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EFFECTS OF WASHING OF RAW MATERIAL ON PROPERTIES OF CARBON NANOTUBE CONTAINING POLY(ETHYLENE-TEREPHTHALATE) COMPOSITES

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Our interest has been focused on mechanical recycling of poly(ethylene-terephthalate) (PET) bottle waste, because recycling of plastic waste has crucial importance nowadays. The present article deals with the effects of washing of the secondary raw materials on properties of carbon nanotube (CNT) reinforced composites. In the first step advantageous washing compounds and their concentration were determined. After selecting the proper washing method extrusion moulding characteristics of PET granulates were investigated, and effects of carbon nanotubes as reinforcing additives and also application of coupling agents on the mechanical and rheological properties of composites were studied.

Keywords: carbon nanotubes, coupling agent, poly(ethylene-terephthalate), bottle waste recycling

Introduction

Almost all human activities result in waste generation either directly or indirectly. Satisfying the daily needs for growing amounts of products results in higher consumption of raw materials, higher quantities of processing waste, and also higher amounts of wastes after the end of product life [1–4].

Selectively collected PET bottles derived from municipal solid waste considered as waste plastics of a specific type, but the liquid stored in them contaminates their surfaces. *Fig.1* shows the typical treatment cycle and possible recycling methods for plastic wastes, especially for the PET bottles collected selectively. Washing the surface of the waste materials is an important issue as biofilm can be formed. Therefore, this raw material will be contaminated with some biological content. Removing biofilm can be carried out in water, acidic or alkaline solvents. Effectiveness of the method is measured by using reactions with Folin reagent.

PET has excellent mechanical and chemical properties, therefore, its resistance against chemicals and irradiation is outstanding; however, it can also have serious impact on the environment, because the biodegradation requires a long time, and expensive pre-treatment methods are needed in order to bring them within reach of decomposing enzymes [3–8].

Carbon nanotubes (CNT) are members of the family of fullerenes with cylindrical shapes, where carbon atoms are located at the surface of a cylinder. Typical diameter is between the 1–50 nm regime, length can exceed even the 10 μm scale. Carbon nanotubes have non-polar character. Their surface contains only a few functional groups, which can react with polymers. In order to enhance the interaction between nanotubes and polymer matrices, the nanotube surface needs to be modified by application of coupling agents [7–11].

The given study deals with mechanical recycling of PET bottle wastes by applying secondary raw material for polymer matrix of CNT reinforced composites. After selecting the proper washing method, extrusion moulding characteristics of PET granulates were investigated. Furthermore, the effects of carbon nanotubes as reinforcing additives, and application of coupling agents on the mechanical and rheological properties of composites were studied.

Experimental

Materials

Selectively collected PET bottles waste was used as the polymer matrix in the composites in washed and

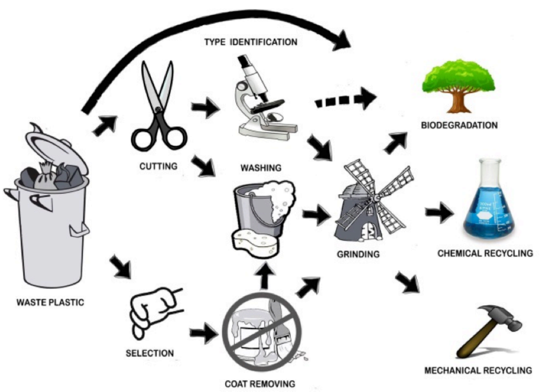

Figure 1: Pre-treatment and recycling of plastic wastes

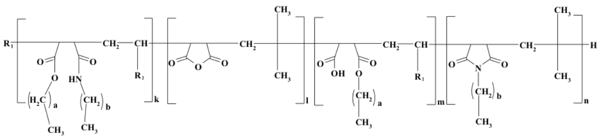

Figure 2: Structure of the ester-amide-imide derivative of the experimental olefin-maleic-anhydride copolymer (R_1: alkyl group with length of the olefinic monomer (C_{16}-C_{18}); R_2: alkyl group with R_1-2 carbon number; a: 3-40, b: 3-32; k: 0,2-2; l: 1-7; m: 1-7 and n: 0,3-2)

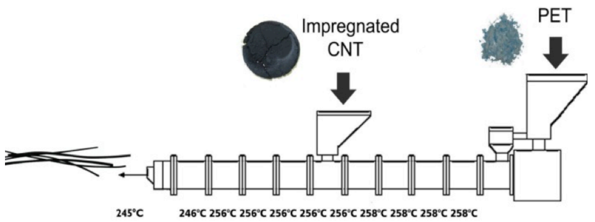

Figure 3: Production of PET composites in a twin-screw extruder

unwashed form. MFI values of the PET granulates were measured, and changed in the interval of 10–14 g (10 min)$^{-1}$ (255 °C, 2.16 kg). Multi-walled carbon nanotubes (MWCNT) were produced at 700 °C by chemical vapour deposition (CVD) process over Fe-Co bimetallic catalyst at the Department of Chemical Engineering, Institute of Chemical and Process Engineering, University of Pannonia. Purity of MWCNT was higher than 90 wt%, diameter was between 10 nm and 20 nm, the average length was above 30 μm and the BET-surface was 200 m^2 g^{-1}. Carbon nanotubes were applied in PET matrix in pristine and surface treated form. For treating surface of the carbon nanotubes experimental olefin-maleic-anhydride copolymer based coupling agents *(Fig.2)* were used with the properties summarized in *Table 1*. The ratios of the functional groups in coupling agents were determined by measuring acid value and saponification number by classical analytical methods and on the second hand the ratios were estimated by a previously developed FT-IR method [12].

Production of Composite Samples

CNT/PET composites were produced by a laboratory twin/screw extruder (LTE 20-44, LabTech Engineering, *Fig.3*). Temperature profiles and screw rotation speed for production were previously determined [13].

Washing of the Waste Material

After the washing process, raw materials from selectively collected PET and PET derived directly from waste deposit were compared. The solutions with 0.05 M concentration were used for both acidic and alkaline washing method. Citric acid and potassium hydroxide were chosen for the acidic and the alkaline wash.

Measurements

To determine the tensile properties of the extruded strings (namely strength, modulus, and extension) an INSTRON 3345 universal tensile testing machine was used. The temperature in the laboratory was 23 °C, while relative humidity was 37% during the mechanical tests that were carried out at 90 mm min^{-1} crosshead-speed. Rheological measurements were carried out in a CEAST Smart RHEO 2000 capillary rheometer at 265 °C. Before measurements, 180 second preheating was applied to all samples.

Structural information about the developed coupling agent was obtained by IR technique using a TENSOR 27 FTIR spectrometer (resolution: 3 cm^{-1}, illumination: SiCGlobar light, detector: RT-DLaTGS type) in the 400–4000 cm^{-1} spectral range.

Scanning Electron Microscopy (SEM) was used to study the morphology of fractured faces of specimens and to follow possible interaction between the reinforcements and matrices on a Phillips XL30 ESEM instrument.

Table 1: Main properties of coupling agents

property	CA-1	CA-2
acid value, mg KOH (g sample)$^{-1}$	12.8	33.1
saponification number, mg KOH (g sample)$^{-1}$	95.3	126.5
molecular weight (M_w)*, g mol^{-1}	3520	3660
polydispersity factor	1.10	1.40
ratio of functional group, %		
anhydride	7.9	12.0
semi-ester	2.7	37.6
ester-amide	44.7	25.2
imide	44.7	25.2

* related to PS standard

Table 2: BET-surface of different carbon nanotubes

samples	surface area
pristine	191.1 m^2 g^{-1}
20% CA-1 coupling agent	125.5 m^2 g^{-1}
15% CA-2 coupling agent	172.3 m^2 g^{-1}
20% CA-2 coupling agent	102.1 m^2 g^{-1}

Results and Discussion

Surface Treating

Effects of surface treatment were studied in two applications. Firstly, the coupling agents on the CNT surface was investigated, thereby properties of pristine CNT were compared to properties of two different coupling agent treated CNTs. BET-surface was measured and surface energy measurements were conducted. Secondly, the effects of concentration of the coupling agent applied on the CNT surface were studied with additive concentration to be 15% and 20%. By the surface treatment the BET surface of pristine CNT reduced at least by 35–40% *(Table 2)*.

On the basis of mesopore volume distribution results *(Fig.4)*, it was determined that coupling agents mainly attached to pores with diameters below 10 nm, because numbers of that pore size decreased the most. Structure

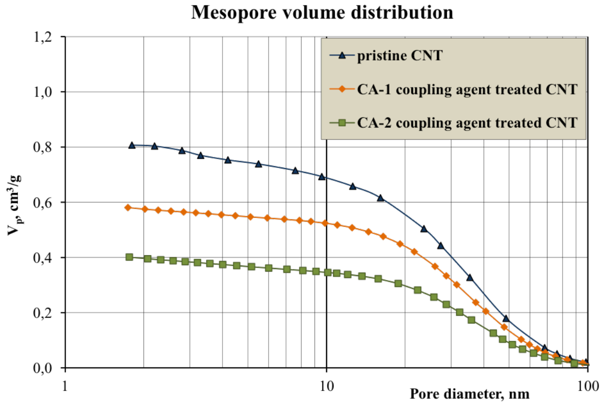

Figure 4: Changes in mesopore volume distribution due to surface treatment (20% coupling agent)

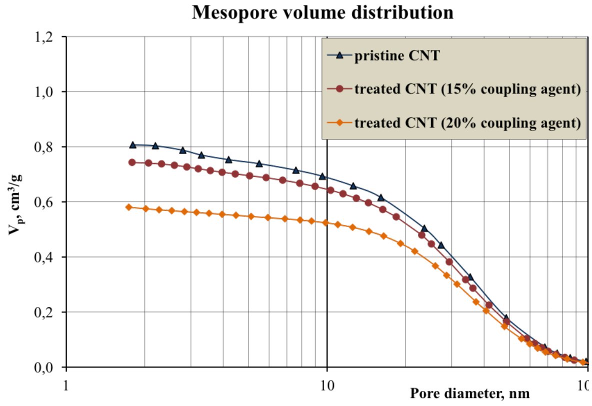

Figure 5: Changes in mesopore volume distribution due to surface treatment with various coupling agent (CA-2) concentrations

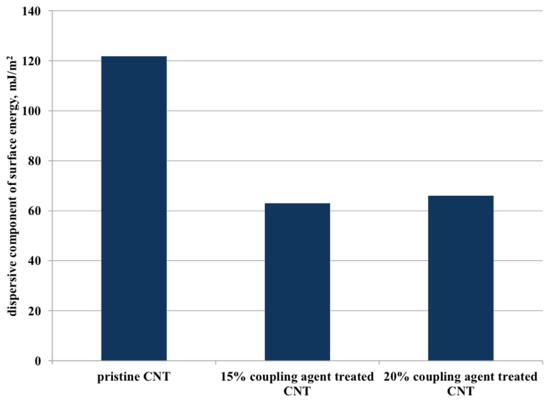

Figure 6: Dispersive surface energy based on Schultz-method (temperature: 70 °C)

of the coupling agent had considerable impact on the distribution since different ratios of decrease were measured in the mesopore volumes, therefore surface interactions with different strength may were evolved between the coupling agent and the CNT.

Concentration of the coupling agent on the CNT surface also influenced the results *(Fig.5)*. Decreasing the concentration from 20% to 15% resulted in an increase in the mesopore volumes to such an extent that almost the values for pristine CNTs were achieved.

Properties of heterogeneous polymer systems are influenced by interfacial interactions and structure; however, no direct method is available to determine strength of interactions. Therefore, models are used generally for their estimation. Inverse gas chromatography measurements can be a useful tool for measuring the surface properties of different fillers and thus, the strength of interactions can be estimated. The dispersive component of surface energy describes London-interactions that can be used for estimation of the non-polar character, while other types of interactions (hydrogen-bond, polar, acid-base, etc.…) are included in the specific component *(Fig.6)*. We found that the dispersive surface energy of the coupling agent treated CNT was half of the pristine one at 70 °C *(Fig.6)*. This is indicative of the surface treated carbon nanotubes likely having lower tendency for agglomeration than pristine CNTs. Constant for the acid-base interactions were calculated based on the GUTMANN equation [14] as summarized in *Table 3*.

Table 3: Acid-base constants calculated by GUTMANN equation [14] at 70 ºC

sample			R^2
pristine CNT	K_a	0.086	0.928
	K_b	0.000	
15% coupling agent treated CNT (CA-1)	K_a	0.086	0.806
	K_b	0.253	
20% coupling agent treated CNT (CA-1)	K_a	0.090	0.849
	K_b	0.213	

On the basis of these results it can be stated that acid character of the pristine CNTs do not change significantly after surface treatment but the basic character improved. On the surface of the treated CNT-s weak basic active centres were predominant over acidic ones.

Effects of Washing

Both acidic and alkaline washing were shown to be effective by which biofilm had been removed from surface of PET granulates with 100% efficiency. Since biofilm cannot stick to the surface of PET due to its crystalline structure biofilm can be removed by application of weak acid or lye.

FT-IR spectra of the granules before and after washing gave the opportunity to study the changes in functional groups of the plastic. It is important to highlight that no significant differences were observed between FT-IR spectra of acidic and alkaline washed samples. Therefore, none of the compounds during washing deteriorated structure of PET *(Fig.7)*.

Effect of Screw Rotational Speed

PET samples were produced at various screw rotational speeds to study their rheological behaviour and also their mechanical properties. Screw rotational speed during processing caused significant differences in viscosities in the low shear rate regime (beyond 500 s^{-1}) *(Fig.8)*.

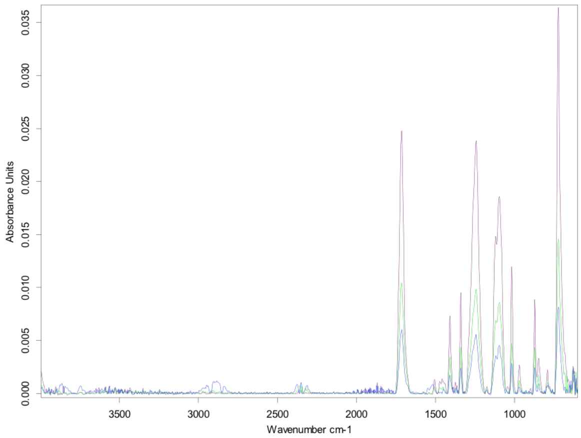

Figure 7: FT-IR spectra of PET sample in the 4000-600 cm^{-1} wavenumber range (purple: potassium-hydroxide; green: citric acid; blue: without washing)

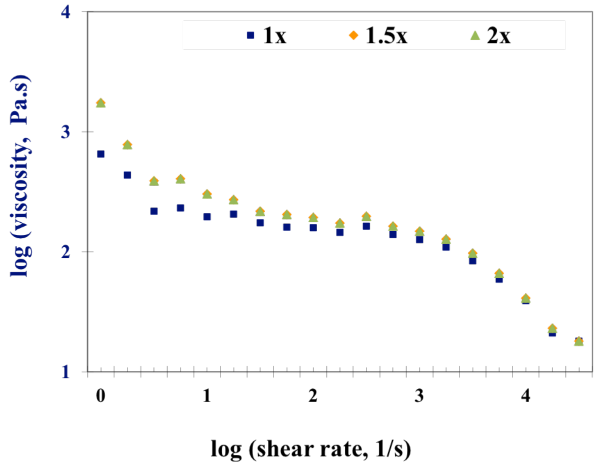

Figure 8: Effect of screw rotational speed on rheological behaviour of PET raw material

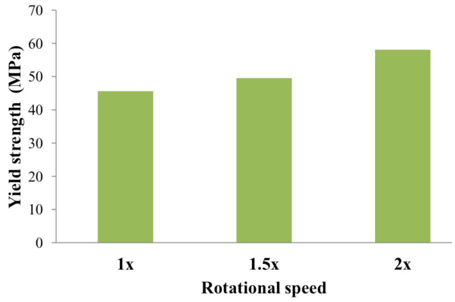

Figure 9: Effect of screw rotational speed on yield strength of PET raw material

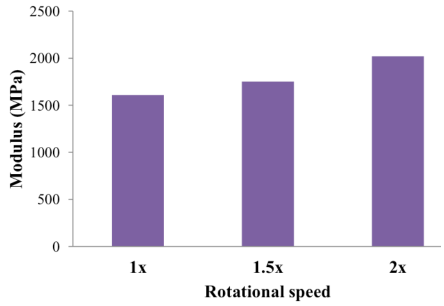

Figure 10: Effect of screw rotational speed on tensile modulus of PET raw material

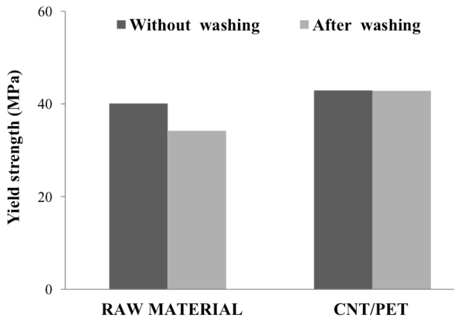

Figure 11: Effects of CNT application on yield strength of PET

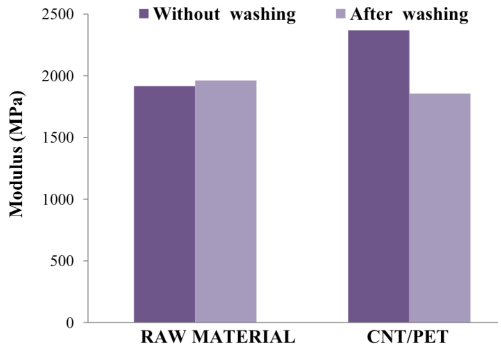

Figure 12: Effects of CNT application modulus of PET

In the medium shear rate region (500-5000 s^{-1}) differences among the viscosities of the samples continuously disappeared. No differences were observed at higher shear rates, above 5000 s^{-1} dedicated to shear rates characteristic for injection moulding. That indicated that all the samples could probably be injection moulded at the same parameters. All the tensile properties (yield strength, modulus) improved by increasing screw rotational speed during processing (*Figs.9* and *10*).

The highest values for the tensile properties were measured for samples produced at the highest screw rotational speed. Sample produced at the lowest rotational speed had values nearly identical to literature data [15]. However, samples processed at the highest rotational speed had 35–40% higher yield strength than the original material used for bottle production. It is important to note that washed PET granulates with the lowest rotational speed could not be produced at the same temperature profile as the plastic melted.

PET Composites Containing Pristine CNT

Washing the raw material caused 15% deterioration in yield strength, but the modulus did not change. Untreated CNT could be introduced into the polymer melts at 2 wt% level both into washed and unwashed PET raw materials by the same side feeder screw rotational speeds. Application of pristine CNT did not influence yield strength of the composites *(Figs.11 and 12)*, so yield strength of CNT/PET samples did not depend on the previous washing of the raw material.

The PET raw materials had *ca.* 2000 MPa tensile modulus either for washed and unwashed plastic, so rigidity of the samples was stated to be the same.

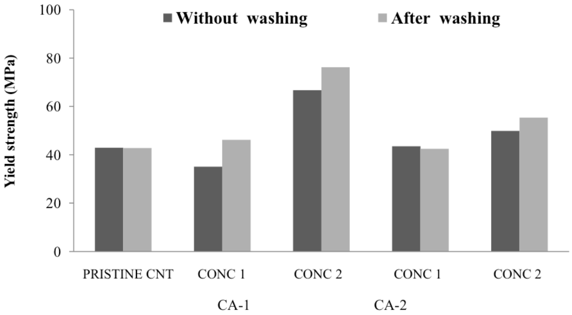

Figure 13: Tensile properties of surface treated CNT containing PET composites

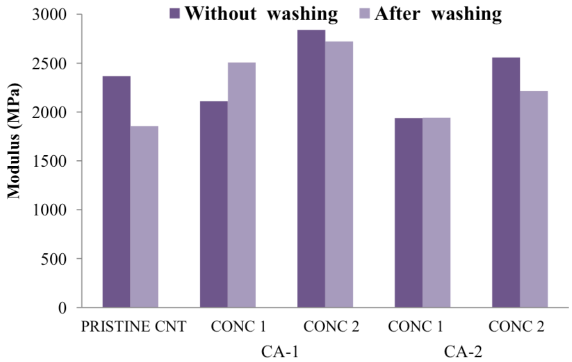

Figure 14: Tensile properties of surface treated CNT containing PET composites

Pristine CNT containing washed PET had 20% lower modulus than unwashed PET based samples had, thereby; the property of the PET raw material was achieved. Adding pristine CNT to washed PET plastic no difference was measured in the modulus compared to the washed PET without any reinforcing.

Effects of Type and Concentration of Coupling Agent

Two different, previously successfully applied coupling agents [13] were used on the surface of CNTs. Concentration of the coupling agents varied from 15% (CONC-1) to 20% (CONC-2) related to the weight of the pristine CNT. With respect of processing, surface treated CNTs were much easier to introduce into the polymer melt. CNT concentration could be elevated up to 2.7–2.9 wt% in the polymer matrix at the same processing parameters using coupling agent treated CNTs instead of pristine type.

Yield strengths of washed PET based composites increased with increasing concentration in the presence of both coupling agents compared to the pristine CNT containing PET sample *(Figs.13 and 14)*. Improvement of 78% for CA-1, and 30% for CA-2 was realized in the presence of coupling agents at the higher concentration (20%). Using unwashed PET, as raw material also resulted in enhancement of yield strength, but to a different extent, such as CA-1 resulting in 55%, while CA-2 causing 16% increase.

Based on the above results, the CA-1 additive was worth applying in higher (20%) concentration due to the achieved more than 50% higher yield strength relative to the pristine CNT containing PET composite. Raw material is worth washing before processing if cost of washing could be balanced by the advantage of the 10 MPa increase in yield strength applying CA-1 coupling agent in 20% concentration. In case of CA-2 additive washing did not influence the properties at the lower (CONC-1) concentration level, but with higher additive concentration (CONC-2) a 14% difference was measured between the composites made from the two raw materials.

Comparing the samples with various additive concentrations an increase was observed in the modulus with increasing concentration for both raw materials and coupling agents. Applying unwashed raw material 34% improvement was realized with CA-1 coupling agent and 32% with CA-2 additive if the concentration increased from 15% to 20%. A lower degree of improvements were measured for washed PET based samples making the same comparison.

Comparison of pristine and surface treated CNT containing samples showed that coupling agent was advantageous to be applied in higher concentration from the point of view of the modulus either. For unwashed PET based composites application of coupling agents resulted in 10–15% decrease in modulus related to the pristine CNT containing sample. For washed PET based samples making the same comparison changes were calculated to be +45% in case of CA-1, and +20% for CA-2 additive.

The most advantageous observation based on the results is the lack of an effect on the mechanical properties in the investigated interval of raw material quality with respect of washing PET bottle waste, when used as polymer matrix for CNT reinforced composites. This could be realized in easier handling and pre-treating of the raw material before recycling.

SEM graphs

Broken surfaces of samples were studied by Scanning Electron Microscopy. CNTs concentrated at one side of the extruded string in pristine CNT containing samples *(Fig.15A)*. Diameter of the probable carbon nanotube nucleation centres varied *(Figs.15B and C)*. There were agglomerates with diameter of 30–40 μm and also with 5-10 μm number of the latter seemed to be higher. In addition, there were only a few nucleation centres both for washed and unwashed PET based composites.

On the cross section of the extruded strings a crystalline part was rendered likely in larger areas in coupling agent treated CNT containing samples than in pristine CNT/PET samples. In PET containing 15% CA-2 coupling agent a likely crystalline part was found at the middle of the extruded sample *(Fig.16)*. More nucleation centres and more homogeneous structure were observed *(Fig.16)* than in pristine CNT containing sample from the same PET raw material. It is in accordance with the 15% lower CNT content of the pristine CNT/PET composite than the treated CNT containing one. The diameters of the nucleation parts were in the range of 20–30 μm.

Area related to the probable crystalline structure was higher in washed PET based sample on the SEM graphs of the extruded strings *(Fig.17A)*. Nucleation parts were

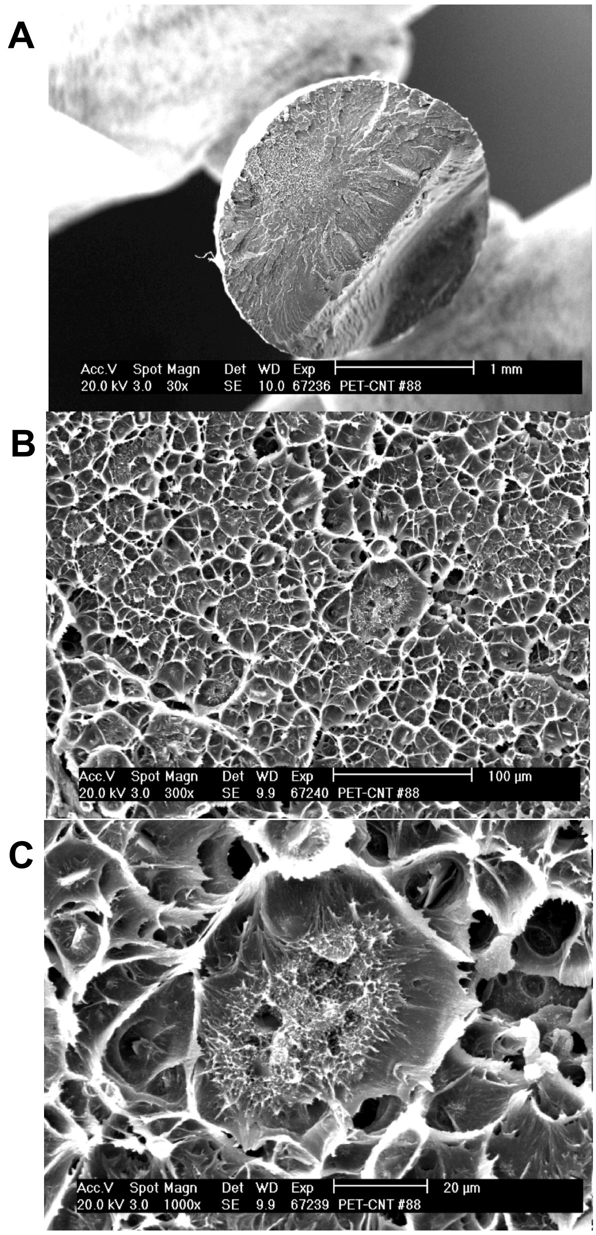

Figure 15: SEM graphs of PET sample containing pristine CNT

located in the middle of the sample and connected to each other diameters were identical to the former sample that was treated *(Fig.17B)*.

Based on the SEM graphs it was concluded that carbon nanotubes were easier to handle and distribute more homogeneously due to surface treating both for washed and unwashed PET raw material, and on the other hand numbers of the nucleation parts and sizes could be influenced.

Conclusions

The present article gave a brief insight into mechanical recycling of PET bottle wastes by applying that secondary raw material for polymer matrix of CNT reinforced composites. After selecting the proper washing method extrusion moulding characteristics of PET granulates were investigated and it was concluded

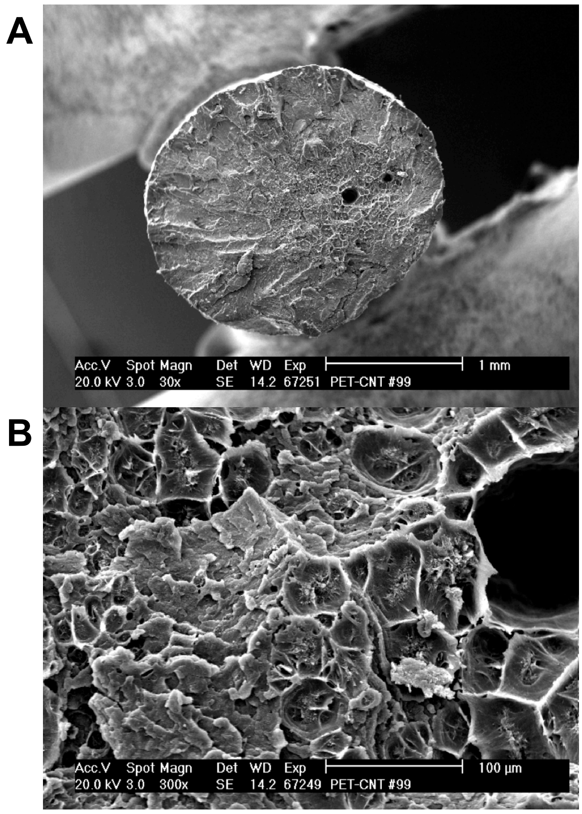

Figure 16: SEM graphs of unwashed PET based sample containing 15% CA-2 coupling agent treated carbon nanotube

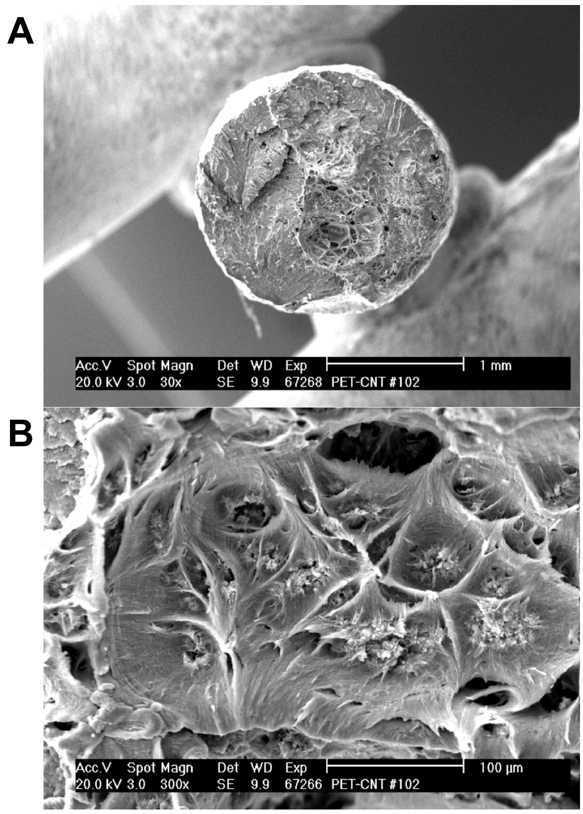

Figure 17: SEM graphs of washed PET based sample containing 20% CA-1 coupling agent treated carbon nanotube

that tensile properties improved by increasing screw rotational speed.

Effects of washing in carbon nanotubes containing PET composites were also investigated where carbon nanotubes were applied either in pristine or surface treated form. Washing of the waste plastic did not affected yield strength in case of pristine carbon nanotubes containing samples but for coupling agent containing composites mechanical properties significantly changed. If the proper coupling agent was applied in higher concentration, 20% e.g. yield strength improved by higher than 60% while modulus increased at least 20%.

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