

# Mechanical and Thermal Properties of Recycled Mixed Waste Polymers Reinforced with Reclaimed Newsprint Fibres

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**Abstract:** This study investigates the mechanical, thermal and morphological properties of rHDPE (Recycled High Density Polyethylene) and a mixture of rPE HD/LD (High and Low Density Polyethylene), both reinforced with rNP (Reclaimed Newsprint Paper) fibres. To enhance the composite properties, the addition of highly grafted maleic anhydride polyethylene wax, as CA (Coupling Agent), and semi crystalline copolymer of propylene and ethylene, as IM (Impact Modifier), was included into the material formulation by a twin-screw extruder. Mechanical and morphological properties were studied on tensile test specimens, prepared by injection moulding, by tensile testing machine and SEM (Scanning Electron Microscope), respectively. Thermal properties, i.e. melting and crystallization behaviour, were investigated by DSC (Differential Scanning Calorimetry). Mechanical analysis showed that the addition of rNP in both composites increased the young modulus and significantly decreased the elongation at break. The DSC results revealed that the addition of the rNP in the rHDPE matrix led to a substantial decrease of crystallinity, which consequently affects the tensile strength of the composite (17 MPa) in contrast to the neat rHDPE (25 MPa). On the contrary, fibre addition in rPE HD/LD matrix had no specific impact on the crystallinity index, but did contribute to the increased tensile strength (26 MPa) when compared with neat rPE HD/LD (16 MPa). SEM photomicrographs of the impact fracture surfaces demonstrated a solid adhesion bond between the natural fibres and the rPE HD/LD matrix. Reclaimed newsprint fibres can thus be considered as a perspective alternative to the inorganic fillers in the rPE HD/LD composite.

Key words: Recycled high and low density polyethylene, natural fibres, mechanical properties, DSC, recycling.

# 1. Introduction

In recent years, the extensive production of fossil-based plastics poses a great threat to the possibilities of maintaining the quality of the environment and diminishing the non-renewable petrol sources. Global demand for petrochemical feedstock in plastic processing industry accounts for 12 million bpd (Barrels Per Day), or roughly 12 percent of the total fossil oil demand in 2017. This figure is forecasted to grow to almost 18 million bpd in 2050 [1]. To maintain the quality of our daily lives and to limit the use of non-renewable sources, i.e. fossil fuel, the search for the alternative materials that are aligned with the European environmental directives and strategies on resource efficiency (COM (614) 2015; COM (125) 2009; COM (98) 2008/CE; COM (211) 2013; COM (397) 2014), has been stimulated significantly in recent years. Reasons for this green shift transition can be found in the growing ecological, social and economic awareness and evermore restricted law regulatives [2]. The world-wide availability of natural fibres, abundant access of agro-wastes, relative cheapness and their ability to be recycled, are the catalysators for the ever-increasing

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interest in research of these new sustainable concepts [3]. Besides the listed motivations, natural fibres have found several applications across the manufacturing industry, mainly because of their desired characteristics, such as low density, less abrasive processing conditions and its reinforcing potential to impart the mechanical properties of the resulted thermoplastic composites. The idea of using natural fibres as a reinforcement in composite materials is not a new or recent one. It has been a part of man's technology since the first ancient builder used straw to reinforce mud bricks [4].

Composite properties are however dependent on the characteristics of polymer matrix, properties, content and dispersion of the filler and the interface compatibility, of which influence was studied in the past [5-9]. However, finding some alternative sources of natural fibres from post-consumer waste and how they will be processed with the recycled solid waste plastic for the mass production of new products is a new concept, driven by the circular economy business model.

The aim of the present study was to characterize the mechanical, thermal and morphological properties of environmentally friendly composites, that were developed within the LIFE CEPLAFIB project (LIFE17 ENV/SI/000119) for its further use in several industrial applications, such as industrial packaging, automotive and construction sector. They are made of the reclaimed newsprint fibres and recycled polyolefins, rHDPE and rHD/LD PE, both obtained from post-consumer wastes. The effect of the maleic anhydride grafted polyethylene addition, serving as a compatibilizer, and the semi-crystalline copolymer of propylene and ethylene (VISTAMAXX<sup>TM</sup>), as an IM (Impact Modifier), were investigated as well. The

effect of high filler content (i.e. 40 wt.% of newsprint fibres) on final properties of recycled HDPE and HD/LD PE blends was investigated by a two-step process technology; twin-screw extrusion and injection moulding.

# 2. Experimental Part

## 2.1 Materials

Recycled high density polyethylene (rHDPE) and a mixture of recycled high density and low density polyethylene (rPE HD/LD) of a ration 30:70 were obtained by recycling company Omaplast (Grosuplie, Slovenia). According to the manufacturer, the density of the recycled polymers was between 0.955 and 0.965 g/cm<sup>3</sup> and MFR (Melt Flow Rate) values were in the range of 0.5-1.0 g/10 min. The reclaimed newsprint paper (rNP) fibres were supplied by Ecopulp Oy (Koria, Finland). Highly grafted maleic anhydride polyethylene wax Licocene® PE MA 4351, supplied by Clariant Produkte (Deutschland) GmbH, Germany, was used as CA (Coupling Agent), and VistamaxxTM 6202, supplied by HSH Chemie, Slovenia, served as IM in the composite mixtures. The material formulations with weight percentages of individual blend components are compiled in Table 1.

### 2.2 Processing Methods

All together four main material components were involved in this study, two reference materials, i.e. rHDPE and rPE LD/HD, and two composite blends based on reference polymer matrices, both reinforced with 40% of rNP and modified with CA and IM. To ensure the desired reinforcing potential and as uniform distribution of the filler as possible, the rNP fibres were first shredded to obtain smaller particles of scale

Table 1Investigated material formulations.

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Material designation	rHDPE (wt. %)	rLDPE (wt. %)	rNP (wt. %)	CA (wt. %)	IM (wt. %)
rHDPE	100	0	0	0	0
rHDPE + rNP	52	0	40	3	5
rPE (HD/LD)	30	70	0	0	0
rPE (HD/LD) + rNP	15.6	36.4	40	3	5

range between 1.5 and 2 mm. The prepared fillers were then dried in a ventilating oven for 12 h at 60 °C to eliminate the undesired moisture and to avoid the hornification phenomenon during the extrusion processing. To obtain the composite blends in granulated form, all the raw components were manually mixed in the container prior to the extrusion process. Mixture of components was afterwards compounded on the Labtech LTE 20-44 twin screw extruder. The barrel temperature was maintained between 170 and 180 °C and the screw rotation was set to 200 rpm. Extruded strand was cooled down in a water bath with a temperature of 20 °C and pelletized. Pellets were dried over-night at 60 °C prior to the injection moulding. Preparation of tensile test specimens was performed on injection moulding machine Krauss Maffei KM 80-380 CX.

### 2.3 Characterization Analyses

Tensile testing was conducted on a Zwick/Roell Z005 (Zwick GmbH & Co. KG, Ulm, Germany) universal machine in compliance to ISO 527-1-2 at ambient conditions. The crosshead speed was 5 mm·min<sup>-1</sup> and the distance between the grips was 60 mm. The crosshead extension was elaborated as a specimen deformation. The presented values of MOE (Modulus of Elasticity, Et), TS (Tensile Strength,  $\sigma_M$ ), and EB (Elongation at Break,  $\epsilon b$ ) are an average from at least six replicates from each final material.

DSC (Differential Scanning Calorimetry) was used to study the thermal characteristics of the investigated materials. Analysis was carried out on HP DSC 1 instrument Mettler-Toledo. Weight of analysed samples was between 10.8 and 11.4 mg. Standard procedure of heating, cooling and second heating was performed in the following order. Samples were first held at 25 °C for 1 min, and then heated from 25 °C to 180 °C at 10 °C/min, and held again at 180 °C for 1 min to eliminate the thermal history. Then cooling run was performed at 10 °C/min back to 25 °C and held at 25 °C for 1 min. In last step, samples were heated again from 25 °C to 180 °C with a heat rate of 10 °C/min.  $T_{\rm C}$  (Crystallization Temperature) and  $T_{\rm M}$  (Melting Temperature) were determined during the crystallization and melting phase, respectively. The heat of fusion  $\Delta H_0$  was calculated from the integrated peak area of the DSC curve. The degree of crystallinity was calculated using the following equation [5].

$$X_C = \frac{\Delta H_f \cdot 100}{\Delta H_0 \cdot w}$$

where  $\Delta H_f$  is the heat fusion of the sample,  $\Delta H_0$  is the heat of fusion of a 100% crystalline PE = 293 J/g [8] and w mass fraction of PE in composites.

The surface morphology of the plain matrices and its composites was investigated by JEOL 5500 LV SEM (Scanning Electron Microscope), working in high vacuum and accelerating voltage of 20 kV. Samples were coated with a highly conductive carbon film using a BAL-TEC/SCD\_500. SEM images were taken at different magnifications, ranging from  $100 \times$ to 5,000×.

### 3. Results and Discussion

### 3.1 Mechanical Analysis

Results for tensile properties, i.e. MOE, TS and EB, are compiled in Table 2 and graphically presented in Fig. 1. The results indicated that the fibre addition significantly increased the modulus of elasticity for both sets of the investigated materials. rHDPE reinforced with 40% of rNP compared to the plain rHDPE stated for 24% higher modulus of elasticity, while the composite based on rPE HD/LD revealed for 86% higher modulus compared to plain rPE HD/LD. Such results were however expected, since rNP possesses had higher stiffness compared to the neat polymer. These findings are also in accordance with other studies investigating the influence of newsprint fibres as a reinforcing agent [5, 10, 11]. On the other hand, elongation at break was significantly affected by fibre content in both materials, since composites become

Material designation	Modul of elasticity (MPa)	Tensile strength (MPa)	Elongation at break (%)
rHDPE	304	25	63
rHDPE + rNP	377	17	8
rPE (HD/LD)	208	16	266
rPE (HD/LD) + rNP	386	26	8
450 (e 400 350 300 300 300 300 300 208 208 208 208 208 208 208 2	86 86 86 87 87 87 87 87 87 87 87 87 87	26 300 16 250 16 250 16 150 100 € 100	266 33 8 8 DPE © HDPE+NP @ PE (HD/LD) = PE (HD/LD) + NP

 Table 2
 Mechanical properties of studied materials.

Fig. 1 Mechanical properties of newsprint fibre reinforced composites with respect to the type of recycled polyolefin matrix.

more brittle with the addition of reinforcing phase. Newly created composites based on rHDPE and rPE HD/LD indicated 87% and 97% lower elongation at break, respectively, compared to the referenced materials.

The tensile strength of the composites varied dependently of the selected matrix. In rPE HD/LD, the addition of rNP gave a rise of the composite stiffness for up to 63%, while the inclusion of fibres in rHDPE resulted in 32% lower strength compared to the plain matrix. The results are in accordance with the results of the DSC investigation. In rPE HD/LD + rNP, a significant decrease in crystallinity was observed. In PE, the crystallinity rate is an important factor in terms of the final mechanical properties. Higher level of crystalline phase in polymeric materials contributes to higher stiffness and tensile strength and vice versa [12]. Consequently, decrease of crystallinity in rHDPE+rNP resulted in lower tensile strength of composite (17 MPa) in contrast to the neat rHDPE (25 MPa). On the other hand, fiber addition in PE HD/LD matrix did not significantly affect the crystallinity index, which resulted in increase of tensile strength for the composite sample (26 MPa), when compared to TS of plain PE HD/LD (16 MPa).

Table 3, Figs. 2 and 3 show how the presence of newsprint fibres affects the polymer crystallization

kinetics. The melting temperature of the composites has not been drastically changed after the fibre inclusion. The addition of rNP in rHDPE lowered the melting temperature of the resulting composite by 3 °C due to the formation of less stable crystal entities that melt at lower temperatures. Similar findings were proved also by Ardekani, et al. [5] for the NP reinforced recycled poly(ethylene terephthalate). On the other side, rNP in rPE (HD/LD) matrix had the opposite effect on crystal formation, which resulted in 5.5 °C higher  $T_m$  compared to the neat rPE (HD/LD) and more thermally stable crystalline phase.

The presence of recycled newsprint fibres in rHDPE matrix revealed a negative impact on the crystallinity index (22.95%) of the composites, compared to the neat rHDPE (90.47%), which could be correlated to the hindered movement of the molecular chains and reduced space available to be occupied by the molecular chains. Similar findings were observed also by Chafidz, et al. [13]. For rPE (HD/LD), the crystallinity degree (50.82%) was not significantly affected by the addition of rNP (44.15%), which led to improved mechanical parameters, in specific, increased tensile strength.

SEM photomicrographs of the impact fracture surfaces were used to verify the distribution of rNP fibres in the matrix and interfacial bonding between

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		-		
Material designation	Melt. temp. (°C)	Melting entalphy (J/g)	Crystal. temp. (°C)	Crystallinity (%)
rHDPE	131.07	159.05	114.87	90.47
rHDPE + rNP	128.25	40.35	112.30	22.95
rPE (HD/LD)	127.72	89.34	112.41	50.82
rPE (HD/LD) + rNP	134.36	77.61	112.77	44.15

Table 3 DSC results of neat rHDPE and rPE (HD/LD) and composites, reinforced with rNP.



Fig. 2 DSC results of plain rHDPE and rHDPE reinforced with 40% of rNP during (a) 2nd heating scan, and (b) cooling scan.



Fig. 3 DSC results of plain rPE HD/LD and rPE HD/LD reinforced with 40% of rNP during (a) 2nd heating scan, and (b) cooling scan.

the reinforcing and matrix component. In Figs. 4a and 5a, the surface morphology of plain rHDPE and rPE (LD/HD) is presented at the magnification scale of  $100\times$ . Morphology of the composite cross-sections is presented in Figs. 4b and 5b. In general, the fibres are homogenously distributed across composite matrices, despite the high loading percentage of the reinforcing agent. A solid adhesion bond in fiber-matrix composite is crucial for transmitting the load stresses from polymer to the fibres and consequently for obtaining

improved mechanical properties [14, 15]. To enhance the compatibility between the hydrophilic natural fibres and hydrophobic polymers, physical or chemical pre-treatment of the first or second component is crucial [16]. For that manner, highly grafted maleic anhydride polyethylene wax was used as CA. In Fig. 4c, some relatively large pores can be observed, attributed to the pool-out effect of the fibres. This indicates the inadequate fiber-matrix interaction, which results in deterioration of mechanical properties, i.e.



Fig. 4 SEM micrographs of (a) plain rHDPE, (b) rHDPE-rNP, and (c) rHDPE-rNP.



Fig. 5 SEM micrographs of (a) plain rPE (LD/HD); (b) rPE (LD/HD)-rNP and (c) rPE (LD/HD)-rNP.

lower tensile strength (17 MPa) in contrast to neat rHDPE (25 MPa).

Composite based on rPE (LD/HD) demonstrated a much better adhesion bonding between the fiber and the matrix, which can be observed in Fig. 5c. As a result, significantly improved mechanical characteristics have been declared by the tensile test results.

## 5. Conclusions

Mechanical, thermal and morphological properties of rNP reinforced rHDPE and rPE (HD/LD) were investigated to determine the influence of fibres addition, obtained from post-consumer wastes, as an alternative to the artificial reinforcing fibres, like glass, aramid, carbon, etc.. It has been confirmed that the addition of rNP deteriorated the crystallinity degree of rHDPE. SEM images identified an inadequate adhesion bond between the natural fibres and matrix. Both findings align well with the mechanical results, which proved inferior mechanical characteristics for the composite sample. On the other hand, the mechanical improvements that were achieved for the composite based on rPE (HD/LD), represent the prosperous potential for their use in different industrial applications. The addition of recovered NP fibers affected the rPE (HD/LD) based composite properties in a positive way. The mechanical parameters were improved, melting temperature was increased and the degree of crystallinity was not significantly changed compared to plain matrix. Morphology of the fractured composite surfaces demonstrated a solid adhesion bond between the fibres and matrix. With the addition of filler, the hindered movement of molecular chains was noted, which resulted in higher material stiffness and lower elongation at break. Reclaimed newsprint fibres can thus be considered as a perspective alternative to the inorganic fillers in the rPE (HD/LD) composite.

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