Novel Thermoplastic Composites from Commodity Polymers and Man-Made Cellulose Fibers

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Summary: A new class of fibre reinforced commodity thermoplastics suited for injection moulding and direct processing applications has been developed using man-made cellulosic fibres (Rayon tire yarn, Tencel, Viscose, Carbacell) and thermoplastic commodity polymers, such as polypropylene (PP), polyethylene (PE), high impact polystyrene (HIPS), poly(lactic acid) (PLA), and a thermoplastic elastomer (TPE) as the matrix polymer. For compounding, a specially adapted double pultrusion technique has been employed which provides composites with homogeneously distributed fibres. Extensive investigations were performed with Rayon reinforced PP in view of applications in the automotive industry. The Rayon-PP composite is characterized by high strength and an excellent impact behaviour as compared with glass fibre reinforced PP, thus permitting applications in the field of engineering thermoplastics such as polycarbonate/acrylonitrile butadiene styrene blends (PC/ABS). With the PP based composites the influence of material parameters (e.g. fibre type and load, coupling agent) were studied and it has been demonstrated how to tailor the desired composite properties as modulus and heat distortion temperature (HDT) by varying the fibre type or adding inorganic fillers. Man-made cellulose fibers are also suitable for the reinforcement of further thermoplastic commodity polymers with appropriate processing temperatures. In case of PE modulus and strength are tripled compared to the neat resin while Charpy impact strength is increased five-fold. For HIPS mainly strength and stiffness are increased, while for TPE the property profile is changed completely. With Rayon reinforced PLA, a fully biogenic and biodegradable composite with excellent mechanical properties including highly improved impact strength is presented.

Keywords: cellulose man-made fibers; injection moulding; mechanical properties; rayon; reinforced thermoplastics

Introduction

Natural cellulosic fibers from wood or annual plants are being used for reinforcing thermoplastic materials and thermosets for a number of years already.[1] Presently, there are many attempts to replace glass fibers by bast fibers (jute, flax, hemp) in mainly PP based composites processed by injection moulding or press technologies. This is motivated by advantages over glass fibers such as lower cost, lower density (1.5 g/cm^3 *vs.* 2.5 g/cm^3), lack of abrasion to the processing equipment and ease of incineration. However, the property variation of the natural fibers due to the varying growing and processing conditions and the typical deficits as possible smell and impact behaviour of the natural fibre reinforced materials are considered as serious disadvantages.

Spun Cellulose fibers, on the other hand, possess all the advantages of a man-made

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industrial fibre in terms of supply, quality control, and uniformity, maintaining the advantages mentioned above for natural fibers. At moderate price they offer remarkable mechanical properties; strengths can be above 50 cN/tex (750 MPa), moduli up to 2000 cN/tex (30 GPa), which make them a promising candidate for reinforcing thermoplastic matrices. In recent years, the potential of man-made cellulosic fibers for reinforcing PP and other thermoplastic matrix polymers has been demonstrated by several groups[2–5] including our laboratory.[6–11] Rayon-PP based composites suitable for injection moulding, extrusion and press technologies were developed in a Fraunhofer project and offered on the web-page www.new-composites.com, among others.

As a summary of the recent developments at Fraunhofer IAP, in the present paper the capabilities of spun cellulose fibers of various origin to reinforce thermoplastic matrices, i.e. PP, PE, HIPS, PLA, and a PP-based TPE are explored. A special two-stage pultrusion process developed in this laboratory is used to incorporate and cut cellulosic spun yarns in the polymer matrix and produce pellets ready for injection moulding. Structural features of injection moulded test bars are revealed by scanning electron microscopy. Tensile and impact properties are studied and the thermal stability is examined by HDT measurements. A more detailed account concerning variations in fibre load, type of coupling agent, and fibre length distributions is given elsewhere.[8,9]

Experimental

Materials

Cellulose Fibers

The mechanical properties of man-made cellulose fibers, including those used in the composites are presented in Table 1 in comparison with natural cellulosic fibres (wood, bast fibres) and glass fibres. Cordenka 700 is a rayon tyre cord yarn provided by Cordenka GmbH Obernburg, Germany and is produced by a special variant of the viscose process. Most of our work and our major development of cellulose fibre reinforced PP were based on Cordenka 700 as a high level technical cellulose fibre. Additionally we studied the influence of deviating fibre properties on the composite properties by using some

Table 1.
Mechanical Properties of Glass Fibers, Natural and Man-made (spun) Cellulose fibers (Fibers Indicated by * are used in this Study).

	Density	Strength		Elongation	Modulus	
	g/cm^3	cN/tex	GPa	%	cN/tex	GPa
E-glass fibre	2.54		1.4. . .2.6 (3.6)			75
Wood fibers						
Hard wood fiber	1.53. . .1.54		0.14. . .0.5			20
Soft wood fiber			0.5. . .1.5			40
Bast fibers						
Flax	1.43. . .1.52		0.3. . .0.96	1.5. . .4.0		27. . .80
Hemp			0.5. . .1.04	1.0. . .6.0		32. . .70
Jute *			04. . ..0.8	0.8. . .2.0		13. . .26.5
Man-made cellulosic fibers						
Cordenka 700 *		56	0.833	13	1300	20
Enkaviscose		21	0.308	24	704	11
Viscose sliver *	1.50. . .1.55	23	0.338	12	730	11
NewCell		40	0.603	9	2060	31
Tencel sliver *		37	0.552	11	1500	23
CarbaCell*		24	0.365	8	1450	22

* own measurements.

textile cellulose fibres. Enkaviscose is a typical viscose fibre for textile applications produced by Enka GmbH and Co. KG, Oberbruch, Germany. Viscose sliver was kindly provided by Kelheim Faser GmbH, Germany, and taken from the staple fibre production line (nonwovens applications) by separating a sliver of approximately 2 ktex. NewCell is a prototype of a lyocell type filament yarn produced by former Akzo, Obernburg. Another Lyocell fibre is Tencel, kindly provided by Tencel Ltd., Grimsby, UK, again separated from a staple fibre sliver (textile and nonwovens applications) to give an appropriate overall titre for incorporation into the composite matrix. Finally, CarbaCell[12] is a cellulose fibre spun in this institute on a pilot plant scale via the carbamate process as another environmentally friendly alternative to the viscose process.

Matrix Polymers

The matrix polymers used in this study as well as some important characteristics as given by the producers are listed in Table 2. The PP is a relatively light flowing block copolymer suited for injection moulding applications. The PE is a high density polyethylene for injection moulding of larger parts, like crates and boxes. HIPS is an impact modified polystyrene used for the manufacture of TV cabinets and audio equipments. PLA is a biogenic and biodegradable poly (lactic acid) polymer for extrusion and thermoforming applications. An injection moulding grade in this price segment is not available at present. Finally, TPE is a thermoplastic elastomer on the basis of PP with processing conditions similar to PP and rubber like behaviour at room temperature.

Coupling Agents and Additives

For coupling the cellulose fibers to the PP and the TPE matrix, maleic anhydride grafted polypropylene (MAPP) has been used (Fusabond MD353D, Du Pont). PE has been coupled with Fusabond E MB-100D. For HIPS poly(styrene-co-maleic anhydride) of different compositions were used. PLA has not been coupled at all, due to the absence of a suitable product. Talcum used as an additive in one case was Luzenac A7C (Luzenac Naintsch, Austria), a compacted product with diameters below 6.5 μm for 90% of the material.

Methods

Compounding

A two stage pultrusion technique[6] was applied with a conventional co-rotating twin screw extruder (Haake Rheocord 9000 PTW 25) equipped with a coating die assembly to cover a number of (continuous) filament tows or sliver with the molten matrix-coupling agent mixture which was premixed before fed into the extruder.

Injection Moulding

Standard test specimens were prepared according to DIN EN ISO 527-2 (for tensile test) and DIN EN ISO 179 (for bending and Charpy impact test) using an injection moulding machine (Allrounder 270 M 500-90, Arburg, Germany), operating with a nozzle temperature of 210 °C and specific

Table 2.
Matrix Polymers Used in This Study and Selected Manufacturer's Data.

Trade Name	Abbrev.	Producer	MFI	Strength	Modulus
			g/10 min	Mpa	GPa
Stamylan P412MN40	PP	Sabic	37 at 230 °C, 22 N	26 (yield)	1.55 (bend)
Hostalen GC 7260	PE	Basell	23 at 190 °C, 50 N	30 (yield)	1,35 (tensile)
Lacqrene 4240	HIPS	Atofina	4 at 200 °C, 50 N	26 (yield)	2 (bend)
PLA 2002D Nature Works	PLA	Cargill Dow	4–8 at 190 °C, 22 N	53	3.5
Sconablend TPE 60 × 111	TPE	Ravago	not specified	4[a]	0.02[a]

[a] own measurement.

injection pressures between 400 and 700 bar.

Mechanical Testing

Tensile and bending strength, tensile modulus and bending resistance (called modulus in the standard) of the composites were measured according to DIN EN ISO 527 and 178, respectively, with a universal testing machine (Zwick 020) using the injection moulded standard test specimen. However, the bending resistance was determined as the maximum derivative at the beginning of the stress-strain curve. Compression resistance (called modulus in the standard) was measured according to DIN EN ISO 604, sample type B. In all the above experiments, except for tensile modulus, cross head motion was used for strain determination. Charpy impact strengths of the composites were determined with an impact tester (PSW 4J) according to DIN EN ISO 179 standard in the flatwise, unnoched, or the edgewise notched (notch type A) modes.

Heat Distortion Temperature (HDT)

Heat distortion temperature was measured along the lines of DIN EN ISO 75, practice A. However, a DMA (TA Instruments 2980) was used as the temperature chamber and the force applying device and therefore air instead of oil was used as the surrounding medium. Comparison to proper ISO 75 measurements performed elsewhere showed that the DMA generated values are somewhat lower (in the order of 5 °C) than the proper ones.

Scanning Electron Microscopy

Cryo-fractured surfaces were generated by breaking the test bars under liquid nitrogen conditions and subsequent sputtering with Pt with a thickness of 4 nm. Cut surfaces were produced with a Leica VT 1000E (Leica Corp. Germany) vibrating knife perpendicular to the flow direction. The fracture und cut surfaces were studied with an SEM Jeol JSM 6330 (Jeol Corp., Japan) at 5 kV.

Results and Discussion

Composites with Polypropylene Matrix

Rayon-PP-Composites Quality and Dependencies

Starting with Rayon tire yarn, the nearly perfect quality of the composite produced by the two stage pultrusion technique is demonstrated in Figure 1, showing an even distribution of the fibers in the composites test bar.

The fibre length distribution is shown in Figure 2, analysed by a specific method described in.[13] Remarkably, the average fibre length is less than 1 mm with a rather broad distribution as the result of fibre cutting during compounding. The effect of MAPP as a coupling agent has been demonstrated very clearly in Figure 3, where a surface of a cryo fractured composite with no coupling (left) and a room temperature notched Charpy generated surface with MAPP coupling (right) are shown. From this and a series of similar pictures not shown here it is concluded that cryo fracture surfaces do not differ from fracture surfaces generated by Charpy impact testing (both notched and un-notched) at room temperature, such that cryo fracture could be used as a convenient tool for studying the coupling efficiency. Moreover, even under a light microscope, the typical ‘‘naked’’ fibers can be detected in cases where the coupling efficiency is low.

The effects of different types (degrees of grafting) and amounts of MAPP were investigated with the conclusion that there are no big differences for different MAPP types on the one hand, and that already 1 wt% additive is sufficient for the full effect of coupling.

Tensile modulus, and bending and compression resistance of Cordenka-PP injection moulded test bars as a function of fibre load are shown in Figure 4 (left). As expected, the modulus and resistance increase with increasing fibre content. Compression resistance is considerably lower than the tensile counterparts, highlighting the anisotropic properties of the

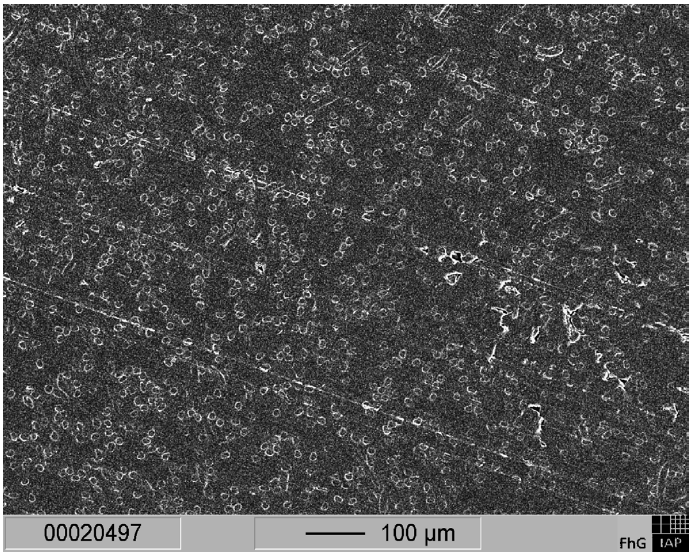

Figure 1.
Scanning electron microscopy picture of cut surface cut perpendicular to test bar axis of Cordenka-PP composite (25%).

"soft" cellulose fibers as compared to glass fibers. The latter act more like stiffening rods, while the former can be pictured as reinforcing "ropes". Bending resistance, in between the two others as expected, is rather close to the compression values, indicating a shift of the neutral plane separating compression and tension regions in the sample towards the lower sample surface thus diminishing the thickness of the layer loaded in tension.

The tensile strength and bending stress at 3.5% strain of the outer fibre of Cordenka-PP injection moulded test bars as a function of fibre load are shown in Figure 4 (right). The bending stress at 3.5%

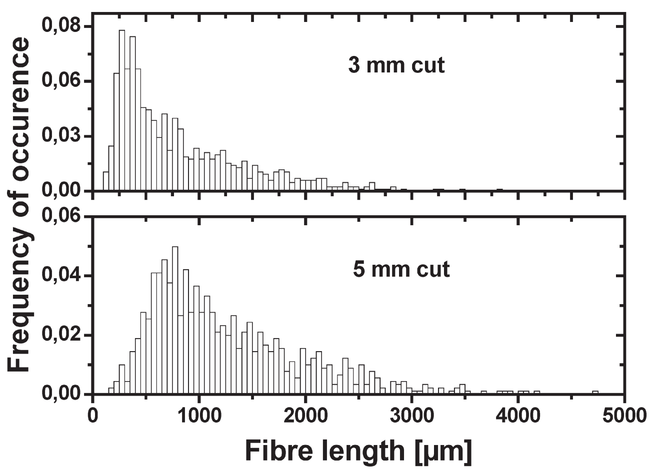

Figure 2.
Fibre length distribution of Cordenka-PP injection moulded bar with 25% fibre load and 3mm (above) and 5 mm (below) cut length in both extruder runs.

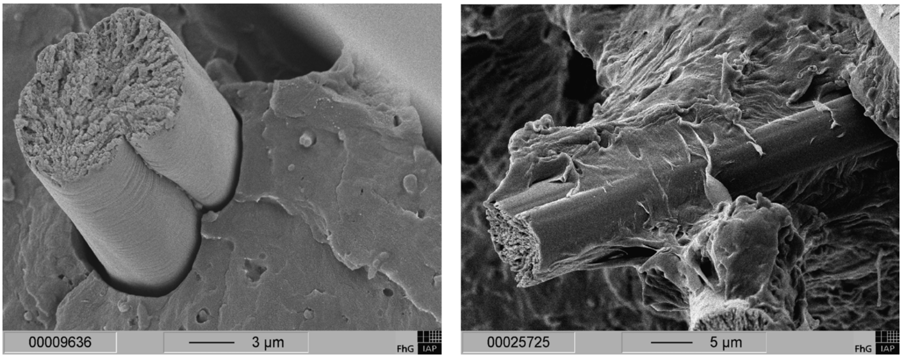

Figure 3.
Scanning electron microscopy cryo fracture micrographs of Cordenka-PP composites with 25% fibre load and no coupling agent (left) and a Charpy generated surface with 3% MAPP coupling (right).

strain of the outer fibre has been chosen as the characteristic value for the bending behaviour since no break was observed in the experiments and the approximations inherent in the calculations (simple beam theory) lose their validity at higher deformations.

For the reinforced samples, the bending stress is generally lower then the tensile strength due to the better performance of the material in tension then in compression (as also indicated by the moduli).

The Charpy impact strengths (flatwise, unnotched) of Cordenka-PP injection moulded test bars as a function of fibre load were measured at 23 °C und −18 °C. Throughout, a high level of 80 to 90 kJ/m^2 is obtained, even at the lower temperature Figure 5, left. This is clearly superior to glass fibre reinforced materials and one of the most important advantages of Rayon as a reinforcing fibre. A clear trend to increased values for increased fibre content, similar to the behaviour with glass is found for the notched Charpy impact strength as demonstrated in Figure 5, right. Already for 24 wt% fibre load the values are doubled at 23 °C and more than tripled at −18 °C as compared to the neat resin. The rather poor impact behaviours of the neat polypropylene, especially below its glass transition temperature of roughly 10 °C, is therefore drastically improved by the addition of the cellulose man-made fibers.

Fibre Type Variation

In Figure 6, tensile strength, tensile modulus and elongation at break are shown for

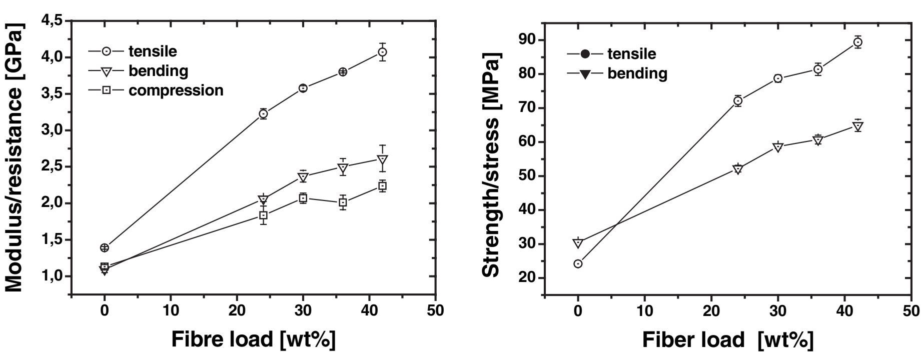

Figure 4.
Tensile modulus, and bending and compression resistance of Cordenka-PP injection moulded composites (left) as well as tensile strength and bending stress (right) as a function of fibre load.

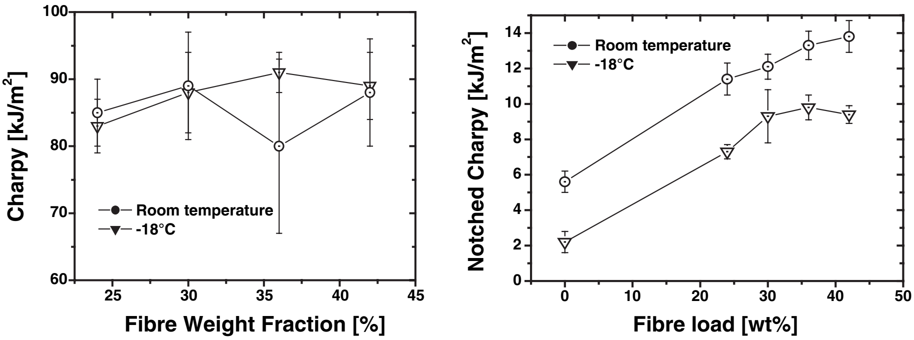

Figure 5.
Charpy impact strength unnotched (left) and edgewise V-notch (right) of Cordenka-PP injection moulded composites as a function of fibre load at 23 °C und −18 °C.

injection moulded composite standard test bars with 25 wt% fibre load as a function of fibre type. For comparison, the values for the pristine matrix polymer are included. A clear reinforcing effect for all fibre types is obvious: strength and modulus are increased considerably, while the elongation is reduced, as expected. Cordenka and Tencel give the best effects in terms of strength with values of 74 MPa and 66 MPa, respectively. Modulus is best for Tencel and jute with 3.6 GPa and 3.3 GPa, respectively. This is accompanied with the lowest values for elongation at break, both 4%, in sharp contrast to Cordenka, which has the highest elongation (10%) for all reinforced materials. The high scatter in elongation for the pristine PP is due to the statistic nature of the necking process. No necking is observed for the reinforced samples.

In Figure 7, Charpy unnotched impact strength, Charpy notched impact strength and heat distortion temperature are displayed in the same manner as in Figure 6.

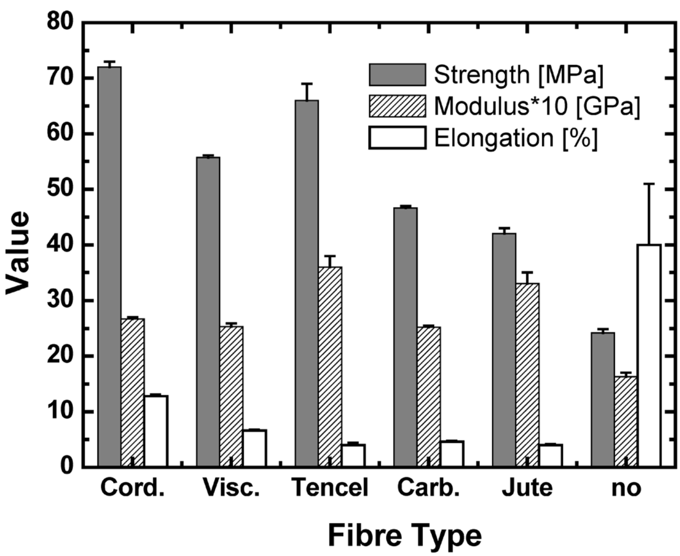

Figure 6.
Strength, modulus, and elongation for injection moulded composite test bars with 25% fibre load as a function of fibre type and for the pristine polypropylene.

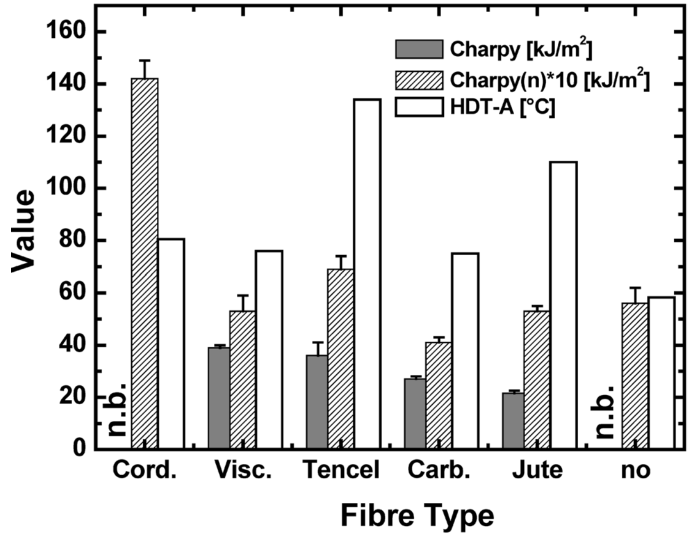

Figure 7.
Charpy and notched Charpy impact strength, and heat distortion temperature for injection moulded composite test bars with 25% fibre load as a function of fibre type and for the pristine polypropylene.

By far the best Charpy values among the reinforced samples are found for Cordenka. Notched Charpy impact strength is 14 kJ/m^2 and the unnotched experiment it does not even fail (as the pure PP). The high stiffness level for Tencel and jute found in Figure 6 is confirmed in Figure 7 by the high HDT values. That means even under elevated temperatures a good bending stiffness is maintained for these composites.

On the other hand, the Cordenka reinforced composites, i.e. the best performing material in terms of strength and impact strength, give values in the range of 80 °C, which is somewhat low for a series of applications, e.g. in the automotive industry (see below).

Mixed Reinforcement
In order to obtain a balanced property profile in terms of stiffness/HDT on the one hand and strength/impact strength on the other, the results of the preceding section suggest a combination of reinforcement fibre types. The combination of Cordenka and Jute has been investigated previously.[9] Additionally, the classic stiffener talcum has been used to reach this goal. In Figure 8, results for mixed reinforcement are presented in the same manner as in Figures 6 and 7. The composition of the composites were as follows: Cord./talc. (25 wt% Cordenka + 10 wt% talcum), Cord./Jute (22 wt% Cordenka + 8 wt% jute), Cord./Tencel (18 wt% Cordenka + 7 wt% Tencel). In each case 3 wt% of MAPP coupling agent has been added to the PP matrix. Obviously, for all compositions, a good stiffness (around 3 GPa) and HDT (>100 °C) is combined with high strength (>65 MPa) and high impact strength (>70 kJ/m^2 for unnotched and >12 kJ/m^2 for notched Charpy). Finding even higher notched Charpy values for the Cord./Jute composite than for the pure Cordenka one is ascribed to the slightly higher overall fibre load and the scatter of the values.

Composites with Alternative Matrices

Polyethylene
Polyethylene, like PP, belongs to the class of inexpensive commodity thermoplastics and is worth testing as a matrix material. Results for the mechanical testing of Cordenka reinforced polyethylene (PE)

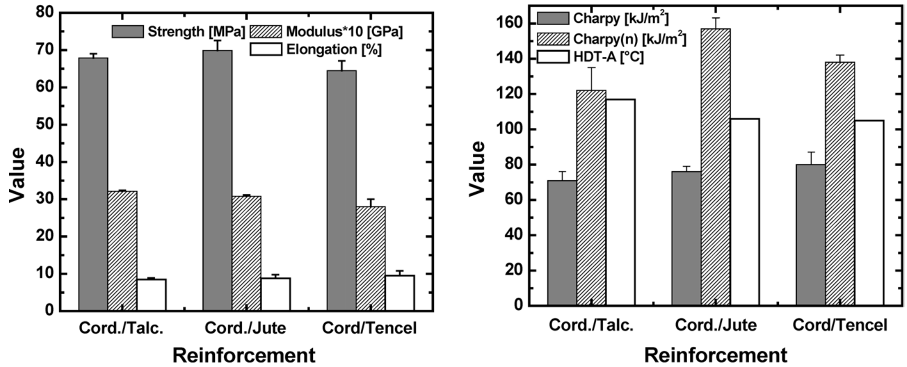

Figure 8.
Strength, modulus, elongation, impact strengths, and HDT for injection moulded composite test bars with mixed reinforcement.

composites together with the values for the pure PE are shown in Figure 9. The effective reinforcement of the matrix by the cellulose spun fibre is obvious. Tensile modulus is almost tripled, strength and notched impact strength are more than tripled and increased five-fold, respectively. With 79 kJ/m^2 unnotched Charpy is on a very high level. The pure PE does not fail in this experiment. This is, of course, the best result that can be obtained. However, it must be kept in mind that the modulus of the pristine PE is quite low. Therefore, the forces acting on the sample surface during impact, which are responsible for crack initiation, are comparatively low. In that way, low modulus materials are favoured in such kind of test.

High Impact Polystyrene

In line with PP and PE, polystyrene (PS) is another inexpensive commodity polymer, giving clear but rather brittle products. Therefore, the polymer is often modified with rubber components giving so called high impact polystyrene (HIPS). Due to its brittleness, the unmodified polystyrene could not be reinforced with the processing method used in this study and thus HIPS was tested as a still inexpensive matrix

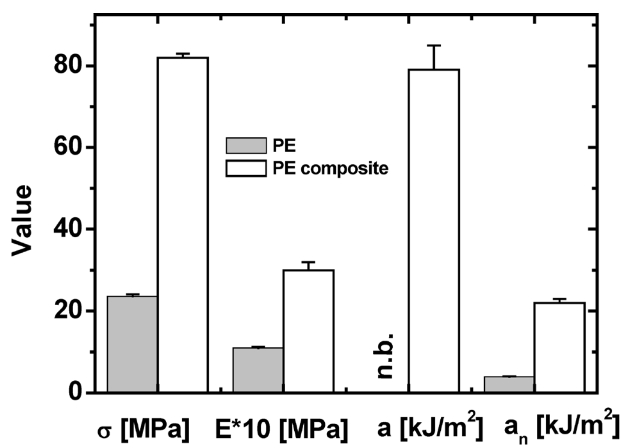

Figure 9.
Tensile strength (σ), modulus (E), Charpy unnotched (a) and notched (a_n) impact strength for injection moulded PE test bars with 25 wt% Cordenka and for the pristine PE.

polymer. Results for mechanical properties of the pristine material and of composites with 25 wt% Cordenka reinforcement are presented in Figure 10.

The pure polymer has good impact properties, but a rather low modulus and, in particular, tensile strength. The latter are increased by reinforcing with Cordenka already without using a coupling agent. The right two sets of columns in Figure 10 represent the values for composites with 3 wt% coupling agent of different architecture. 25%MA means the styrene-maleic acid anhydride copolymer with 25% maleic acid anhydride, while 7%MA stands for the 7% maleic acid anhydride product mentioned there. Obviously, the lower MA concentration favours both strength and impact strength. This can be explained by the characteristics of the coupling mechanism. On the fibre side, the anhydride group reacts with the cellulose hydroxyl groups to form ester linkages[14], and on the matrix side, the styrene loops of the coupling agent are entangled in the matrix polymer. The loops are very short for 25% maleic anhydride (MA) and become longer for the 7% MA coupling agent improving in that way the anchorage in the matrix polymer. Further improvement is therefore to be expected by (a) decreasing the MA concentration and (b) using a grafted product instead of o copolymer to improve the accessibility.

Poly(lactic acid)

A quite different matrix type investigated in this study is PLA. This is a biogenic and biodegradable polymer with remarkable mechanical properties available in various types (mostly thermoforming and extrusion) at moderate prices. Reinforcing this material with a cellulosic (spun) fibre opens up new opportunities to design biogenic and biodegradable composites with excellent mechanical performance. However, care must be taken to avoid the presence of water during processing to prevent degradation of the polyester backbone by hydrolysis. Results for composites with 25% Cordenka and for the pristine PLA are presented in Figure 11. The increase in strength and modulus is about 50%. Again, the Cordenka fibre proves to be an excellent impact modifier: unnotched impact strength is doubled and notched Charpy values tripled. All these values are obtained without using a coupling agent, which, to the authors knowledge, is not available at present.

Polypropylene Based Thermoplastic Elastomer

Finally, a thermoplastic elastomer has been tested for its possibilities to be reinforced

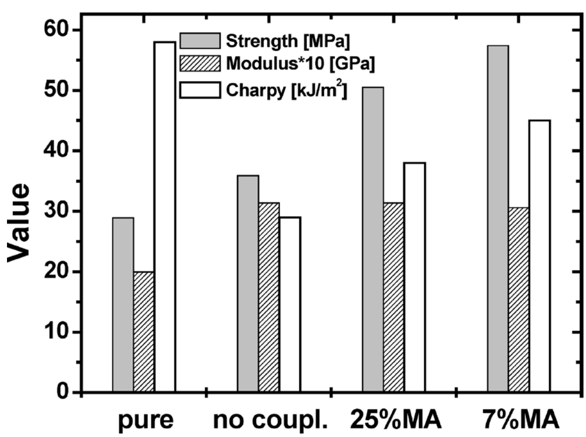

Figure 10.

Strength, modulus, and unnotched Charpy impact strength for pure HIPS and composites with 25% Cordenka without coupling and with two different coupling agents with 25% and 7% maleic anhydride (MA).

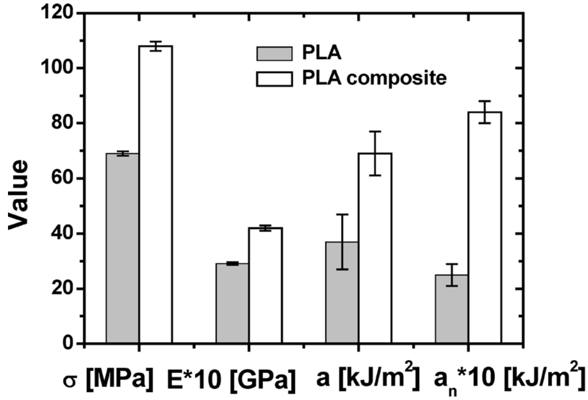

Figure 11.
Tensile strength (σ), modulus (E), Charpy unnotched (a) and notched (a_n) impact strength for injection moulded PLA test bars with 25 wt% Cordenka and for the pristine PLA.

with the cellulosic spun fibre Cordenka, as shown in Figure 12 by the stress-strain curves of injection moulded TPE composite test bars with 25% Cordenka with and without MAPP coupling agent and for the pristine TPE.

Again coupling with MAPP is very effective. The property profile of the material is changed drastically. Strength is increased five fold to 20 MPa and the modulus is 38 times higher than for the pristine matrix. The elongation of the pure TPE of 650% is reduced to 12%, a value found for the reinforcing fibre. In that way, a different type of material is formed for the present fibre content of 25 wt%. By variation of the fibre load it should be possible to tailor the mechanical properties in a way to obtain intermediate values between the extreme cases pure TPE and 25% fibred composite.

Conclusion

Cellulose man-made fibers are suited for reinforcing thermoplastic polymers such as polypropylene, polyethylene, high

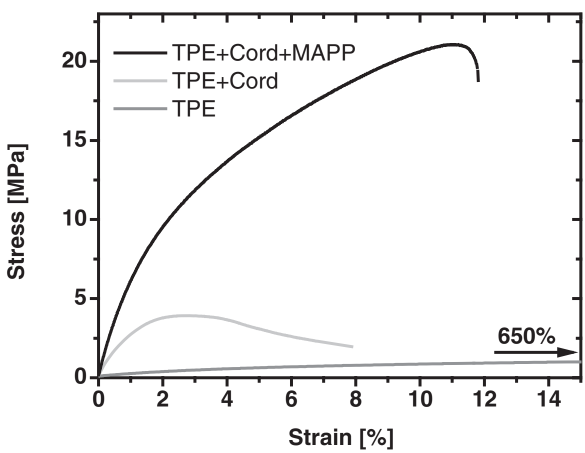

Figure 12.
Stress-strain curves for injection moulded TPE composite test bars with 25% Cordenka with and without MAPP coupling agent and for the pristine TPE.

impact polystyrene, poly(lactic acid) and polypropylene based thermoplastic elastomers. Important mechanical properties like strength, stiffness and impact strength are increased considerably; often they are doubled or tripled. In particular, high tenacity technical viscose fibers like tire cord yarn prove to be excellent strength promoters and impact modifiers, while Lyocell type fibers act as stiffeners enhancing the heat stability for polypropylene composites. An appropriate combination of fibers (or addition of inorganic fillers) leads to a well balanced property profile in terms of stiffness *vs*. impact strength in the polypropylene case. For all the matrix materials, except for poly(lactic acid)(PLA), the cellulose fibers are coupled to the respective matrix by adding small amounts of maleic acid anhydride grafted or copolymerised matrix material. In the case of biogenic and biodegradable PLA composites, excellent mechanical properties are obtained without coupling.

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