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Mechanical Properties of Polypropylene Biocomposites Reinforced with Man-Made Cellulose Fibres and Cellulose Microfibres

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Abstract. This paper presents the influence of man-made cellulose fibres and cellulose microfibres on the mechanical properties of reinforced composites based on polypropylene matrix. The hybrid combination of these reinforcements was also used. The man-made cellulose fibres and cellulose microfibres were compounded with polypropylene. The volume fractions of reinforcement and compatibiliser were maintained at the proportional levels to enable correlation of mechanical properties. The manufactured composite compounds were subsequently injection moulded into testing specimens. Mechanical properties such as tensile and flexural strength, tensile and flexural modulus were determined. The data obtained from experiments have shown that addition of the cellulose fibres and microfibres to the polypropylene matrix has reinforcing effect on its tensile and flexural properties, which depends mostly on volume fraction of reinforcement and its type. The hybrid combination has shown higher than expected properties, especially at higher volume fractions.

1. Introduction

Polymer structures and composites reinforced with materials of natural origin like wood and cellulose fibres are becoming significantly important for the production of a large variety of products owing to their advantages reflected in cost-effectiveness, mechanical properties, low weight and recyclability [1-3].

In recent years, composites reinforced with cellulosic fibres, such as man-made cellulose fibres, have become the focus of research. Application of cellulose fibres both of man-made and natural origin as reinforcement gives relatively good mechanical properties and higher elongation at break in comparison to glass reinforcement [4-6]. These fibres provide potential for lightweight applications in comparison to common glass fibre reinforcement on the one hand, while on the other they are obtained from raw-renewable resources and offer better recyclability and disposal [7-8].

The choice of polymer as a matrix material is important for the man-made cellulose fibres reinforcement. The use of polypropylene in the development of new composites is of great interest due to its low density, design flexibility and low price compared with other polymers [9]. It can be easily compatibilised with cellulosic fibres using polypropylene waxes with maleic anhydride functionality

[10]. Polypropylene matrix composites possess improved mechanical properties and offer new possibilities for technical and engineering applications.

The potential of short-cut rayon fibre (man-made cellulose) as reinforcements in polypropylene matrix was studied by Amash et al. [11-12]. Injection moulding compounds with high strength man-made cellulose fibres such as tyre cord yarn Cordenka (product name of tyre cord man-made cellulose) and polypropylene block copolymer were first reported by Weigel et al. [13]. Ganster et al. studied reinforcing effect of cellulose fibres in thermoplastic matrices in order to obtain a balanced property profile in terms of strength [14]. Khan et al. demonstrated that the property profile of Cordenka fibre reinforced polypropylene composites can be tailored by a partial replacement of the Cordenka by natural fibres such as jute. The jute/Cordenka hybrid composites were produced by a pultrusion process and subsequent injection moulding [15]. Recently, novel selective tailoring of dual interface in polypropylene reinforced with man-made cellulose fibres, as well hybridisation with polyethylene terephthalate fibres were developed by Franciszczak et al. [16-17].

The main purpose of this study was an investigation and comparison of the influence of man-made cellulose fibres and cellulose microfiller, as well as their hybrid combination on the mechanical properties of the reinforced composites based on polypropylene matrix. For this purpose injection moulding grade polypropylene HP400R was applied as a matrix polymer and man-made cellulose Cordenka fibres and HM400X cellulose microfibres were used as fibres and microfiller, respectively. The manufactured composite compounds were subsequently injection moulded into test specimens. Tensile and flexural characteristics of composites reinforced with different filling ratios of man-made cellulose Cordenka fibres, HM400X cellulose microfibres and their hybrid combination is presented. This research shows that the relatively costly man-made cellulose fibres may be partially substituted with HM400X, which results in a diminishing of tensile and flexural properties but to lesser extent than it would be expected by averaging of these properties of both Cordenka and HM400X composites. Especially elongation at break is maintained on the level of man-made cellulose reinforced composite after partial replacement these fibres with cellulose microfibres.

2. Materials and methods

2.1. Materials

Moplen HP400R was used as matrix material. This material is homopolymer polypropylene (PP) used for injection moulding applications in granulate form with a melt flow rate (MFR) of 25 g/10 min at 230 °C and 21.6 N.

For reinforcement, the man-made regenerated cellulose fibres Cordenka 610F having a linear density of 1.8 dtex (fibre diameter ~18 μm) and 1000 filaments were used. The initial length of fibres was approximately 1.7 mm [8, 17].

Cellulose microfibres Jelucel HM400X with a cellulose content of 99.5% and a bulk density of 55 g/l were added as a microfiller. They are irregular in shape with dia. ~21 μm and length of ~170 μm [8].

TP Licocene PP MA 6452, a maleic acid anhydride grafted polypropelene wax (MAH-g-PP) from Clariant was applied as an efficient compatibiliser between fibres/fillers and the matrix. 4 vol% of the compatibiliser for ∼28 vol% of the reinforcement and 2 vol% of the compatibiliser for ∼14 vol% of the reinforcement was applied in a composite respectively.

2.2. Methods

Due to their hydrophilic properties Cordenka fibres and HM400X microfibres were dried before compounding at temperature of 103°C in an oven for ~16 h [16]. Then materials were compounded at temperatures ranging from 150 to 200 °C to avoid decomposition of cellulose and at 40 RPM in order to reduce fibre shear damage. Native HP400R reference was processed without drying.

The pre-dried fibres and PP granulated were mixed with MAH-g-PP granulate. The extruded strands were cooled in a water tank and cut subsequently into granulate. Then granulate was dried before injection moulding at the same conditions as prior compounding.

Standard test specimens were prepared with these granulates according to DIN EN ISO 527 (Type A for tensile test) and DIN EN ISO 178 (Type B for 3-point bending test) using an injection moulding machine ARBURG ALLROUNDER 270 S 350–100 (clamping force 350 kN, screw diameter 25 mm, L/D = 20). The L/D ratio is the ratio of the flighted length of the screw to its outside diameter.
Static mechanical properties of manufactured test specimens were measured in a tensile and flexural test according to DIN EN ISO 527 and 178 using an Instron E3000 testing machine. All mechanical tests were performed at 23°C and 50% relative humidity after conditioning. Testing speed was 1 mm/min. Gauge length of extensometer in tensile testing was 50 mm. The presented values represent the averaged results of measurements performed on 10 samples for each type of composite.

3. Results and discussions

3.1. Volumetrict filling ratios

The filling ratios of the manufactured composites are collated as volumetric contents in Table 1. Filling volumes were calculated from the weight contents and densities.

For the composites the volume fraction of matrix was calculated according to:

$$M_{\mathrm{vol.}} = \frac{M_{\mathrm{wt-\%}} \cdot \rho_{\mathrm{Tcomp}}}{\rho_{\mathrm{Rmat.}} \cdot (1 - V_{\mathrm{vol.}})} \quad (1)$$

while volume fraction of fibres was calculated according to:

$$F_{\mathrm{vol.}} = \frac{F_{\mathrm{wt-\%}} \cdot \rho_{\mathrm{Tcomp}}}{\rho_{\mathrm{Rfib.}} \cdot (1 - V_{\mathrm{vol.}})} \quad (2)$$

where theoretical density of composite was calculated according to:

$$\rho_{\mathrm{Tcomp.}} = \frac{100}{\frac{M_{\mathrm{wt-\%}}}{\rho_{\mathrm{R\,mat.}}} + \frac{F_{\mathrm{wt-\%}}}{\rho_{\mathrm{Rfib.}}}} \quad (3)$$

The void fractions were calculated from obtained real values of densities and theoretical densities:

$$V_{\mathrm{vol.}} = 1 - \frac{\rho_{\mathrm{Rcomp}}}{\rho_{\mathrm{Tcomp}}} \quad (4)$$

where $M_{wt\text{-}\%}$ is weight content of matrix, $F_{wt\text{-}\%}$ is weight content of fibres, $\rho_{Rmat.}$ is measured density of matrix, $\rho_{Rfib.}$ is measured density of fibres, $\rho_{Tcomp.}$ and $\rho_{Rcomp.}$ is theoretical density and measured density of composite respectively.

Table 1. Volumetric filling ratios of the manufactured composite

Composite	Matrix [vol%]	Fibre [vol%]	Filler [vol%]	Fibre+Filler [vol%]	Voids [vol%]
HP400R	-	-			-
HP400R/HM400X	94.3	0.0	5.1	5.1	0.7
HP400R/HM400X	90.1	0.0	9.2	9.2	0.7
HP400R/HM400X	85.7	0.0	13.9	13.9	0.4
HP400R/HM400X	81.2	0.0	18.4	18.4	0.4
HP400R/HM400X	71.1	0.0	27.9	27.9	1.1
HP400R/Cordenka	94.7	4.5	0.0	4.5	0.8
HP400R/Cordenka	90.8	8.9	0.0	8.9	0.4
HP400R/Cordenka	86.3	13.0	0.0	13.0	0.8
HP400R/Cordenka	81.1	17.5	0.0	17.5	1.4
HP400R/Cordenka	69.4	27.4	0.0	27.4	3.2
HP400R/HM400X/Cordenka	91.0	4.3	4.4	8.8	0.2
HP400R/HM400X/Cordenka	84.7	6.9	7.1	14.0	1.3
HP400R/HM400X/Cordenka	81.4	8.7	8.9	17.5	1.0

HP400R/HM400X/Cordenka	71.6	13.2	13.5	26.6	1.8

3.2. Mechanical properties of the composite

3.2.1. Tensile and flexural strength
Tensile and flexural ultimate strength of composites reinforced with different filling ratios of Cordenka man-made cellulose fibres, HM400X cellulose microfibres and their combination are presented in Figure 1 and Figure 2, respectively.

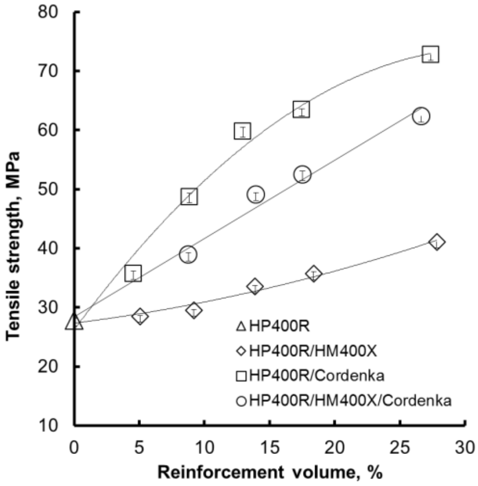

Figure 1. Tensile strength of composites with different filling ratios of cellulose reinforcements and their combination.

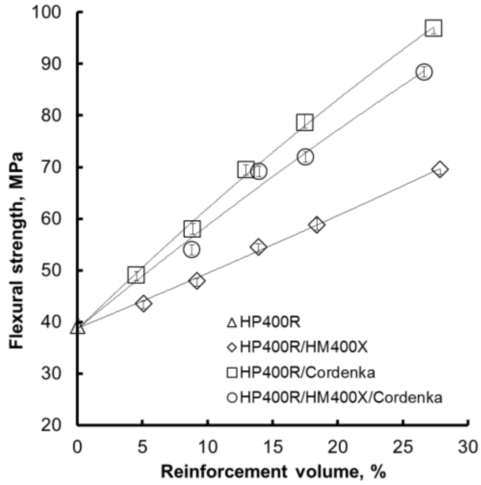

Figure 2. Flexural strength of composites with different filling ratios of cellulose reinforcements and their combination.

Tensile and flexural strength of composites increases with an increase of the reinforcement filling ratio. The greatest improvement was obtained with Cordenka fibres. The maximum stress reached 72.8 MPa and 96.9 MPa for tensile and flexural stress respectively, at ~27% reinforcement volume fraction. It can be explained by the significantly higher tensile strength of the Cordenka fibres, as well as their higher aspect ratio in comparison to HM400X microfiller [8, 17].

The composite with HM400X cellulose microfibres achieved lower strengths, which were 41 MPa and 70 MPa for tensile and flexural stress respectively at reinforcement volume of ~27%. The much lower improvement achieved in composites reinforced with microfibres is likely to be due to the fact that microfibres have lower aspect ratios than Cordenka fibres [6]. At this reinforcement volume fraction composite with Cordenka fibres had ultimate tensile strength higher by 45% and ultimate flexural strength by 28% in comparison to composite with HM400X microfibres. Lower strength of the composite with HM400X cellulose microfibres may be improved by using hybrid combination with Cordenka fibres. The differences of the tensile and flexural stress between composite with Cordenka fibres and composite with combination of man-made cellulose fibres and microfibres in ratio 1:1 was 14.3% (ultimate tensile stress) and 8.8% (ultimate flexural stress).

Averaged tensile stress-strain curves of manufactured composites with ~18% volume fraction of Cordenka man-made cellulose fibre, HM400X cellulose microfibres and their combination are presented in Figure 3.

The stress-strain characteristics of the composite with ~1:1 ratio of Cordenka man-made cellulose fibres and HM400X cellulose microfibres is more similar to the stress-strain characteristics of the composite reinforced with only Cordenka man-made cellulose than the composite reinforced with only HM400X microfibres . Comparing to the HM400X cellulose microfibres the ultimate tensile strength of composites increased from 36 MPa to 53 MPa for hybrid combination of man-made cellulose fibres and microfibres. The ultimate tensile strength of the reinforcement composite with Cordenka fibres achieved the maximum of 63 MPa.

The elongation at break had similar values for the composite reinforced with Cordenka fibres and hybrid composite with combination of Cordenka fibres and HM400X microfibres (8.5%). The composite with HM400X cellulose microfibres was breaking at lower elongation (4.4%).

Figure 4 shows representative flexural stress-strain curves of the manufactured composites with the same filling ratios as presented for tensile results. Comparing to the composite with HM400X cellulose microfibres the ultimate flexural strength of hybrid combination of Cordenka and HM400X increased from 59 MPa to 72 MPa, while the composite reinforced only with Cordenka fibres reached 79 MPa. In the same manner as for tensile testing, also in 3-point bending the stress-strain characteristics of hybrid was closer to stress-strain characteristics of composite reinforced with Cordenka man-made cellulose, as well as the elongation at break of Cordenka reinforced composite and hybrid reinforced with Cordenka and HM400X of 1:1 ratio, had similar values of approximately 13-15%, while the composite reinforced solely with HM400X microfibres broke at ~ 6%.

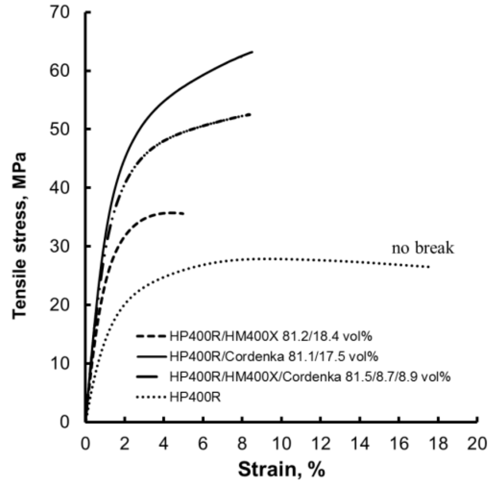

Figure 3. Tensile stress-strain curves of composites with similar filling ratios of cellulose reinforcements and their combination.

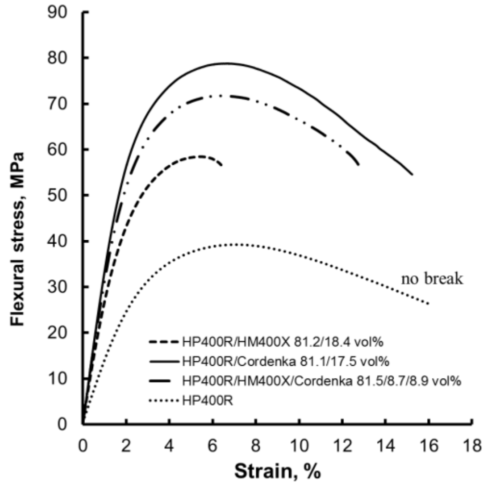

Figure 4. Flexural stress-strain curves of composites with similar filling ratios of cellulose reinforcements and their combination.

3.2.2. Tensile and flexural elastic modulus

Additional investigations were carried out to evaluate an influence of filling ratios on the tensile and flexural modulus. The results obtained for the tensile and flexural modulus with different filling ratio of the manufactured composites are presented in Figure 5 and Figure 6, respectively.

It can be seen that the values of elastic modulus significantly increase with an increase of the volume fraction of Cordenka fibres, HM400X microfibres and their combination. An addition of the cellulose microfibres in the composite increases tensile and flexural modulus for ~160% and ~130% respectively at reinforcement volume of ~5% compared to reinforcement volume of ~27%. The replacement of a cellulose microfibres by Cordenka fibres gives an increase of 61% in the tensile modulus and 58% in the flexural modulus. A similar increase is observed for the tensile and flexural modulus in the manufactured composites with combination of Cordenka man-made cellulose fibres and HM400X cellulose microfibres.

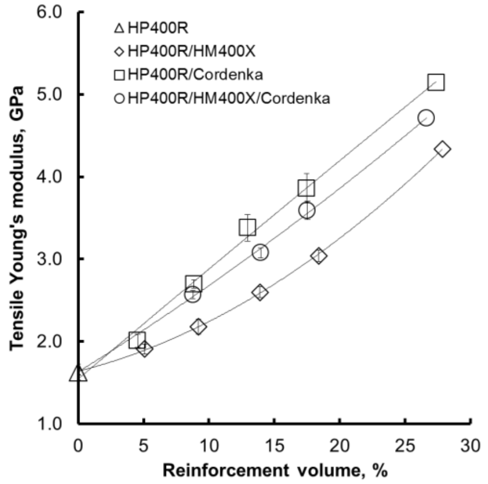

Figure 5. Tensile Young's modulus of composites with different filling ratios of cellulose reinforcements and their combination.

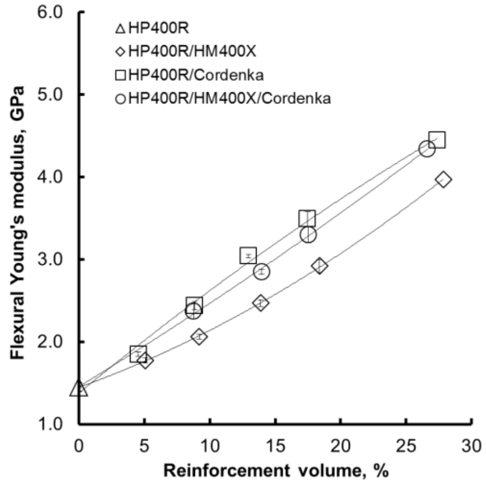

Figure 6. Flexural Young's modulus of composites with different filling ratios of cellulose reinforcements and their combination.

4. Conclusions

The effect of Cordenka man-made cellulose fibres, HM400X cellulose microfibres and their combination on the tensile and flexural strength, elastic and flexural modulus in the composites based on polypropylene matrix was investigated. Increasing volume fractions of Cordenka man-made cellulose fibres, HM400X cellulose microfibres and their combination were used in the research.

The reinforcing with HM400X cellulose microfibres had the smallest influence on the tensile and flexural strength. An addition of the man-made cellulose fibres together with cellulose microfibres increased tensile and flexural ultimate stress by 34% and 21%, respectively, at ~27%reinforcement volume. The maximal ultimate strength was obtained for the composite reinforced with highest filling ratio of Cordenka man-made cellulose fibres. Its tensile strength was higher by 45% and flexural strength by 28% in comparison to the composite reinforced with HM400X microfibres. It can be observed that hybridisation by partial substitution of more expensive man-made cellulose Cordenka fibres with cheaper HM400X cellulose microfibres is beneficial owing to maintaining the tensile and flexural characteristics closer to Cordenka fibre reinforced counterpart. The effect is more profound at higher volume fractions of reinforcement, which also give the highest performance in the investigated range of volume fractions. Especially elongation to break of hybrids is maintained close to Cordenka man-made cellulose composites of equivalent reinforcement volume. The manufactured hybrids have mechanical performance higher than WPC's and engineering plastics like polyamides, but are inferior to polypropylene reinforced with compatibilised glass fibres especially in terms of Young's modulus and strength, although their higher elongation to break might be desired in some particular applications.

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References

[1] E. Labans, K. Kalnins, C. Bisagni, "Flexural behavior of sandwich panels with cellular wood, plywood stiffener/foam and thermoplastic composite core," Journal of Sandwich Structures and Materials, 2017. https://doi.org/10.1177/1099636217699587

[2] A.K. Bledzki, J. Gassan, "Composites reinforced with cellulose based fibres," Prog Polym Sci, Vol. 24, pp. 211–274, 1999. https://doi.org/10.1016/S0079-6700(98)00018-5

[3] R. Merijs-Meri, J. Zicans, T. Ivanova, I. Bochkov, M. Varkale, P. Franciszczak, A.K. Bledzki, J. Gravitis, "Some aspects of the development of oat husks containing polypropylene composites," AIP Conference Proceedings, Vol. 1981, 020128, 2018. https://doi.org/10.1063/1.5045990

[4] A.K. Bledzki, A. Jaszkiewicz, "Mechanical performance of biocomposites based on PLA and PHBV reinforced with natural fibers – a comparative study to PP," Compos Sci Technol, Vol. 70(12), pp. 1687–1696, 2010. https://doi.org/10.1016/j.compscitech.2010.06.005

[5] M Das, Chapter 2, Man-made cellulose fibre reinforcements (MMCFR). In: Biocomposites for High-Performance Applications, edited by D. Ray, Woodhead Publishing 2017, p. 336.

[6] J.K. Pandey, S.H. Ahn, C.S. Lee, A.K. Mohanty, M. Misra, "Recent advances in the application of natural fiber based composites," Macromol Mater Eng, Vol. 295(1), pp. 975–989, 2010. https://doi.org/10.1002/mame.201000095

[7] J. Ganster, H-P. Fink, "Novel cellulose fibre reinforced thermoplastic materials," Cellulose, Vol. 13, pp. 271–280, 2006. P. Franciszczak, K. Kalnins, A.K. Bledzki. "Hybridisation of man-made cellulose and glass reinforcement in short-fibre composites for injection moulding – effects on mechanical performance". Composites: Part B, Vol. 145, pp. 14-27, 2018. https://doi.org/10.1016/j.compositesb.2018.03.008.

[8] P. Franciszczak, K. Kalnins, A.K. Bledzki. "Hybridisation of man-made cellulose and glass reinforcement in short-fibre composites for injection moulding – effects on mechanical performance". Composites: Part B, Vol. 145, pp. 14-27, 2018. https://doi.org/10.1016/j.compositesb.2018.03.008

[9] J. Ganster, H-P. Fink, "Novel cellulose fibre reinforced thermoplastic materials," Cellulose, Vol. 13, pp. 271–280, 2006. https://doi.org/10.1007/s10570-005-9045-9

[10] A.K. Bledzki, P. Franciszczak, A. Mamun, "The utilization of biochemically modified microfibers from grain by-products as reinforcement for polypropylene biocomposite," eXPRESS Polymer Letters, Vol.8. pp. 767–778, 2014. Doi: 10.3144/expresspolymlett.2014.79

[11] A. Amash, P. Zugenmaier, "Study on cellulose and xylan filled polypropylene composites," Polym Bull, Vol. 40(1-2), pp. 251–258, 1998. https://doi.org/10.1007/s002890050

[12] A. Amash, P. Zugenmaier, "Morphology and properties of isotropic and oriented samples of cellulose fibre–polypropylene composites," Polymer, Vol. 41(4), pp. 1589–1596, 2000. https://doi.org/10.1016/S0032-3861(99)00273-6

[13] P. Weigel, J. Ganster, H-P. J. Fink, J. Gassan, K. Uihlein, "Polypropylene–cellulose compounds-high strength cellulose fiber strengthen injection moulded parts," Kunststoffe Plast Europe, Vol. 92, pp. 35–37, 2002.

[14] J. Ganster, H-P. J. Fink, M. Pinnow, "High-tanacity man-made cellulose fiber reinforced thermoplastics-injection moulding compounds with polypropylene and alternative materials," Composites: Part A, Vol. 37, pp. 1796–1804, 2006. https://doi.org/10.1016/j.compositesa.2005.09.005

[15] M. A. Khan, J. Ganster, H-P Fink, "Hybrid composites of jute and man-made cellulose fibers with polypropylene by injection moulding," Composites: Part A, Vol. 40(6-7), pp. 846–851, 2009. https://doi.org/10.1016/j.compositesa.2009.04.015

[16] P. Franciszczak, A.K. Bledzki, "Tailoring of dual-interface in high tenacity PP composites – Toughening with positive hybrid effect," Composites: Part A, Vol. 83, pp. 185-192, 2016. https://doi.org/10.1016/j.compositesa.2015.07.001

[17] P. Franciszczak, R. Merijs-Meri, K. Kalnins, A.K. Bledzki, J. Zicans, "Short-fibre hybrid polypropylene composites reinforced with PET and Rayon fibres – Effects of SSP and

interphase tailoring," Composite Structures, Vol. 181, pp. 121-137, 2017. https://doi.org/10.1016/j.compstruct.2017.08.075