

Mechanical Properties of *Eobania vermiculata* (Müller) Shell Powder Polypropylene composites

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ABSTRACT

This research paper is focusing on the mechanical properties of polymer / *Eobania vermiculata* (EV) shell powder composites. The samples used in this work were prepared through melt compounding, using Polypropylene (PP) doped with *Eobania vermiculata* shell powder (EVSP). PP/ EVSP composites were prepared at different concentration of EVSP in PP composites at 1wt% to 5wt% by using a Plastograph-Mixer through twin-screw extruder. XRD examination did not show any change in the degree of crystallinity. It was found that the EVSP have a good dispersion inside the polymer matrix as examined by using SEM. By using the DSC, it was found that there was no significant change in the melting point of the prepared samples. On other hand, the thermal stability decreased by increasing the EVSP concentration in the PP/ EVSP composites, as seen from TGA examination. The mechanical properties have been improved by adding EVSP inside the PP matrix. Both the modulus of elasticity (M_E) and the maximum stress (σ_p) of PP/EVSP was found to have a peak value at 3 wt%.

Key words: Land snails; polymer composites; mechanical properties, waste management

Introduction

Gastropod animals belong to phylum Mollusca, those can be considered the third most important after vertebrates and arthropods. Snails are gastropod animals which live in marine and fresh water, but others have successfully colonized land and known as pests in many places of the world. Some of land snails are very important pests of agricultural crops, in addition to the role as intermediate hosts for many parasitic diseases which infest human, animals and birds (Goden, 1983; Barker 2002 and Mahrous *et al.*, 2002).

Eobania vermiculata is a land snail which can be considered as a harmful agricultural pest and can cause great damage to many species of plants (Notton, 2006). These useless and harmful land snails in many places are collected and burnt. These agricultural pests can be used as useful materials. The land snails are used in many useful food industries for other animals such as poultry and fishes. On the other hand, the shells of these snails are ground and used in many industries such as a filler or/and reinforcing materials in the concrete and polymers

The agricultural wastes are enormous and often constitute environmental menace. The most of these wastes are coming from the crops residual wastes which in many cases are burnt in the harvest seasons, which is very harmful for the environment. Recently, most of these agricultural wastes are used in industry for reinforcement and filler materials in plastics industry. Wood polymer composites are very promising industry in last two decades. After minor treatments, different lignocellulose coming from maize stems and hulls, rye straw, rice straw and husk, banana bundles, switch grass, wheat straw, sorghum stems and leaves, pineapple, coconut, nettle, velvet, empty palm fruit bunch, hemp, flax, kenaf, cotton, soy hulls ...etc. have been used in wood polymer composites .

Over the last decade, polymer composite materials attracted attention of the researchers because of their promising physical properties, and can be used in many applications (Advani, 2007 and Park *et al* 2004). Therefore, enormous effort has been exerted to develop polymer/ceramic composites. The ceramics powder changes the physical and the mechanical properties of the host polymer dramatically by using small quantities of the nanofillers. These polymer composites have unexpected thermal and mechanical properties, e.g. more thermal and dimension stability, flame resistance, higher modulus...etc. (Advani 2007). On other hand, still many difficulties to create such a homogenous polymer/clay composites such as the preparation processes and how to make good dispersion of the ceramics powder inside the hosting polymer. Many techniques to produce the polymer/ceramics powder composites have been devolved.

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There are three most suggested methods, in situ polymerization, the solution cast method, and melt intercalation. Among the preparation methods, melt intercalation is considered to be the most promising approach for the fabrication of composites because of its versatility, its compatibility with polymer-processing equipment, and its environmental friendliness because of the absence of any solvent (Park *et al.*, 2004).

In recent years, there has been much interest in the developments of polypropylene (PP) composites to improve the properties of this low cost, commodity polymer by reinforcement materials. Mixtures of PP and different types of ceramics have been prepared with a significant improvement in mechanical, flame retardant and barrier properties compared with the pure PP. These enhancements have been obtained with only low ceramics powder loading, typically in the range of 1-10 wt%. Therefore, the PP / ceramics powder so-called PP/ ceramics powder (PPCPs) are regarded as promising new materials in many industrial fields (Advani, 2007).

In the light of the research, this study aims to use the snail shells in polymer industries as reinforcement materials. Then, the study extends to investigate the effects of *Eobania vermiculata* shell powder (EVSP) on the morphology, thermal and mechanical properties on Polypropylene. Extrusion process is the melt blending method to produce the nanocomposites.

Experimental Technique

Materials

PP was supplied from Sidpec egyptene, Alexandria, Egypt, stearic acid as a lubricant and DOP as a plasticizer were used to prepare PP/Snail shell powder. Empty shells of *Eobania vermiculata* were collected by hand from different plants, under the herbs and beside the plants and canals and transported in white cloth bags to Zoology laboratory of Plant Protection Department, Faculty of Agriculture, Benha University. The empty shells were full sun dried for one week, then cleaned carefully and dried in oven at 80 °C for 2hrs. After that, the shells were grind by WiseMix Ball in the Faculty of Science, Benha University. The powder was sieved by 212 µm sieve.

Samples preparation

The PP/ EVSP composite was melt-blended at 170 °C for 10 min and at a speed of 90 rpm at different concentrations (0%, 1%, 2%, 3%, 4%, 5% wt%) of EVSP, DOP as a plasticizer and stearic acid as a lubricant then putting the result in a hot mold (dog bone) in a hot piston at 170 °C at pressure of 10 MPa for 10 min.

Measurements

X-Ray diffraction (XRD) analysis was carried out with (SHIMADZU X-Ray Diffractometer 6000, 60 KV, 80 mA, Cu-X-ray TUBE). For polymer composites, XRD can be used to examine the influence on the crystallinity caused by adding filler. The surface morphology of these polymer electrolytes was observed using JEOL JSM 5600 LV SEM. Thermogravimetric (TGA) data were obtained by using thermogravimetric analyzer pyres 6 TGA perkin Elmer at a heating rate of 10.0°C/min, under N₂ (20 ml/min) flow. The range investigated from 10 to 600°C. Perkin-Elmer DSC-7 power compensation differential scanning calorimeter (DSC) was used to measure the absorbed and the released heat. Tension tests were determined by using mechanical testing machine type HT-9112 which was supplied by Hung-Ta Instruments Co. LTD, Taiwan.

Results and Discussion

X-ray diffraction studies

Representative X-ray diffraction pattern of PP/EVSP composites is presented in Fig.1 (Papageorgiou *et al.*, 2012). One can see that there is an obvious peaks at $2\theta=30$ and $2\theta=50$ reference to EVSP and there is no significant change of the peaks with the change of EVSP concentrations (Singh and Purohit, 2011).

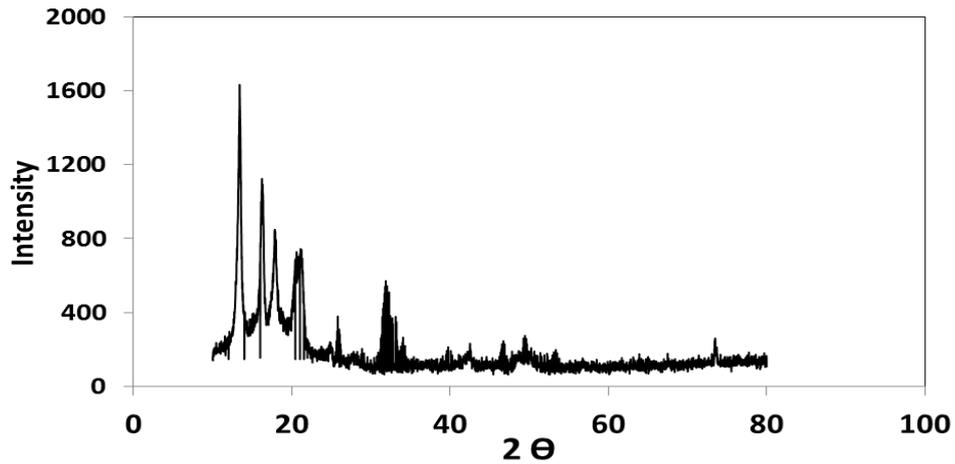


Fig. 1: XRD of different concentrations of PP/EVSP composites

Observation of morphology of the composites

The morphologies of the PP/EVSP composites were observed using scanning electron microscopy (SEM). Fig. 2 shows the SEM image for PP/EVSP composites at concentration 3%wt of EVSP. The EVSP has good dispersion inside the matrix and dispersed homogeneously in the polymer matrix and having single structure morphology (Muthiah *et al.*, 2015).

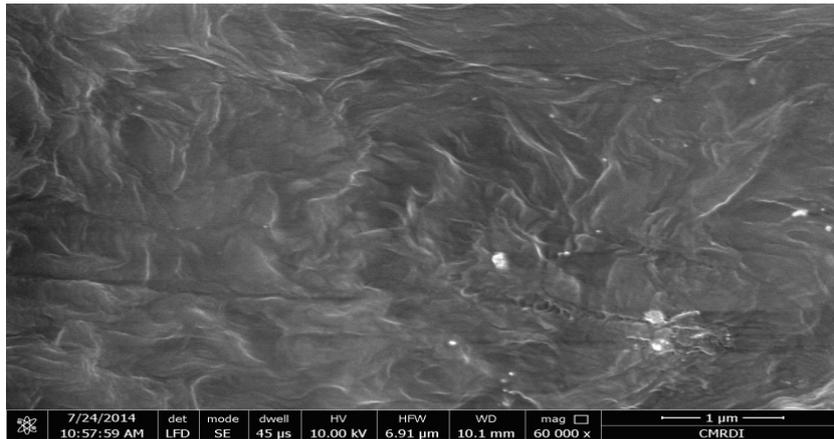


Fig.2: SEM image for PP/EVSP composite at concentration 3%wt of EVSP

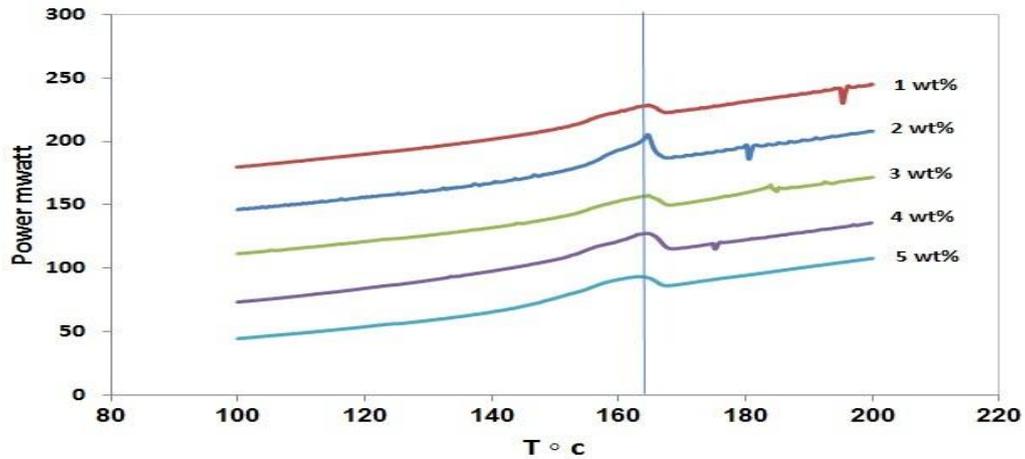


Fig. 3: DSC of different concentrations of PP/EVSP composites

From the DSC analyses of PP/EVSP composites during heating it is possible to determine the melting point, level of crystallinity and the presence of different phases in semicrystalline polymers. As shown in Fig.3, the melting temperature of PP was not influenced by the incorporation of EVSP particles. On the other hand, from this figure, it is possible to see that for the composites with EVSP content of all studied samples, there is a second peak around 157 °C, representing β phase of PP. The formation of β phase in the presence of inorganic fillers is a result of the nucleation effect of the filler in the matrix crystallization process. Moreover β phase is known to be tougher than α phase due to β - α polymorphic transition (Chen *et al.*, 2002 ., and Li *et al.*, 1999) and some authors attributed this to the presence of the metastable phase to the higher toughness of PP/filler composites (Furukawa *et al.*, 2006) .

The degree of crystallinity ($\%_{cryst}$) of the samples was calculated from the melting enthalpy results (ΔH_m) of each sample using Equation (1), X_{PP} is the mass fraction of the PP in the samples, (ΔH_m) is the experimental melting enthalpy and ΔH_m^0 is the melting enthalpy for 100% crystalline PP, (207.1 J/g) (Fitaroni *et al.*, 2015).

$$\%_{cryst} = \frac{\Delta H_m}{X_{PP} \Delta H_m^0} \times 100 \quad \dots\dots\dots (1)$$

The results for the samples studied are summarized in Table 1.

Table 1: DSC Characterization of polypropylene samples

Sample (EVSP content)	ΔH_m (J/g)	T_m °C	T_c °C	T_{onset} °C	Crystallinity (%)
PP 1%	36.24	164.3	142.06	153.8	17.7
PP 2%	55.74	164.6	141.4	160.3	27.5
PP 3%	130.6	164.6	148.8	141.2	65
PP 4%	48.3	164.2	127.16	145.9	24.3
PP 5%	60.02	162.7	138.6	144.2	30.5

From Table 1, one can see that, the T_m , T_c and T_{onset} didn't change, i.e are independent on EVSP concentration. On the other hand, the ΔH_m and crystallinity percentage of PP/EVSP composites increase gradually by increasing the EVSP concentration up to 3 wt% then decrease again.

Fig. 4 shows TGA of PP/EVSP composites, one can see a single step weight loss in the temperature ranged from 15 to 600 °C. Very low stable loss in weight of 10 % for all samples is up to 340 °C. This weight loss can be attributed to the dehydration of the samples. Then it does lose its weight of 90% in the temperature span of 362 to 490 °C. This main mass loss could be due to the decomposition of the PP and CO and CO₂ release. The plain PP/EVSP composite is completely decomposed after 500 °C.

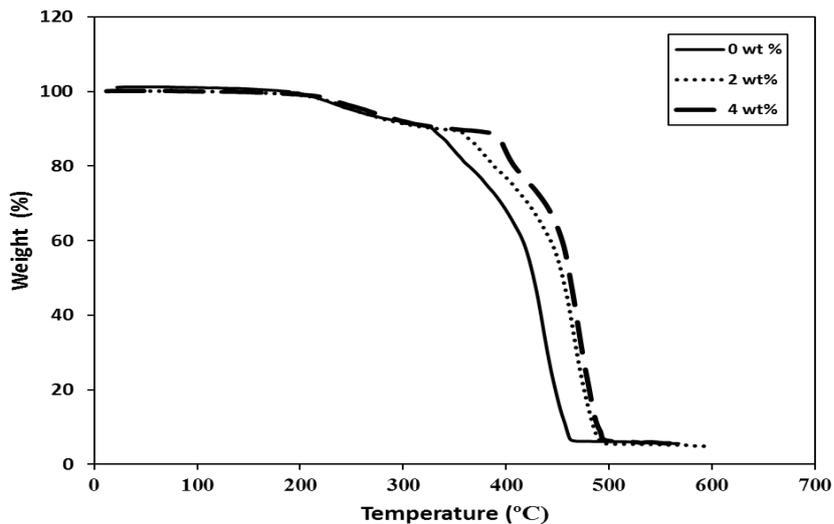


Fig.4: TGA of different concentrations of PP/EVSP composites

Mechanical properties

The mechanical properties have been investigated at different concentrations of EVSP for polypropylene at 1, 2, 3, 4 %wt.

Stress-Strain curves

Fig. 5. Illustrates the stress-strain curve for different concentrations of PP/EVSP composites respectively. It is noticed that the strain increases by increasing applied stress up to maximum σ_p , and then still increase while the stress decrease until the break point. The peak in the stress-strain curve was shifted upward by increasing EVSP concentration, until 3 wt % and it decreased again. This may be attributed to, at small amount of EVSP; there was good dispersion of the particles through the polymer chain increasing the strength of the composites. At higher concentration, the particle agglomerate together, which has a negative effect on the mechanical properties, and this is clear from SEM at higher concentrations. Furthermore, one can see that the maximum strain decreases with increasing the EVSP concentrations; this is because the EVSP decreases the elasticity of the polymer chains.

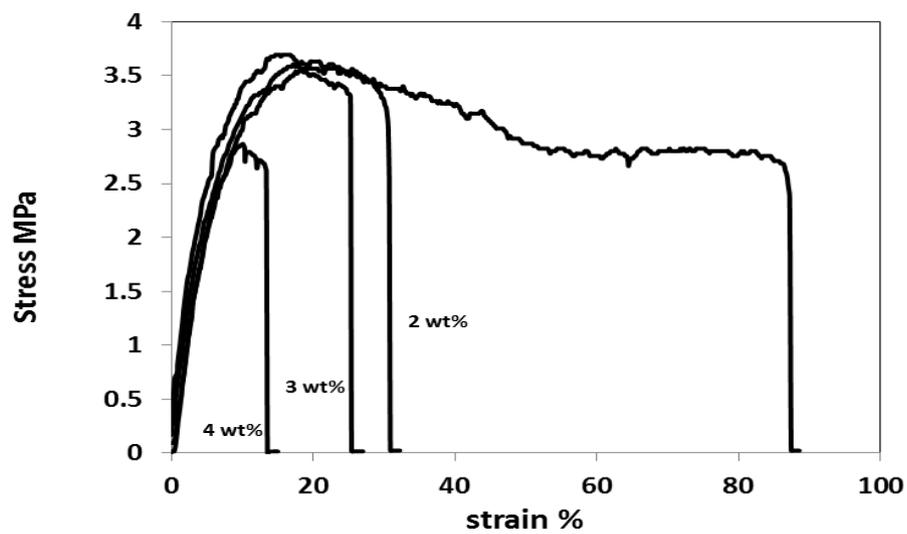


Fig.5: The Stress-Strain curves of PP/EVSP composites at different concentrations.

Young’s Modulus (Modulus of elasticity).

The obtained values of M_E for PP/EVSP composites are plotted versus EVSP concentrations in Fig. 6. One can note that M_E increases by increasing the EVSP concentration up to 3 wt% of EVSP and then it decreases again by increasing EVSP concentration.

Strength (Maximum stress σ_p)

The applied stress at peak σ_p is plotted against the EVSP concentration for PP/EVSP composites Fig. 7. It is noticed that, σ_p increases with increasing EVSP concentration until 3% of EVSP, then σ_p decreases again with increasing EVSP concentration.

For PP/EVSP composites, the absorbed energy E_a by the sample has been calculated (the area under the curve of stress-strain curve per unit volume of the sample) using the following relation (2)

$$E_a = a / lbd \dots\dots\dots(2)$$

where a is the area under the stress-strain curve obtained for EVSP/PE composites, l, b and d are the length, width and depth respectively.

From Fig. 8, it could be noticed that the absorbed energy increase by increasing EVSP concentration until 2 wt% then decreases again.

The maximum strain (the maximum elongation before break) of the PP/EVSP composites as a function of the EVSP concentrations is shown in Fig. 9. It is clear from Fig. 9 that, the maximum strain

decreases dramatically by adding the EVSP inside the PP matrix. This behavior is predictable, because the EVSP makes the PP matrix more rigid with lower elasticity.

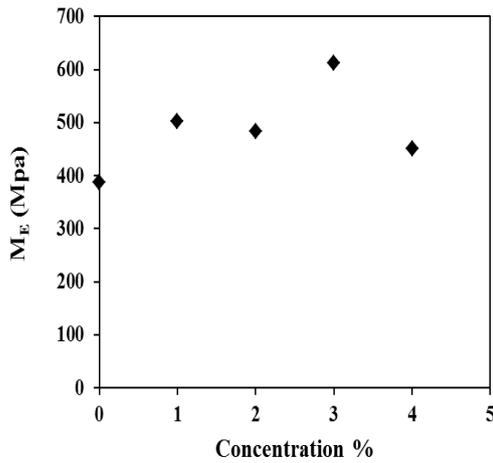


Fig. 6: M_E versus the concentration of EVSP in the PP/EVSP composites.

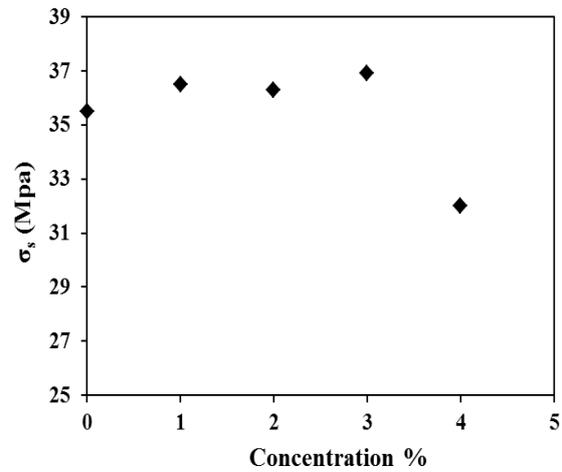


Fig. 7: The Maximum Stress σ_p versus the concentration of EVSP in PP/EVSP composites

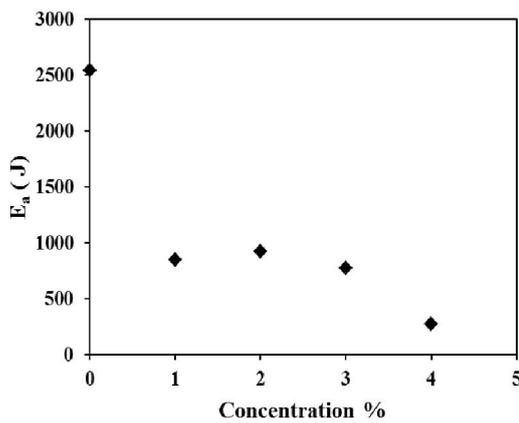


Fig.8: Absorbed Energy (E_a) versus the concentration of EVSP in the PP/EVSP composites

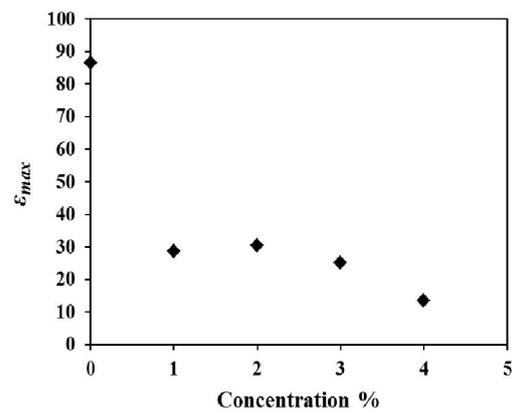


Fig.9: Maximum strain (ϵ_{max}) versus the concentration of EVSP in the PP/EVSP composites

Conclusion

From the presented results, it could be concluded that there was an obvious increase in tensile strength, Young's modulus of the sample with filler content until 3 wt % of EVSP in PP composites and more rigid. Also there was a thermal stability in the samples due to small filler content. SEM analysis confirmed the homogeneity of the surface morphology.

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