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# Increasing the Impact Toughness of Cellulose Fiber Reinforced Polypropylene Composites—Influence of Different Impact Modifiers and Production Scales

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Received: 29 June 2019; Accepted: 4 August 2019; Published: 8 August 2019



**Abstract:** While cellulose fiber reinforced polypropylene (PP) composites typically offer good stiffness and strength in combination with ecological benefits and a high potential for lightweight construction, they often require measures taken to improve their impact performance. In this work, the influence of different types of impact modifier on the mechanical performance of a PP–cellulose composite was systematically investigated, with a particular focus on the improvement of the notched impact strength and the accompanying loss of stiffness. Among the tested impact modifiers, ethylene-octene copolymers appeared to be the most suitable class to achieve a good overall performance. A high modifier viscosity increased its potential to improve the notched impact strength of the composite. Additionally, composite production on a larger scale improved the impact performance without significantly affecting the tensile properties. Several composites from this study surpassed the overall mechanical performance of a benchmark commercial PP–cellulose composite. While the impact strength of commercial high-impact PP–talc composites could not be reached, the considerably lower density of the PP–cellulose composites is worth mentioning.

**Keywords:** cellulose fiber; polypropylene; impact modification; mechanical properties; injection molding

## 1. Introduction

Natural-fiber reinforced composites (NFC) based on polypropylene (PP) can be of special interest for the automotive industry as a substitute for conventional composites (e.g., with talc or glass fibers), as they offer comparable stiffness and strength while at the same time exhibiting a higher potential for lightweight construction due to their lower density. In addition, they provide the ecological benefit of partially consisting of renewable raw materials [1,2]. In 2017, the European production of wood polymer composites (WPC) and NFC was 410,000 tons, distributed over three main application fields: Decking, siding, and fencing (49%); automotive (36%); and technical applications, furniture, and consumer goods (15%). The latter sector was the strongest growing application in recent years, with an annual growth rate of roughly 30% between 2012 and 2017. In total, 80,000 t of granules for injection molding or extrusion were produced and traded, with PP being one of the most widely used base polymers (other important polymers for WPC and NFC are biopolymers such as polylactic acid (PLA), polyethylene (PE), thermoplastic elastomers, acrylonitrile butadiene styrene (ABS), polycarbonate (PC), polyvinyl chloride (PVC), and poly(methyl methacrylate) (PMMA) [3]. One very interesting type of natural fillers is Kraft pulp fibers, i.e., cellulose fibers obtained from the sulphate process. These offer a good combination of perennial availability, good reinforcing potential, and price, and thus appear particularly suitable for the production of composites for the automotive industry.

Because of the low intrinsic impact toughness of PP, often a heterophasic copolymer instead of a homopolymer is used as a base polymer for composites. Otherwise, additives are often introduced to improve the impact strength. The most common approach to enhance the mechanical performance of PP-based NFCs is to increase the fiber-matrix interaction [4]; commonly used coupling agents are maleic anhydride (MA) grafted polymers [5–10] or silanes [11]. However, the addition of a coupling agent can adversely affect the notched impact strength, as effective energy dissipation during crack propagation requires debonding and pull-out of the fibers from the matrix [12]. If this is prevented by a very strong fiber-matrix interaction, the fibers will break upon impact; for the materials used in this study, this has been shown to dissipate less energy than the fiber pull-out, which is why no coupling agents were used for the present work.

Recently the addition of polymer fibers, such as polyvinyl alcohol (PVA) [13] or polyethylene terephthalate (PET) [14] has been shown to improve the mechanical performance of PP composites considerably.

A different approach, especially in the case of PP-based composites, is to add an elastomeric phase to improve the impact performance of the matrix. Next to ethylene-propylene-based rubbers (EPR, EPDM) [15–17], an important class of materials for the impact modification of polymers are thermoplastic elastomers [18]; among those, the most relevant modifiers for PP are styrenic elastomers (SBS, SEBS) [19], which are often used in combination with coupling agents [20–23], and polyolefinic elastomers [24,25]. The use of ethylene vinyl acetate (EVA) as impact modifier for PP has also been reported [26].

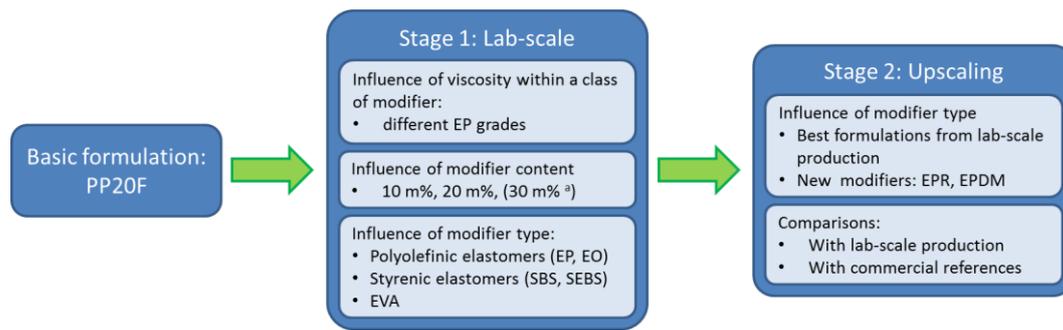
While much literature on the mechanical performance of NFCs is available, a systematic investigation of the influence of different impact modifiers is so far lacking. Therefore, the main objective of the present study is to fill this gap. With regard for the possible application of impact-toughened NFCs in the automotive industry, the aim for the mechanical performance was to achieve the highest possible notched impact strength, while at the same time limiting the reduction of the tensile modulus. A target value for the modulus of 1.8 GPa or higher was set, as this was approximately the average of the moduli of the commercial automotive-grade reference materials that were used for comparison (see Section 3.3).

## 2. Materials and Methods

### 2.1. Materials

The basic formulation for all composites that were investigated in this study consisted of an injection molding grade, metallocene-catalyzed polypropylene (PP) homopolymer with a melt flow rate (MFR) of 140 g/10 min (230 °C, 2.16 kg), and bleached Kraft cellulose fibers with an average fiber length of 800 µm (prior to processing) and a thickness of 15 µm. The fiber content in all composites was 20% by weight. The reference formulation consisting of 80 wt% PP and 20 wt% fibers will subsequently be referred to as “PP20F”. The neat PP was characterized as well in order to show the effect of the fibers on the mechanical properties.

The experimental work for this study consisted of two main parts: First, a screening of different types of impact modifiers that were added to the basic formulation on a laboratory scale; these included several grades of metallocene-catalyzed polyolefinic elastomers (POE; ethylene-octene (EO) and ethylene-propylene (EP)), styrene-butadiene-based elastomers (SBS, SEBS), and ethylene vinyl acetate (EVA). Second, the preparation of selected formulations from the first part, in an upscaled production in order to emulate the processing conditions of commercial materials more realistically than on a laboratory scale; additionally, for this step, an ethylene-propylene rubber (EPR) and an ethylene-propylene-diene rubber (EPDM) were introduced due to their historic importance as impact modifiers for PP. A schematic of the experimental program is illustrated in Figure 1. A complete list of the impact modifiers is shown in Table 1.



**Figure 1.** Flow chart to illustrate the experimental program. <sup>a</sup> Formulations with 30 m% of modifier were only prepared with the ethylene-propylene (EP) grades and with styrenic elastomers (SBS).

**Table 1.** List of impact modifiers; melt flow rate (MFR) data as measured at Wood K plus unless otherwise stated, other material data as shown on the technical data sheets.

Code	Density (g/cm <sup>3</sup> )	Hardness Shore A	MFR <sup>(2.16 kg; 190/230 °C)</sup> (g/10 min)	Additional Material Information
<i>Only laboratory scale production</i>				
EP1	0.865	A 71	18.5 <sub>(190 °C)</sub> /48 <sub>(230 °C)</sub>	13% ethylene content
EP2	0.863	A 64	8.5 <sub>(190 °C)</sub> /20 <sub>(230 °C)</sub>	15% ethylene content
EP3	0.862	A 67	1.5 <sub>(190 °C)</sub> /3 <sub>(230 °C)</sub>	16% ethylene content
EO1	0.885	A 84	30 <sub>(190 °C)</sub> <sup>a</sup>	Mooney viscosity 2 MU
SBS	0.94	A 71–81	<1 <sub>(200 °C, 5 kg)</sub> [Datasheet] <sup>b</sup>	31% styrene content
SEBS	0.90	A 47	1.8 <sub>(190 °C)</sub> /9.4 <sub>(230 °C)</sub>	13% styrene content
EVA	0.952	A 75	2.5 <sub>(230 °C)</sub> <sup>c</sup>	28% VA content
<i>Laboratory scale and upscaled production</i>				
EO2	0.870	A 70	5 <sub>(190 °C)</sub> /10.8 <sub>(230 °C)</sub>	Mooney viscosity 9 MU
EO3	0.857	A 57	1 <sub>(190 °C)</sub> /2.2 <sub>(230 °C)</sub>	Mooney viscosity 25 MU
EO4	0.870	A 51	0.5 <sub>(190 °C)</sub> /1.4 <sub>(230 °C)</sub>	Mooney viscosity 45 MU
<i>Only upscaled production</i>				
EPR	n/a	n/a	n/a <sup>d</sup>	72% ethylene content Mooney viscosity 44 MU
EPDM	n/a	n/a	n/a <sup>d</sup>	69% ethylene content 4.4% diene content Mooney viscosity 60 MU

<sup>a</sup> Viscosity of EO1 at 230 °C was too low for reliable MFR measurement. <sup>b</sup> Viscosity of SBS was too high at either temperature for MFR measurement with a load of 2.16 kg. <sup>c</sup> Viscosity of ethylene vinyl acetate (EVA) at 190 °C was too high for reliable MFR measurement. <sup>d</sup> Viscosity of ethylene-propylene-based rubbers (EPR and EPDM) was too high at either temperature for reliable MFR measurement.

The amounts of impact modifier in the composites were 10% and 20% by weight, and 30% in selected formulations. Regarding the nomenclature, the formulations used for this study will subsequently be referred to according to the scheme “*ModifierCode\_wt%*”; e.g., the designation “EP1\_30” describes the formulation consisting of 30 wt% EP1, 50 wt% PP and 20 wt% fibers. For the comparison of production scales, the suffix “\_Lab” is used for the laboratory scale production, and “\_Up” is used for the upscaled production.

Two commercially available talc-reinforced polypropylene copolymers that are being used as high-impact grades for the automotive industry were tested as reference materials: Hostacom TRC 333N (20% talc filled) and Hostacom EKC 330N (16% talc filled), both from LyondellBasell. As a reference, specifically for PP–cellulose composites, the mechanical properties of the commercially available high impact grade Formi EXP 20 (20 wt% cellulose filled PP) from UPM Biocomposites, according to the technical data sheet [27], were taken into account.

## 2.2. Sample Preparation

For the laboratory-scale production, the compounds were prepared on a Brabender DSE20/40D twin screw extruder (Brabender GmbH & Co KG, Duisburg, Germany) with a 20 mm screw diameter, at a screw speed of 600 rpm and a throughput of 5 kg/h. The upscaled production was performed on a Leistritz ZSE 50 MAXX 48D twin screw extruder (Leistritz Extrusionstechnik GmbH, Nürnberg, Germany) with 50 mm screw diameter, a screw speed of 400 rpm and a throughput of 240 kg/h.

For the mechanical characterization, standard shoulder bars according to ISO 527-2 were prepared on a Battenfeld HM1300/350 injection molding machine (Battenfeld Kunststoffmaschinen GmbH, Kottlingbrunn, Austria). Prior to testing, the specimens were conditioned at 23 °C and 50% RH for at least 120 h.

## 2.3. Characterization Methods

Tensile tests according to ISO 527 were carried out on a Messphysik BETA20-10 universal testing machine (Messphysik Materials Testing GmbH, Fürstenfeld, Austria). The tensile modulus  $E$  was determined in the range between 0.05% and 0.25% elongation at a rate of 1 mm/min, afterwards the elongation rate was gradually increased to 50 mm/min to determine the tensile strength  $\sigma_M$ . Charpy unnotched ( $a_cU$ ) and notched ( $a_cN$ ) impact strength according to DIN EN ISO 179-1eU (unnotched) or -1eA (notched) were tested on an Instron CEAST 9050 impact pendulum (ITW Test and Measurement Italia S.r.l., INSTRON CEAST division, Pianezza, Italy). Depending on the impact toughness of the materials, a pendulum with an energy of 0.5 J, 2 J or 7.5 J was used. The heat deflection temperature (HDT-B) according to DIN EN ISO 75 was determined on an Instron CEAST HDT Vicat Series 3 Station Tester, using a load of 0.45 N/mm<sup>2</sup>. This test was carried out for selected samples. Melt flow rate (MFR) according to ISO 1133 was tested on a Zwick 4105 Extrusion Plastometer, at a temperature of 230 °C and using a load of 2.16 kg. The density  $\rho$  was measured according to DIN EN ISO 1183-1 using a Sartorius BP 301 S Analytical Balance with a YDK 01 Density Kit. The morphology of the samples was investigated via scanning electron microscopy (SEM), using a Phenom ProX desktop microscope.

## 3. Results

### 3.1. Fiber Reinforcement of the Neat PP

Compared to the neat PP, the formulation PP20F shows a very strong increase in stiffness and a moderate increase in tensile strength (cf. Table 2); these changes are in the expected range for NFC [1]. However, the most obvious effect of the addition of the fibers is an increase of the notched impact strength by almost a factor of four, whereas the unnotched impact strength is not significantly affected. The introduction of natural fibers is typically detrimental to the impact performance of PP [1]; however, in the present case the neat PP has a very poor intrinsic impact performance (most likely due to its very low viscosity which indicates a very low molar mass and therefore a high brittleness), which is therefore improved by the addition of the fibers.

### 3.2. Characterization of the Compounds from the Laboratory-Scale Production

Literature comparing different types of impact modifiers for PP-based NFCs is surprisingly scarce. The first experimental stage of this study was therefore to produce and characterize a series of compounds containing different types and amounts of impact modifiers (see the list of materials in Table 1) that were introduced into the basic formulation PP20F.

The three EP grades were supplied by the same manufacturer and mainly differed in their viscosity, while the differences in ethylene content and Shore hardness were considered negligible in comparison. Therefore, these grades were suitable to investigate the influence of the viscosities of otherwise very similar modifiers on the mechanical properties of the compounds. The details of this investigation are described in Section 3.2.1. A similar investigation might have been possible with the four EO grades; however, due to the fact that EO2 was supplied by a different manufacturer than EO1, EO3, and EO4,

and due to the large variation in density and Shore hardness, it would not have been feasible to focus solely on the effect of the modifier viscosity.

**Table 2.** Absolute and specific mechanical properties of the compounds from the lab-scale production. The properties of the neat polypropylene (PP) are shown for comparison.

Code	Absolute Values							Specific Values (Normalized by Density)			
	$\rho$	MFR	HDT-B	E	$\sigma_M$	$a_cU$	$a_cN$	$E_{sp}$	$\sigma_{M\_sp}$	$a_cU_{sp}$	$a_cN_{sp}$
Unit	g/cm <sup>3</sup>	g/10 min	°C	GPa	MPa	kJ/m <sup>2</sup>	kJ/m <sup>2</sup>	GJ/kg	MJ/kg	kJ m/kg	kJ m/kg
PP	0.906	140 <sup>a</sup>	95.8	1.55	34.7	40.1	1.1	1.71	38.3	44.3	1.2
PP20F	0.981	9.2	134.6	2.76	40.1	41.0	4.5	2.81	40.9	41.8	4.6
EP1_10	0.978	7.3	129.4	2.07	35.6	39.4	5.3	2.12	36.4	40.3	5.4
EP1_20	0.978	6.3	119.1	1.74	30.8	40.1	7.5	1.78	31.5	41.0	7.7
EP1_30	0.973	6.0	104.0	1.32	24.7	38.6	9.7	1.36	25.4	39.7	10.0
EP2_10	0.978	7.1	132.6	2.05	35.3	39.0	5.6	2.10	36.1	39.9	5.7
EP2_20	0.978	4.6	122.9	1.72	30.4	41.0	8.1	1.76	31.1	41.9	8.3
EP2_30	0.974	3.6	108.0	1.33	24.2	36.9	11.1	1.37	24.8	37.9	11.4
EP3_10	0.981	5.1	136.1	2.19	36.6	39.3	6.2	2.23	37.3	40.1	6.3
EP3_20	0.976	2.6	127.7	1.83	31.0	39.1	9.2	1.88	31.8	40.1	9.4
EP3_30	0.972	2.2	114.3	1.33	24.3	36.9	12.8	1.37	25.0	38.0	13.2
EO1_10	0.984	6.4	-	2.30	36.7	44.3	6.7	2.34	37.3	45.0	6.8
EO1_20	0.980	5.2	-	1.83	31.9	44.5	8.4	1.87	32.6	45.4	8.6
EO2_10	0.981	6.7	-	2.36	34.2	42.2	7.6	2.41	34.9	43.0	7.7
EO2_20	0.977	4.7	-	2.03	29.4	38.4	10.2	2.08	30.1	39.3	10.4
EO3_10	0.978	6.2	-	2.44	35.1	35.8	7.2	2.49	35.9	36.6	7.4
EO3_20	0.972	3.5	-	2.09	29.3	34.4	10.1	2.15	30.1	35.4	10.4
EO4_10	0.974	5.5	-	2.30	33.6	37.8	7.1	2.36	34.5	38.8	7.3
EO4_20	0.979	3.0	-	2.03	28.8	36.7	11.6	2.07	29.4	37.5	11.8
SBS_10	0.982	4.3	-	2.29	32.7	41.9	6.8	2.33	33.3	42.7	6.9
SBS_20	0.993	2.4	-	2.12	28.5	40.9	9.6	2.13	28.7	41.2	9.7
SBS_30	0.997	1.5	-	1.72	22.3	37.8	14.2	1.73	22.4	37.9	14.2
SEBS_10	0.982	4.5	-	2.27	34.8	41.3	7.5	2.31	35.4	42.1	7.6
SEBS_20	0.980	3.1	-	1.86	28.6	40.4	11.4	1.90	29.2	41.2	11.6
EVA_10	0.990	5.8	-	2.30	35.1	39.3	6.2	2.32	35.5	39.7	6.3
EVA_20	0.996	5.3	-	1.93	31.3	38.2	7.3	1.94	31.4	38.4	7.3

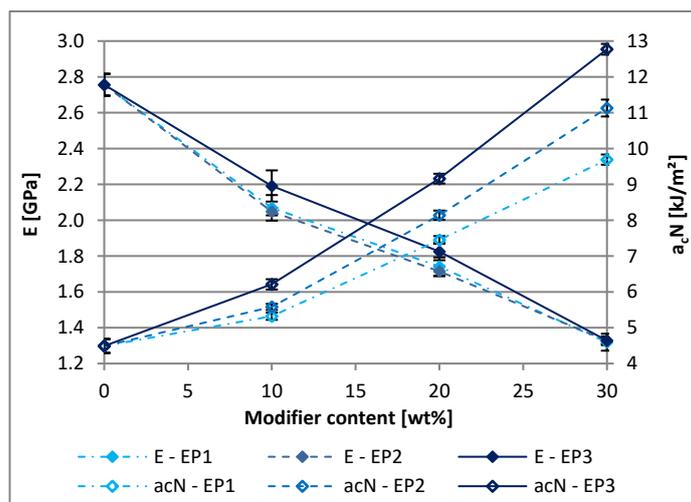
<sup>a</sup> MFR of the neat PP was taken from the technical datasheet; the viscosity was too low for a reliable measurement.

The investigation of the influence of different types of modifiers on the mechanical performance is discussed in Section 3.2.2. For that part of the study, the determination of the heat deflection temperature was omitted, as the results from the comparison of the three EP grades showed a close correlation of the HDT-B to the tensile modulus, and thus the measurement of the HDT-B did not seem to give an additional benefit for the purposes of the present study.

Table 2 shows the measured data, as well as the density-normalized specific values, from the mechanical characterization of all compounds prepared at the laboratory scale.

### 3.2.1. Influence of the Viscosity of the Impact Modifier

For all EP grades, increasing the concentration of the modifiers resulted in a strong increase of the  $a_cN$  and in a reduction of the tensile modulus and strength. Additionally, flowability and HDT were reduced as well. The unnotched impact strength, however, remained largely unaffected by the modifier (cf. Table 2). The effect of the modifier content on the tensile modulus and the notched impact strength is illustrated in Figure 2. The more or less linear reduction of the stiffness with increasing modifier content is consistent with the literature for impact-toughened PP [15,28] and basically follows the rule of mixtures according to which a larger amount of the soft dispersed phase decreases the volume of the stiff matrix and thus the modulus [17].



**Figure 2.** Tensile modulus (filled symbols; left  $y$ -axis) and Charpy notched impact strength (open symbols; right  $y$ -axis) of the compounds containing the EP elastomers.

With increasing viscosity of the elastomer, the effect of the impact modification also increased. The highest  $a_{cN}$  value was thus obtained for EP3\_30, which was 184% higher than the  $a_{cN}$  of the reference NFC material. In comparison, with EP1\_30 the  $a_{cN}$  was increased by 115%. Moreover, a higher viscosity of the modifier slightly reduced the detrimental effect on the HDT. The downside of a higher viscosity of the modifier was obviously an increase in the total viscosity of the compound, as indicated by decreasing MFR values; nonetheless, all compounds could be processed by injection molding without difficulty. Regarding the tensile properties and the unnotched impact strength, the viscosity of the modifier did not appear to have a significant influence. A further illustration of the modulus and the  $a_{cN}$  is given in Figure 2, as the focus regarding the mechanical performance lies mostly on these two properties.

While it has been shown in the literature that a high viscosity of the modifier is generally beneficial for the impact toughness [29], the reason for this cannot be explained in a straightforward way. On the one hand, a high molar mass directly influences the impact strength in a positive way. On the other hand, a high viscosity ratio (i.e., the viscosity of the dispersed phase, divided by the viscosity of the matrix) is likely to increase the particle size [30]. Then again, the processing history also has a strong influence on the morphology [28]. While generally a small particle size improves the impact behavior [16,31], the phase compatibility also has a strong influence on both the impact performance as well as the morphology [28].

SEM pictures of the fracture surfaces of EP1\_20, EP2\_20 and EP3\_20 clearly show the presence of the cellulose fibers; however, no significant differences in the morphology are visible. In fact, a separation between matrix and the dispersed phase cannot be distinguished in these images (cf. Figure 3). Based on the available data, a definite statement on whether the increase in impact performance with increasing modifier viscosity is only related to the molar mass or is also influenced by the morphology can therefore not be made, but given the existing knowledge from the literature, a combination of both factors appears to be the most likely explanation.

### 3.2.2. Effects of Different Types of Impact Modifiers

Because of the poor tensile properties of the previously tested compounds containing 30 wt% EP (1,2,3) (cf. Table 2), for most other modifiers except SBS only formulations with 10% and 20% modifier content were prepared, while formulations with 30 wt% modifier content were omitted. An exception was made in case of the SBS because of the comparatively high stiffness of the formulation SBS\_20.

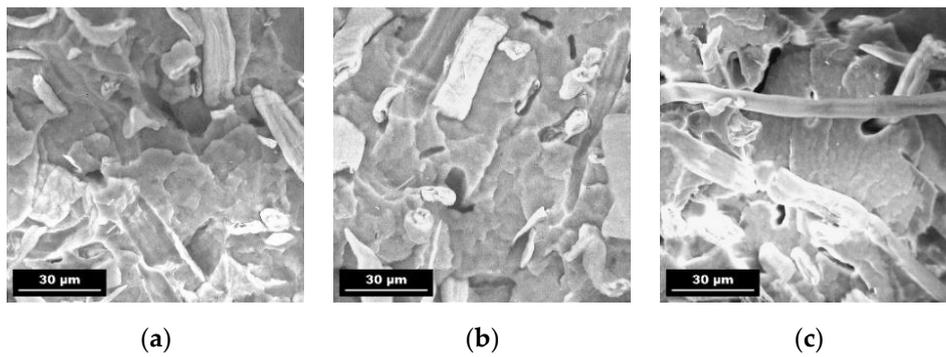


Figure 3. SEM images of cryo-fractured surfaces: (a) EP1\_20, (b) EP2\_20, (c) EP3\_20.

All measured mechanical data are summarized in Table 2. The tensile modulus and the  $a_cN$  of selected formulations are illustrated in Figure 4. In order to improve the visibility, only formulations containing up to 20 wt% of modifier are plotted. In comparison with the EP elastomers, most of the other modifiers led to a further improvement of the  $a_cN$ , the notable exceptions being the EO1 and the EVA (cf. Table 2). The  $a_cU$  was slightly improved with EO1, but reduced with the other EO types, while it was only marginally affected with the other modifiers. The reduction of tensile strength was in a similar range for all modifiers, whereas for the stiffness slightly larger differences were observed, with the best value being reached with SBS. Generally, all observed (positive and negative) effects were stronger with a higher modifier concentration.

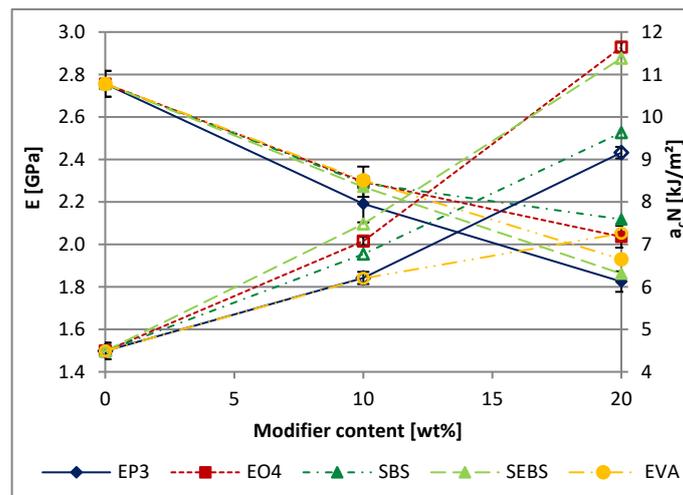


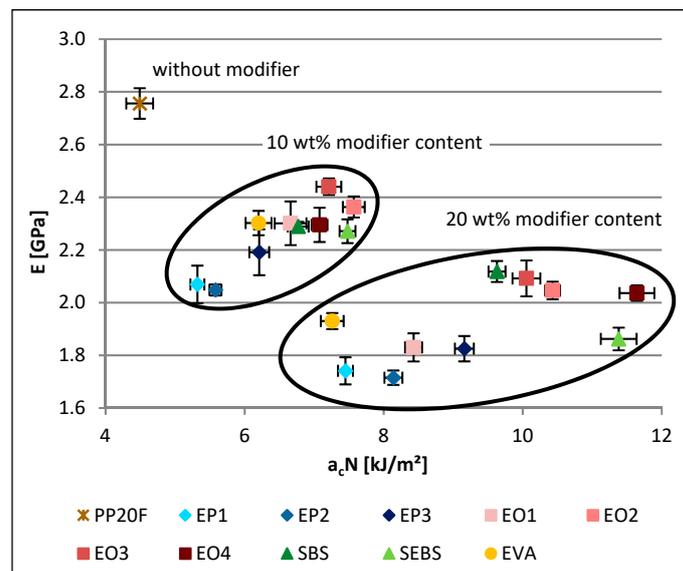
Figure 4. Influence of various impact modifiers on the tensile modulus (filled symbols; left  $y$ -axis) and the Charpy notched impact strength (open symbols; right  $y$ -axis).

Among the POEs, one of the best overall performances was achieved with 20 wt% of EO4, with an increase of the  $a_cN$  by 157% and a comparatively moderate loss of stiffness (−26%). However, a reduction of the  $a_cU$  was observed, which might be related to a rather coarse distribution of the modifier in the PP matrix, as indicated by the SEM images shown at the end of this subsection. In contrast, the best  $a_cU$  of all formulations was achieved with EO1, which may be due to a better compatibility between matrix and modifier. However, the  $a_cN$  and stiffness were noticeably reduced compared to the other EO grades.

Among the other compounds containing 20 wt% of impact modifier, the highest  $a_cN$  was achieved with SEBS (+153%), which is very close to that of EO4\_20 but which came at the cost of a comparatively low stiffness, even though it was still above the abovementioned target value of 1.8 GPa from comparable commercial materials. The formulations containing SBS showed promising mechanical properties, with the  $a_cN$  being slightly lower than that of EO2 but the E-modulus being slightly

higher. Therefore, an additional formulation with 30 wt% SBS was produced. With this material, by far the best  $a_cN$  of all tested samples was achieved (+213% compared to PP20F). The stiffness was significantly higher compared to the compounds with 30 wt% EP elastomer, despite being slightly below 1.8 GPa. The drawbacks of this formulation were a comparatively poor tensile strength and flowability and, especially, a higher density than most other materials. The samples containing EVA showed comparable tensile properties and  $a_cU$  to the other formulations but a significantly lower  $a_cN$  as well as a higher density.

An Ashby plot of the modulus versus the  $a_cN$  is given in Figure 5, which shows that at a concentration of 20 wt%, EO4 gives the best combination of stiffness and notched impact strength, while at 10 wt%, the performance of EO2 and EO3 appears actually better than that of EO4. Among the other impact modifiers, the good mechanical properties of compounds containing SEBS are worth mentioning, but they are surpassed by EO2 and EO3 (at 10 wt%) and by EO4 (at 20 wt%).



**Figure 5.** Ashby plot: Tensile modulus vs. notched impact strength—comparison of all tested impact modifiers from the laboratory-scale production in concentrations of 0, 10, and 20 wt%.

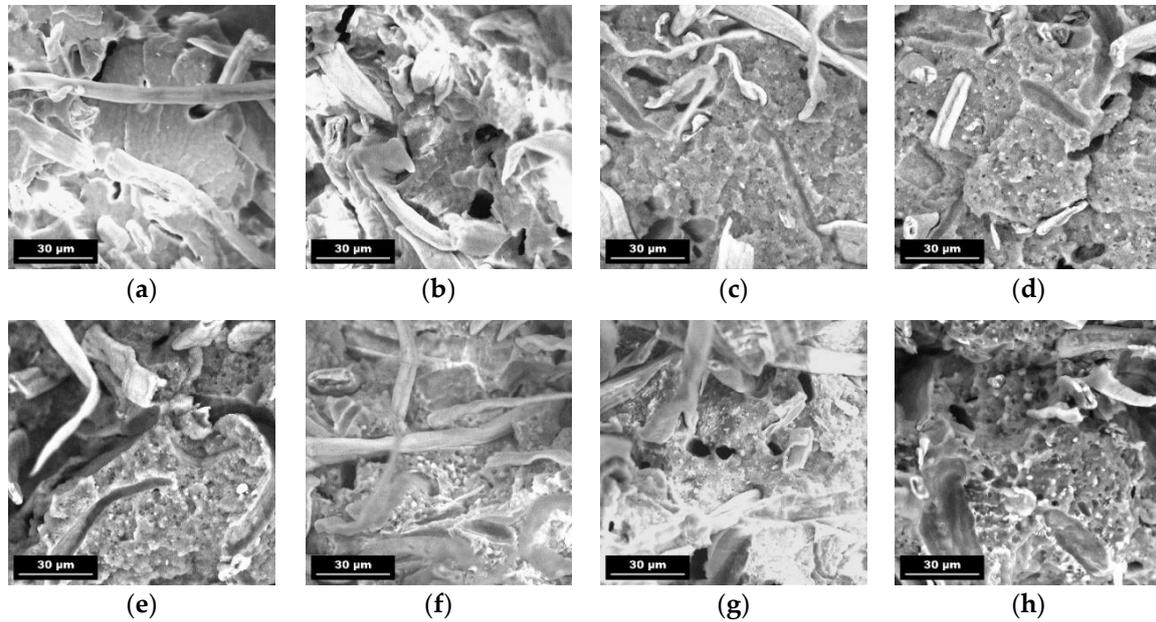
Figure 6 shows SEM images of cryo-fractured surfaces of the compounds containing 20% modifier. In contrast to the EP formulation, the matrix and dispersed modifier phase can clearly be distinguished in all cases except EO1\_20. Between EO2, EO3, and EO4, the morphology appears to become slightly coarser with increasing viscosity of the modifier. The respective dispersions of SBS and EVA are even coarser; this can probably be explained by the high modifier viscosity in combination with a low compatibility with the matrix in both cases. In contrast, the dispersion of the SEBS appears to be clearly finer than that of the SBS, and similar to that of the EO2.

### 3.3. Upscaling and Comparison with Commercial Reference Materials

For the comparison with commercially available high-impact materials, selected formulations from the present study (EO2\_20, EO3\_20, and EO4\_20 and the base material PP20F as a reference) were produced on a larger scale.

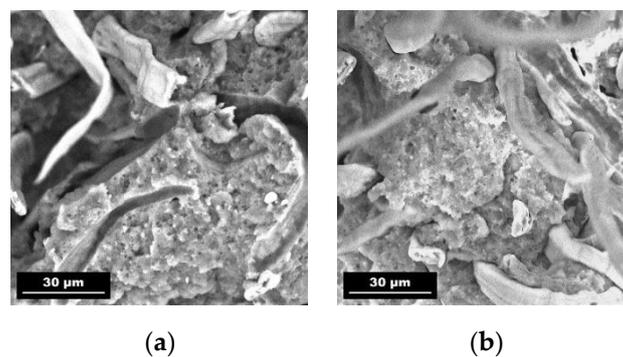
The EO grades were chosen because of the good overall mechanical performance of the compounds containing 20 wt% modifier. Despite their high respective  $a_cN$  values, SBS\_30 and SEBS\_20 were omitted from the up-scaling because of their lower stiffness and, in case of the SBS, also because of its high density. In addition, because of the historic importance of these materials as impact modifiers for PP, a grade of ethylene-propylene rubber (EPR) and a grade of ethylene-propylene-diene rubber (EPDM) were introduced for comparison with the EO grades. As commercial references, the PP-talc

composites Hostacom TRC 333N (H\_TRC; 20% filler content) and Hostacom EKC 330N (H\_EKC; 16% filler content) were tested. Due to its very similar composition, the commercial high-impact PP–cellulose composite Formi EXP 20 (20 wt% filler content) was added as a reference, using mechanical data as given on the technical data sheet [27].



**Figure 6.** SEM images of cryo-fractured surfaces: (a) EP3\_20, (b) EO1\_20, (c) EO2\_20, (d) EO3\_20, (e) EO4\_20, (f) SBS\_20, (g) SEBS\_20, (h) EVA\_20.

According to the data from PP20F, EO2\_20, EO3\_20, and EO4\_20, the compound production on a larger scale resulted in a notable improvement of the impact properties, especially the unnotched impact strength. This may be related to a reduced damage of the polymers and fibers during compounding (because of the higher normalized throughput in the upscaled production and thus a reduced energy input), and in the case of the impact modified compounds, also to a better dispersion of the modifier, as illustrated by a comparison of the SEM images of EO4\_20\_Lab and EO4\_20\_Up (cf. Figure 7). Meanwhile, the tensile properties remained almost unaffected (cf. Table 3).



**Figure 7.** SEM images of cryo-fractured surfaces: EO4\_20\_Lab (a) and EO4\_20\_Up (b).

A comparison of the ethylene-octene grades EO2, EO3, and EO4 shows that the viscosity of the modifiers increases in the order EO2 < EO3 < EO4, while the Shore hardness decreases in that order. Likewise, the  $a_cU$  and  $a_cN$  values of the corresponding compounds from the up-scaled production increase in this order, while the tensile strength and (albeit not significantly) the modulus decrease.

These trends are much clearer in the up-scaled production compared to the lab-scale production, especially between EO2 and EO3, which may again be related to a better dispersion.

**Table 3.** Absolute and specific mechanical properties of the compounds from the upscaled production (suffix “\_Up”), comparison with laboratory-scale production (suffix “\_Lab”) and commercial reference materials (these are, by definition, “Up”).

Code	[g/cm <sup>3</sup> ]	Absolute Values				Specific Values (Normalized by Density)			
		E [GPa]	M [MPa]	a <sub>c</sub> U [kJ/m <sup>2</sup> ]	can [kJ/m <sup>2</sup> ]	E <sub>sp</sub> [GJ/kg]	M <sub>sp</sub> [MJ/kg]	a <sub>c</sub> U <sub>sp</sub> [kJ m/kg]	a <sub>c</sub> N <sub>sp</sub> [kJ m/kg]
PP20F_Lab	0.981	2.76	40.1	41.0	4.5	2.81	40.8	41.8	4.6
PP20F_Up	0.980	2.82	41.0	43.4	5.5	2.88	41.9	44.4	5.6
EO2_20_Lab	0.977	2.03	29.4	38.4	10.2	2.07	30.1	39.3	10.4
EO2_20_Up	0.972	2.03	28.9	39.7	10.7	2.09	29.8	40.9	11.0
EO3_20_Lab	0.972	2.09	29.3	34.4	10.1	2.15	30.1	35.4	10.3
EO3_20_Up	0.973	2.01	28.3	41.8	12.2	2.06	29.1	42.9	12.5
EO4_20_Lab	0.979	2.04	28.8	36.7	11.6	2.08	29.5	37.5	11.9
EO4_20_Up	0.976	1.96	26.8	43.3	13.3	2.01	27.4	44.4	13.6
EPR_20_Up	0.973	2.18	29.4	36.1	8.7	2.24	30.3	37.1	9.0
EPDM_20_Up	0.976	2.13	28.6	35.2	8.5	2.18	29.3	36.0	8.7
H_TRC	1.062	1.90	21.4	>160 <sup>a</sup>	31.7	1.79	20.2	>151 <sup>b</sup>	29.9
H_EKC	1.020	1.63	19.4	>160 <sup>a</sup>	27.3	1.60	19.0	>157 <sup>b</sup>	26.8
Formi EXP 20 <sup>b</sup>	0.99	1.80	33	45	8.8	1.82	33.3	45.5	8.9

<sup>a</sup> With both Hostacom grades, no fracture occurred upon impact with a 7.5 J pendulum. <sup>b</sup> Data for Formi EXP 20 were obtained from the technical data sheet [27].

There was little difference in the mechanical properties between the compounds containing EPR and EPDM. Thus, the diene content of the EPDM did not appear to have a significant influence on the mechanical properties. In both cases a slightly higher stiffness and similar tensile strength, compared to the EO grades, were achieved. However, the impact performance, in particular the a<sub>c</sub>N, was considerably reduced.

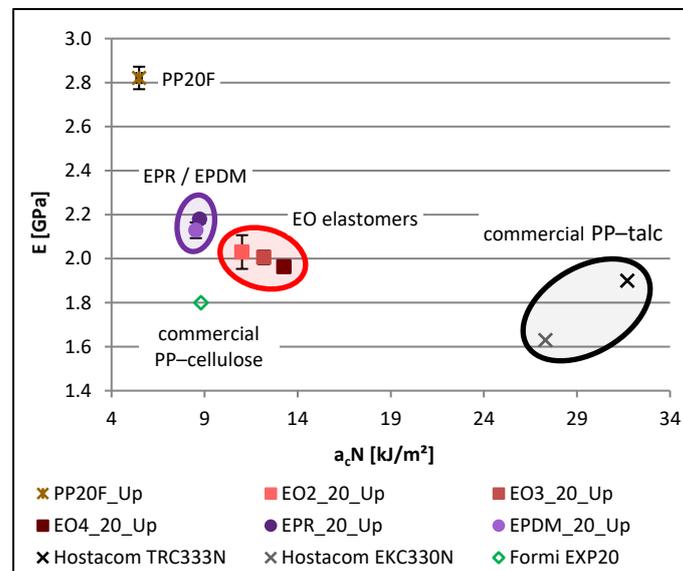
In comparison with the talc reinforced Hostacom grades, none of the materials tested in this study come close to their impact performance. However, all of the cellulose fiber reinforced PPs have a higher tensile strength and a significantly lower density (cf. Table 3). Especially the latter point is of particular importance for all considerations concerning lightweight construction and may therefore be of great interest for automotive applications [2]. The tensile modulus of most formulations containing up to 20 wt% modifier (except EP2\_20, EP3\_20) is comparable or better than that of H\_TRC. The only formulations of which the stiffness values do not clearly exceed that of H\_EKC are those with 30 wt% of any of the EP grades.

If the specific mechanical properties are considered, the advantage of the NFCs in terms of stiffness and strength compared to the talc-filled grades becomes even more obvious, while their deficit regarding the impact performance becomes slightly less pronounced (cf. Table 3).

The cellulose reinforced reference material Formi EXP20 has a higher a<sub>c</sub>U than all other materials prepared for this study; however, the majority of tested formulations containing 20 wt% of modifier, particularly those with the EO grades (except EO1), SBS and SEBS, have a clearly superior a<sub>c</sub>N. Almost all formulations with 20 wt% modifier have a lower tensile strength but a comparable or higher stiffness than Formi EXP20, the exceptions being EP2\_20 and EP3\_20, which have a lower stiffness. With most modifiers, except SBS and EVA, a lower density than that of Formi EXP20 was achieved (cf. Table 3).

Figure 8 shows an Ashby plot of the modulus versus the a<sub>c</sub>N of the formulations prepared in the upscaled production and the commercial reference materials. Evidently the ratio between stiffness and notched impact strength, while at 10 wt%, the performance of EO2 and EO3 appears actually better than that of EO4. Among the other impact modifiers, the compounds containing SEBS show the

best overall mechanical properties, but they are surpassed by EO2 and EO3 (at 10 wt%) and by EO4 (at 20 wt%).



**Figure 8.** Ashby plot: Tensile modulus vs. notched impact strength—comparison of compounds from the up-scaled production with commercial materials.

#### 4. Conclusions

By adding a thermoplastic elastomer, the notched impact strength of cellulose reinforced PP can be considerably improved without significantly affecting the unnotched impact strength. However, the enhanced impact properties come at the cost of a reduction in stiffness and tensile strength; depending on the desired application, this is likely one of the most important limiting factors.

While a high viscosity and a low hardness of the modifier appear to be beneficial for the impact behavior, a soft material also leads to a more pronounced loss in stiffness. Among the materials tested in this study, ethylene-octene-based POE and styrene-butadiene-based elastomers led to the best overall mechanical performance. Within the given boundary conditions, for most of the modifiers a content of 20 wt% yielded the best results; in the case of the used SBS grade with a content of 30 wt%, a very good notched impact strength was achieved while at the same time retaining acceptable tensile properties but at the cost of an increased composite density. An increased production scale did not significantly affect the tensile properties, but a clear tendency towards an improved impact performance could be observed.

Generally, the observed influence of the different types of modifiers on the mechanical performance of the PP–cellulose composite reflects what is known from the impact modification of neat PP—according to the literature, thermoplastic elastomers, in particular ethylene-octene elastomers, appear to be more effective than conventional modifiers such as EPR or EPDM [32,33]. One can therefore conclude that the impact modifiers that were used for this study mainly affect the properties of the PP matrix and that any possible interaction with the fibers plays only a minor role. This conclusion is supported by the SEM images, which do not suggest any adhesion between the fibers and the impact modifiers.

Of all the formulations that were tested in the course of this study, the most well-balanced property profile, with an excellent impact performance and also good tensile properties, was achieved with 20 wt% of EO4. Some of the tested materials showed a clearly improved mechanical performance over the commercial cellulose reinforced reference material. While the impact properties of the commercial talc-filled reference materials were out of reach, their tensile properties could be surpassed. In addition, due to the lower density, a cellulose reinforced compound might find opportunities for applications where weight reduction plays a role.

The mechanical property profiles indicate a high potential for use in automotive interior applications. In that regard, the EO-modified composites are of particular interest, as metallocene-catalyzed polymers offer the additional benefit of a low level of volatile organic compound (VOC) emissions because of their well-defined molar mass distributions [34–36].

**Author Contributions:** Conceptualization, M.M. and L.S.; Investigation, M.M.; Methodology, M.M. and L.S.; Project administration, L.S., C.P. and C.U.; Supervision, L.S., C.P. and C.U.; Visualization, M.M.; Writing—original draft, M.M.; Writing—review & editing, M.M., L.S., C.P. and C.U.

**Funding:** This work was funded within the scope of the COMET programme of the Austrian Research Promotion Agency (FFG). Part of this work was performed within the project BioCarb K, supported by the European Regional Development Fund (EFRE) and the province of Upper Austria through the program IWB 2014–2020.

**Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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