, the shape of material and the filler

distribution inside the polymer composite [19]. Fig. 1 shows the raw data results with regard to the measurements of the unnotched izod impact strength in J/m of the manufactured OSA/PP composite samples of different filler proportions. A higher impact strength suggests that the energy absorbed by the specimen has raised and its toughness also increased. It was observed that the addition of OSA at 10% loading level increased the impact strength by several folds compared to that of neat polypropylene polymer. This can be attributed to the presence of the hard and strong inorganic filler within the polypropylene polymer matrix which agreed well with the published work [20,21].

The tensile stress and stain behaviour of the OSA/PP composite with different filler's weight percentages are given in Fig. 2a-d. All four measured stress and strain characteristics

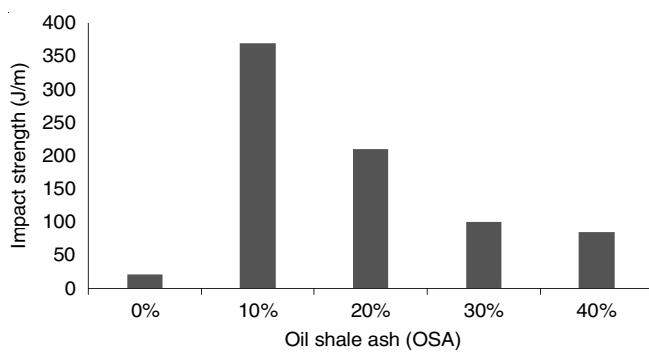


Fig. 1. Impact strength of the OSA/PP composite with different compositions

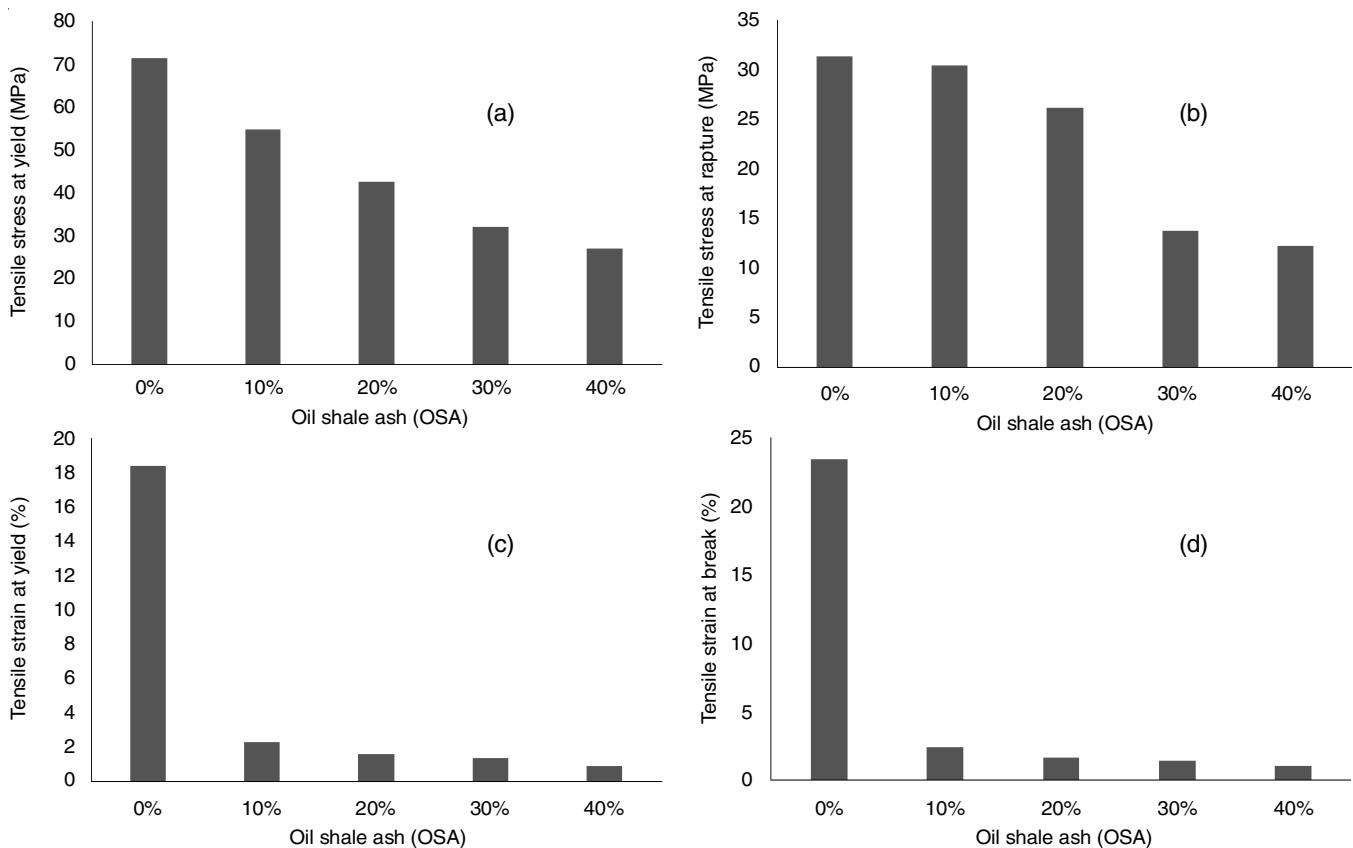


Fig. 2. Mechanical properties of the OSA/PP composite with different compositions: (a) Tensile stress at yield, (b) Tensile stress at rupture, (c) Tensile strain at yield, (d) Tensile strain at break

of the samples decreased with the addition of OSA. These characteristics include: tensile stress at yield (Fig. 2a), tensile stress at rupture (Fig. 2b), tensile strain at yield (Fig. 2c) and tensile strain at break (Fig. 2d). A systematic decrease in these characteristics were observed as filler contents with high volumes incorporated into the polypropylene matrix. The OSA filler agglomeration and the poor dispersion into the polypropylene matrix had a significant impact on the mechanical performance of the composite. The incorporation of the ash to the polypropylene led to more brittle and weaker material, as the tensile strength at break significantly decrease. This effect was more pronounced as ash content increased. In addition, the loss of strength could be attributed to the lack of the interfacial adhesion between polypropylene and OSA. The poor tensile stress and strain may attribute to the particle debonding from the matrix before yielding point as a result of the poor interfacial adhesion, these results were in agreement with the work of Pardo *et al.* [22].

Young's modulus is the ratio of stress to strain [23]. Fig. 3 shows the raw data results with regard to the measurements of Young modulus of the OSA/PP composite samples with various filler proportions. As shown in Fig. 3, the Young's modulus exhibits a different behaviour, which was consistent with the obtained stress and strain characteristics. A significant increase was observed with the addition of OSA, the observed increase in the Young's modulus is due to the greater rigidity of the composite caused by the filler content. Higher filler content led to both higher yield strength and Young's modulus. It is

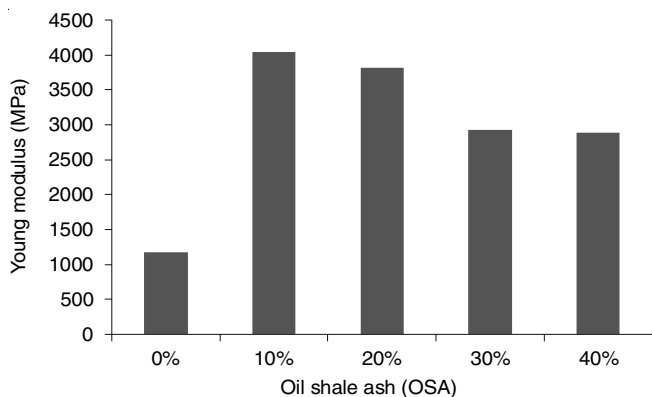


Fig. 3. Young's modulus of the OSA/PP composite with different compositions

possibly that the greater decrease in tensile strain at yield compared to the small decrease in stress at yield of OSA/PP composite is the reason for greater modulus values, where similar results is also confirmed by Huang *et al.* [24].

**Flexural properties:** The flexural strength is the greatest stress of a substance can opposed before yielding and describes how much force is required to fracture a test sample of a given diameter in flexural test [25,26]. Fig. 4a-c show the raw data results with regard to the measurements of maximum flexural stress (Fig. 4a), the flexural stain at maximum stress (Fig. 4b) and flexural modulus (Fig. 4c) of the manufactured OSA/PP composite samples of different filler contents. The pattern is correlated to what have been seen in previous tensile tests. Where the addition of OSA to polypropylene decreased gradually the maximum flexural stress and strain and slightly decreased the flexural modulus.

As shown in Fig. 4a-c, the measured maximum flexural stress, strain and modulus of all OSA/PP composite samples decreased with the addition of OSA. It was observed that the flexural strength decreased because of the particle agglomeration at higher filler contents. Particle agglomeration tends to reduce the strength of a material because the agglomerates are considered as weakness points in material and break easily when a stress is applied to them, these results were also comparable with Gumjadi *et al.* [17] work.

**Scanning electron microscopy (SEM):** The morphology of a material, its internal structure and the distribution of fillers in a polymer matrix was visualized by SEM. The interaction between OSA and polypropylene matrix has great influence on the mechanical properties of the composite. A composite with a better filler/matrix interaction can result in good overall

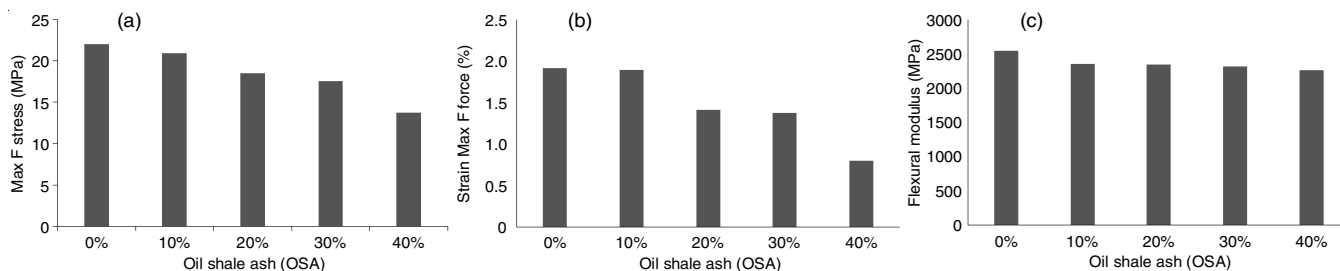


Fig. 4. Flexural properties of OSA/PP composite with different compositions: (a) Maximum flexural stress, (b) Flexural strain of maximum force, (c) Flexural modulus

performance. Fig. 5 represents the morphology of pure polypropylene which apparently showed regular plain surface shapes.

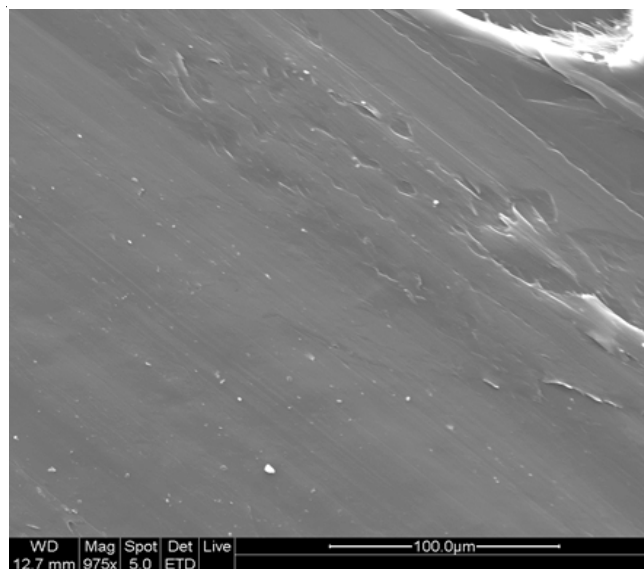


Fig. 5. SEM micrograph of the pure polypropylene

The fractured surfaces of the OPA/PP polymer composites are presented in Fig. 6a-d. The morphology of the filler at low percentage (10% OSA) (Fig. 6a) slightly differs from that of neat polypropylene polymer (Fig. 5). The low level pullout and the formation of some agglomerates was observed which reflects a relatively low tensile stress performance of the polymer composite compared to that of the neat polypropylene. It was thus observed that the agglomerates and filler pullout increased measurably with the addition of OSA filler to the polypropylene polymer matrix (Fig. 6b-c). The highest increase in the agglomerates was seen when 40% OSA was added to polypropylene (Fig. 6d). Increasing the ash content increased agglomerates and filler pullout followed by the development of matrix micro voids, where similar results were obtained by Lin *et al.* [20].

**Differential scanning calorimetry (DSC):** DSC enables the determination of melting and crystallization temperatures and the corresponding enthalpy of melting and heat of crystallization [27]. All mentioned parameters for neat polypropylene and OSA/PP composites extracted from DSC thermograms are summarized in Table-2. The melting temperature ( $T_m$ ) of polypropylene, 166.4 °C, insignificantly affected by the addition of OSA to the polymer composite matrix. The normalized

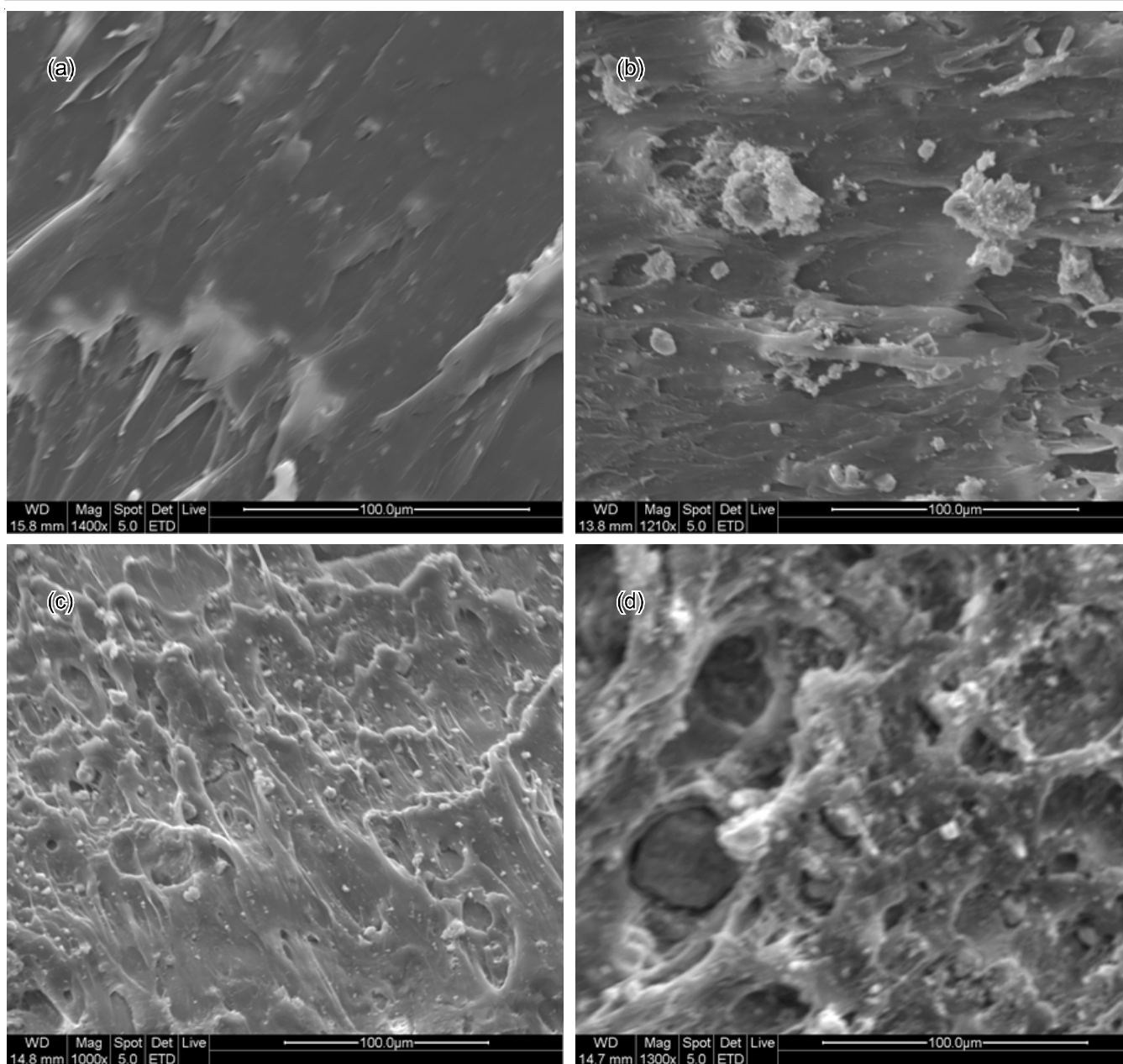


Fig. 6. SEM micrographs of the OSA/PP composite at different compositions: (a) 10% OSA, (b) 20% OSA, (c) 30% OSA and (d) 40% OSA

melting enthalpy ( $\Delta H_m$ ) of OSA/PP composite decreased from 123 J/g for neat polypropylene to 71 J/g for 40% OSA filled polymer composite. The reduction in melting enthalpy values can be explained by the decrease of the crystallinity of the polypropylene due to the filler addition which inhibited the crystallization process because of the limited polymer chain mobility. The heat of crystallization ( $\Delta H_c$ ) and the temperature of crystallization ( $T_c$ ) of pure polypropylene and OSA/PP composites with different weight percentages are shown in Table-2. The crystallization temperature ( $T_c$ ) of polypropylene, 116.6 °C, shifted to 118, 120 and 127 °C when 20%, 30% and 40% OSA were added to the OSA/PP composite, respectively. This indicates that the crystallization of OSA/PP composite material on cooling process, initiated earlier upon adding OSA filler to the polypropylene matrix. We believe that OSA acts as a nucleating

Composite type	Normalized $\Delta H_c$ (J/g)	$T_c$ (°C)	Normalized $\Delta H_m$ (J/g)	$T_m$ (°C)	$X_c$
Pure PP	133	116.6	123	166.4	59
OSA/PP (10%)	115	118.1	110	167.2	53
OSA/PP (20%)	89	117.7	87	166.3	42
OSA/PP (30%)	82	120.5	79	167.4	38
OSA/PP (40%)	71	127.1	71	167.5	34

sites and promotes rapid polymer crystallization but did not develop the crystal size as proved from the percent of crystallinity calculation which decreased on OSA filler addition.

The normalized heat of the crystallization ( $\Delta H_c$ ) of OSA/PP composite decreased from 133 to 71 J/g when 0% and 40%

OSA was added to the OSA/PP composites, respectively. The decrease in  $\Delta H_c$  may attributed to the OSA filler which inhibited crystal growth.

**Water absorption properties:** The water absorption of the OSA/PP composite material as a function of time is shown in Fig. 7. Small incremental increases in water absorption were often observed at first days of immersion then regularly slowed down until saturation was reached after 30 days in most cases. Pure polypropylene showed a very small water absorption, 0.17%. Whereas, the addition of 40% OSA showed the highest water absorption 3.98%. It was observed that the water absorption increased measurably with the addition of OSA filler to the polymer. Increasing the ash content increased water absorption, the OSA filler addition possibly causes the development of micro voids in polymer matrix. The continual hydration process caused changes in pore size magnitude and water absorption, concurrently. Thus, pure polypropylene has virtually negligible water absorption compared to that of OSA/PP composite samples, the results were matched with the reported values [19,28,29].

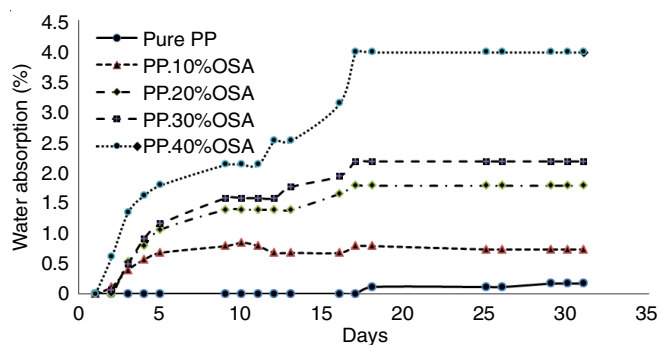


Fig. 7. Water absorption of the OSA/PP composite with different compositions

## Conclusion

The composite materials containing the oil shale ash (OSA) added to a polypropylene matrix were prepared. The investigation of the impact of the OSA filler on the mechanical, morphological, thermal and water uptake properties of the polypropylene matrix composite was studied. Reducing the cost of the polymer composite production and improving its properties by using oil shale waste led to preservation and reduction of the waste in the environment. The experimental results comparing pure polypropylene to OSA/PP composite showed an increase in the measured properties of the impact strength, tensile young's modulus and water uptake. The impact strength tests revealed that the addition of the OSA filler significantly improved the impact strength of OSA/PP composite material. The tensile stress at yield, tensile stress at rupture, tensile strain at yield and tensile strain at break measured characteristics of the samples decreased with the addition of OSA. All these decreases can be attributed to the agglomeration and the poor dispersion of the OSA filler in the polypropylene matrix. The Young's modulus exhibits a different behaviour from the above for the stress and strain characteristics. A significant increase was observed with the addition of OSA is possibly

due to the greater rigidity of composite. Higher filler content led to higher yield strength and an increase in the Young's modulus. The observed water uptake confirmed the insignificant water absorption property of polypropylene, thus demonstrating its hydrophobic nature. The addition of OSA to pure polypropylene resulted in some increase in its water absorption. The SEM micrographs confirmed an increase in filler agglomerates and filler pullout of OSA/polypropylene composite. Finally, DSC results confirmed a significant decrease in the degree of the crystallinity ( $X_c$ ) of the composite.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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