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Novel Blends from Agave Fibers and Poly(methyl methacrylate)

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Summary: Cellulose-rich fibers were isolated from Agave lechuguilla (AL) and Agave fourcroydes (AF) growing in the Mexican northeast. These fibers are a valuable feedstock for the preparation of blends with synthetic polymers like poly(methyl methacrylate), PMMA. Blends of different types of agave fibers (dewaxed, mercerized, and grafted) and PMMA were prepared and investigated by means of tension measurements and dynamic mechanical analysis. The fiber-containing blends are more stable than the plain PMMA. Surprisingly, the mechanical stability of the blends is practically independent of the pretreatment of the fibers.
Methyl methacrylate (MMA) was grafted onto the biopolymer fibers initiated by the cerammonium nitrate redox initiator. Grafting yields of 26.5% were realized with fibers from AL while up to 75.8% MMA was grafted onto fibers from AF. The materials were characterized by means of FTIR spectroscopy and DSC.

Keywords: biopolymers; composites; fibers; graft copolymers

Introduction

Cellulose-rich biomass gains increasing importance as chemical feedstock. Agave plants are wide-spread in Mexico and a typical example for such a renewable resource. From agave plants, biopolymer fibers can be isolated easily as carried out for many years. The fibers are mechanically very stable and consist mainly of cellulose (about 80% in the dry state) and smaller amounts of hemicellulose and lignin. In principle, the functional groups are susceptible to chemical reactions leading to new biopolymer derivatives, on one hand. On the other hand, the polymer chain can be modified by grafting reactions without changing the shape of the material.

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Quite recently, the reactivity of agave fibers was studied under typical conditions for modification of cellulose.[1] An activating treatment with *n*-octanol/aqueous NaOH leads to a voluminous material which is soluble in typical solvents for cellulose. Carboxymethylation, sulfation, acetylation and tritylation reactions as well as subsequent carboxymethylation of the trityl derivative and selective oxidation reactions of the carboxymethylated products with TEMPO/NaBr/NaOCl were successfully carried out under heterogeneous and homogeneous conditions. The products were characterized by means of ^{13}C- and ^{1}H-NMR spectroscopy and HPLC after complete depolymerization as well as by GPC.

Grafting reactions are of particular interest to modify the properties of biopolymers without altering the shape of the fibers. Moreover, selected properties may be imparted without significantly altering others as, e.g., elasticity, thermal stability, and resistance to biological attack. Grafting can be used to improve the compatibility of blends with synthetic polymers. Patra and Singh studied the optimum conditions of graft polymerization of acrylonitrile and methyl methacrylate (MMA) onto purified jute fibers.[2] Also much research has been done on graft copolymerization of acrylonitrile onto pineapple leaf fibers[3] and cotton[4] using redox initiator as, e.g., Ce(IV)/$Fe(NH_4)(SO_4)_2$, Ce(IV)/hippuric acid, $KMnO_4$/thioacetamide, and $IO_4^-/CuSO_4$. Oxidation of alcohol and glycol groups involving free radicals has been used to develop a technique of graft copolymerization onto starch and cellulose. The system most widely used is the initiation by ceric ions, in which high grafting yields have been obtained.[5] Agave was also studied as starting material for grafting reactions with styrene as monomer.[6] Grafting yields of up to 15% can be achieved depending on the agave material and the reaction conditions applied. It was found that the thermal stability was improved and the fibers kept their biodegradability.

In the present study, differently treated agave fibers were used to investigate their influence on the mechanical stability of blends with poly(methyl methacrylate). The treatment consists of dewaxing, mercerization, and grafting with MMA.

Experimental

Materials

Agave lechuguilla (AL) was collected in Jaumave, Tamaulipas and *Agave fourcroydes* (AF) in Gonzales, Tamaulipas, Mexico. Cerammonium nitrate was purchased from Baker and used as 0.1 M solution in water. All other reagents were used without further purification.

Methods

FTIR spectra were recorded on a BioRad FTS 25 FTIR spectrometer. DSC measurements were carried out using a TA Instruments 2010 differential scanning calorimeter. 5.7 mg samples were measured under nitrogen with a heating rate of 10 $Kmin^{-1}$. Data about the mechanical stability were acquired on a Instron model 5564 mechanical testing machine at 22°C. The cell was moved with a speed of 2 inch/min until breakage of the sample occured. Dynamic mechanical analyses were carried out with a TA Instruments 2980 DMA device equipped with a dual cantilever clamp. The rectangular samples (length/width/thickness 3.60/4.78/1.66 mm) were measured in a temperature range from 0 to 180°C.

Dewaxing of agave fibers

The fibers were extracted in a Soxhlet apparatus with ethanol/benzene (1:1, v/v) for 24 h. They were washed with ethanol and dried in a vacuum oven overnight at 50-60°C.

Mercerization of agave fibers

1.0 g of fibers was slurried in 100 ml aqueous NaOH (12%, w/w AL, 10%, w/w AF) solution. Stirring was continued for 2 h at 30°C. The material was collected and neutralized with 100 ml 0.1 M acetic acid followed by washing several times with water and drying overnight at 50-60°C.

Grafting of methyl methacrylate (MMA) onto agave fibers (general procedure)

In a typical procedure, 0.4 g activated fibers were placed in the reaction vessel under nitrogen. Water, 1 M nitric acid, and MMA were added to adjust the selected concentrations and to obtain a total volume of 150.0 ml including the initiator solution (see Tab. 1). The mixture was heated up to the reaction temperature of about 38±2°C and stirred for 1 h. 0.1 M aqueous cerammonium nitrate solution was added to initiate the grafting reaction. The reaction was quenched by adding 40 ml 0.1 M ferric ammonium(II)sulfate. Homopolymers were removed by Soxhlet extraction with methanol/water (1:1, v/v) for 24 h. The material was dried in vacuum at 60°C.

The grafting of 2-4 g agave fibers was carried out in a 1 l laboratory reaction vessel equipped with mechanical stirrer and a nitrogen inlet- and outlet.

Preparation of the blends

The blends were prepared using a laboratory mixing molder from Atlas Polymer Evaluation Products equipped with a 2 cm^{-3} mixing cup. The surface of the mold (bone shape according to ASTM D-170B, 70-0479-00) was covered with oil (vegetable oil for household use, trade name: PAM) to increase the ability to remove the blend from the mold.

The agave fibers were cut into pieces with an average length of 1-2 mm with a household scissor. Poly(methyl methacrylate), PMMA, was grinded in a coffee-grinder. Both components were dried in a vacuum oven at 60°C and stored in a dry place. The agave fibers and PMMA were mixed and placed in the mixing molder. The mixture was allowed to melt for 2 min at 225°C. The melt was rapidly injected into the mold.

Results and Discussion

The starting material, the cellulose-rich fibers were isolated by mechanical disintegration of the leafs from *Agave lechuguilla* (AL) and *Agave fourcroydes* (AF). Soluble impurities were removed by Soxhlet extraction with benzene/ethanol and by washing with ethanol. Subsequent mercerization of the dried fibers with aqueous NaOH was carried out in a concentration range from 10-12% at 30°C for 2 h.

Methyl methacrylate (MMA) was grafted onto fibers from AL and AF. The grafting was carried out in aqueous HNO_3 under nitrogen and initiated by the cerammonium nitrate (CAN) redox system. An amount of water was added in order to obtain a total volume of 150 ml including the initiator solution. A 0.1 M CAN solution was used. The clear part of the liquid becomes turbid indicating the homopolymer formation. The grafting reaction was quenched by addition of ferric(II)ammonium sulfate solution. The samples were isolated and the homopolymer was removed by Soxhlet extraction with methanol/water in the case of rather low graft yields while samples of a high grafting were extracted with toluene. The grafting yield was calculated according to:

$$\text{Grafting yield}\,(\%) = \frac{\text{weight}_{\text{grafted fibers}} - \text{weight}_{\text{fibers}}}{\text{weight}_{\text{fibers}}} * 100$$

Variation of the reaction conditions

The influence of the concentration of MMA, acid and initiator on the grafting yield was investigated. It was found that grafting onto AL occurs even at low concentration of HNO_3 and MMA. A grafting yield of 8.5% was already realized using 0.1 M HNO_3, 0.25 M MMA, and 0.025 M CAN (sample **AL-1**, Tab. 1). An increase of the MMA (0.5 M) yields a higher grafting yield of 26.5% (**AL-2**). The increase of the acid concentration leads to an increased grafting yield. Sample **AL-3** was synthesized using 0.2 M HNO_3, 0.25 M MMA, and 0.025 M CAN yielding a grafting yield of 14.5%. Further increase of the HNO_3 concentration leads to a slightly decreased grafting yield of 21.3% (**AL-4,** 0.2 M HNO_3, 0.5 M MMA, and 0.025 M CAN).

The ratio between fibers and total volume of the reaction mixture was decreased. In case of 1 g of fibers in a total volume of 150 ml containing 0.1 M HNO_3, 0.25 M MMA, and 0.025 M CAN, a grafting yield of 5.3% was found (sample **AL-5**).

Grafting reactions carried out with AF as starting material show that the grafting yields are remarkably higher compared to AL. For instance, a grafting yield of 75.8% was obtained using 0.25 M HNO_3, 0.5 M MMA, and 0.025 M CAN (**AF-1**). Increasing the amount of fibers to 1 g in a total volume of 150 ml leads to a grafting yield of 62.3% (sample **AF-3**). Further increase of the fiber batch up to 2 g in a total volume of 150 ml yields sample a grafting yield of 57.7% (**AF-4**). Sample **AF-2** was prepared with the same concentrations of reactants. In contrast to sample **AF-1** an initiator stock solution containing 0.1 M CAN and 1 M HNO_3 was used. The grafting yield of 61.3% indicates that an aqueous initiator stock solution without additional HNO_3 is even more effective. The higher grafting yields of the AF fibers results from the higher porosity of AF compared with AL. Consequently, more reaction sites are available leading to the higher grafting yield.

The shape of the fibers is not altered by the grafting process. However, the fibers become brittle at higher grafting yields and small particles are released from the material under physical stress.

Table 1. Grafting of methyl methacrylate (MMA) onto agave fibers from *Agave lechuguilla* (AL) mercerized with aqueous NaOH (12%, w/w) and *Agave fourcroydes* (AF) mercerized with aqueous NaOH (10%, w/w) initiated with 0.025 M cerammonium nitrate (CAN) within 2 h in a total volume (V_{total}) of 150 ml.

Sample No.	**Fiber (g)**	**Reaction conditions**			**Yield (g)**	**Grafting yield (%)**	**Remarks**
		HNO_3 (mol/l)	**MMA (mol/l)**	**Temp. (°C)**			
AL-1	0.410	0.1	0.25	35-40	0.445	8.5	
AL-2	0.411	0.1	0.5	36-38	0.520	26.5	PMMA on the fiber surface
AL-3	0.413	0.2	0.25	38-40	0.473	14.5	Yellow-white material on the fiber surface
AL-4	0.408	0.2	0.5	32-36	0.495	21.3	PMMA on the fiber surface
AL-5	1.009	0.1	0.25	34	1.062	5.3	Mixture remained clear, formation of foam
AF-1	0.409	0.25	0.5	32-38	0.719	75.8	CAN 0.1 M in water, yellow-white material on the fiber surface, extraction with aqueous ethanol and toluene, grafted fibers are brittle
AF-2	0.408	0.25	0.5	33-38	0.658	61.3	Initiator solution contains 0.1 M CAN and 1 M HNO_3, yellow-white material on the fiber surface, extraction with aqueous ethanol and toluene, fibers are brittle
AF-3	1.005	0.25	0.5	32-38	1.631	62.3	Extraction with aqueous ethanol and toluene, fibers are brittle
AF-4	2.010	0.25	0.5	32-42	3.169	57.7	Extraction with toluene, fibers are brittle
AF-5	4.007	0.1	0.25	34-52	4.758	18.7	V_{total}= 600 ml; Extraction with toluene, fibers are brittle
AL-6	3.008	0.1	0.5	38-40	3.344	11.2	V_{total}= 450 ml; Extraction with toluene, fibers are brittle
AL-7	3.005	0.2	0.25	35-40	3.027	0.7	V_{total}= 450 ml; Extraction with toluene, fibers are brittle

Characterization of the MMA grafted fibers

The MMA-grafted fibers show typical FTIR spectra. Beside the bands of the cellulose and hemicellulose backbone at 3400 cm^{-1} (νOH), 2900 cm^{-1} (νCH), 1423 cm^{-1} and 1300 cm^{-1} (δCH), and 1085 cm^{-1} (νC-O-C) a strong band at 1750 cm^{-1} indicates the presence of carbonyl groups of the methyl methacrylate moieties.

DSC measurements were carried out in order to get information about the thermal stability of unmodified and grafted fibers. The DSC curves of non-grafted fibers show an endothermic peak in the range of 70-80°C indicating the evaporation of water. The decomposition of hemicellulose occurs at 297°C and of cellulose at 350°C. The shape of the DSC curve from the grafted material is different compared to the plain fiber. For the MMA-grafted fibers an endothermic peak at 350°C appears indicating the decomposition of the MMA grafts. This peak appears in the range of the cellulose decomposition and, therefore, the decomposition temperature of the cellulose in the grafted material can not be detected.

Preparation and characterization of fiber/PMMA blends

Blends of PMMA with unmodified and grafted agave fibers were prepared at a fiber concentrations of 15, 30, and 35%. The fibers were cut into small pieces of 1-2 mm length and mixed with different amounts of grinded PMMA. The mixing molder used to make the blends also enables the preparation of specimens with a defined shape for mechanical tests.

The non-blended PMMA broke at a tension of 14 MPa. A blend with 15% dewaxed AL was more stable (breakage at 25 MPa, Tab. 2). Higher fiber concentrations lead to nearly the same maximum tension values of 17-21 MPa (30 and 35% AL, respectively). A similar result was found for the mercerized fibers. The blend containing 15% mercerized AL fiber broke at a tension of 22 MPa. In any case, the blending of PMMA with AL yields materials which are more stable than the synthetic polymer itself.

Further samples were prepared with MMA-grafted fibers. In comparison to PMMA, an increased mechanical stability was found. One series of samples was prepared using AL fibers with 11.2% grafted MMA (**AL-6**). The blend (15% fiber content) broke at a tension of 24 MPa. At a higher fiber content of 30%, a tension at break of 30 MPa was found. At 35% grafting the value was 27 MPa.

Even fibers with 0.7% grafted MMA (**AL-7**) leed to an increase of the mechanical stability of PMMA. Here, a tension at breakage of 22 MPa appeared for the blend with a fiber content of

15%. Higher amounts of the grafted fibers lead to values of 28 MPa for 30% and 27 MPa for 35% grafting. These results show that the stability of the polymer PMMA can be increased by blending with treated agave fiber. Moreover, MMA-grafted fibers lead to a slightly better stability than non grafted fibers. It is possible to apply these fibers even at rather high concentration.

Blends were also prepared with differently treated fibers of AF. The materials containing the mercerized AF fibers show a high stability at low fiber concentration. A sample with 15% fiber content broke at a tension of 34 MPa which is higher compared to mercerized AL fiber. Higher concentrations of the fibers lead to decreased tensions at break of 31 MPa (30%) and 21 MPa (35% fibers). Grafted AF fibers exhibit similar results which are nearly independent of the grafting yield. Fibers of 57.7% (**AF-4**) and 18.7% (**AF-5**) grafting degree lead to a material with tension at break of about 32 MPa for the blends with 15% fiber which becomes lower if the fiber content is increased. Generally, the blends are more stable than the pure PMMA, especially at low fiber concentration. An influence of the grafting yield of the fibers on the mechanical stability of the blends was not clearly obvious. It appears clearly that the modification of the agave fibers by means of grafting reactions does not lead to a better adhesion of the synthetic polymer PMMA than a simple dewaxing or mercerization of the fibers. In any case, an increased mechanical stability appears.

Selected samples were subjected to dynamic mechanical analysis (DMA) in order to study the dependency of the mechanical properties on the composition of the blends (Fig. 1). The storage moduli measured at 0°C and 25°C as well as the maximum tan δvalues are given in Tab. 2. The tendency of tan δ is similar for all samples. The tan δ, which is the ratio of the loss modulus and the storage modulus, decreases with increasing fiber concentration. Consequently, the storage modulus increases while the loss modulus decreases which is typical for a semi-crystalline polymer like cellulose. The modulus of a semi-crystalline polymer is directly proportional to the degree of crystallinity. Thus, when the amount of amorphous material was increased (PMMA), the larger tan δpeak was found. This is clearly shown by results based on blends of AL with 35%

fiber content. In all cases, increasing PMMA concentration has a more dramatic effect on tan δ than the amount of grafted MMA on the agave fibers.

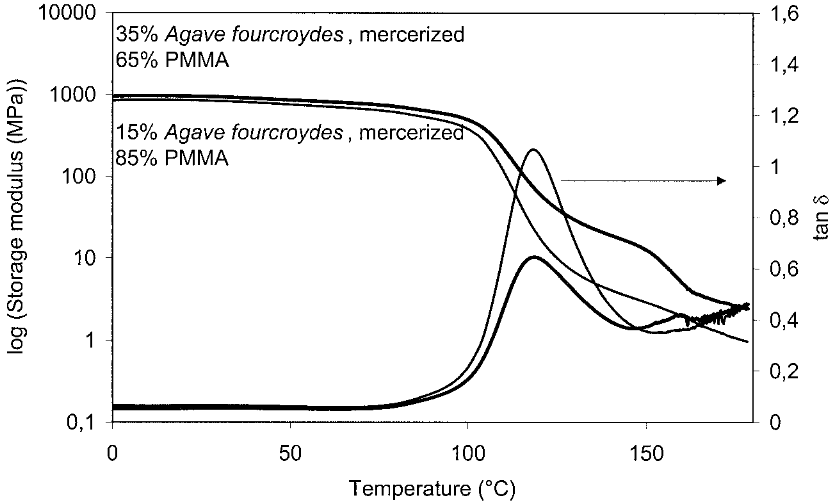

Figure 1. Dynamic mechanical analysis of blends consisting of poly(methyl methacrylate) and mercerized agave fibers (top) and MMA-grafted fibers (bottom). For details of composition, see text in figure.

Table 2. Mechanical stability of composite materials prepared by blending different types of agave fibers with poly(methyl methacrylate), PMMA.

Fiber	Composition Fiber/PMMA	Tension (MPa)	tan δ (max.)	Temperature (°C)	Storage modulus (MPa)	
					at 0°C	at 25°C
	0/100	14	n.d.	n.d.	n.d.	n.d.
Agave lechuguilla, dewaxed	15/85	25[a]	n.d.	n.d.	n.d.	n.d.
	30/70	18[a]	n.d.	n.d.	n.d.	n.d.
	35/65	21[a]	n.d.	n.d.	n.d.	n.d.
Agave lechuguilla, dewaxed, mercerized	15/85	22	n.d.	n.d.	n.d.	n.d.
	30/70	19[a]	n.d.	n.d.	n.d.	n.d.
	35/65	15[a]	0.904	121.67	1019.2	954.5
Agave lechuguilla **AL-6**	15/85	24	1.439	119.03	767.1	766.1
	30/70	30[a]	n.d.	n.d.	n.d.	n.d.
	35/65	27	1.131	119.12	907.9	896.1
Agave lechuguilla, **AL-7**	15/85	22	1.519	119.53	806.7	807.4
	30/70	27	n.d.	n.d.	n.d.	n.d.
	35/65	27	1.156	118.51	1003.4	999.9
Agave fourcroydes, dewaxed, mercerized	15/85	34	1.066	118.39	846.2	847.8
	30/70	31	n.d.	n.d.	n.d.	n.d.
	35/65	21[a]	0.644	118.71	952.0	952.5
Agave fourcroydes, **AF-4**	15/85	33[a]	n.d.	n.d.	n.d.	n.d.
	30/70	30	n.d.	n.d.	n.d.	n.d.
	35/65	14[a]	n.d.	n.d.	n.d.	n.d.
Agave fourcroydes, **AF-5**	15/85	32	1.337	119.91	850.4	844.7
	30/70	26	n.d.	n.d.	n.d.	n.d.
	35/65	21[a]	1.000	119.74	1043.1	1028.5

[a] No average value, because sample was broken during the measurement, n.d.= not determined

This was also shown by G' values. Furthermore, the fibers impart a higher stability to the blends due to their own mechanical properties. The non-grafted fibers (AL and AF) show a similar storage modulus, however, tan δ is higher for AL, as a result of a more viscous behavior (loss modulus). This pattern is also found for the sample having an amount of grafted MMA of 18.7% which exhibits a lower tan δ than AL with 11.2 % grafted MMA.

Fig. 1 shows a typical plot of storage modulus and tan δ in dependence on the temperature between 0 and 180°C. The storage moduli of blends with grafted and non-grafted fibers possess nearly the same shape at low fiber concentration. Contrary, tan δ is higher in case of grafted fibers. If the fiber concentration is increased, the storage moduli of the blends with grafted fibers are higher compared to the non-grafted material, i.e., that the stiffness of the blend containing MMA-grafted fibers is increased.

Conclusion

This study demonstrates an interesting possibility of the utilization of renewable agave fibers for the preparation of novel materials. The properties of the agave fibers were modified by dewaxing, mercerization, and grafting reactions. Thus, the surface becomes more hydrophobic and therefore, more compatible with poly(methyl methacrylate), PMMA. It is worth to note that a simple dewaxing and mercerization yields fibers that form blends with PMMA of high stability. A grafting of methyl methacrylate onto the fibers was successfully carried out, however, this chemical modification is not necessary with regard to reach a compatibility with PMMA. In contrast, blends of polystyrene show good mechanical properties only with styrene grafted fibers as shown by Cruz *et al.*[6]

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