Oak sawdust and hazelnut shells as fillers for a polyester thermoset

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Composites made from a styrene cross linked unsaturated polyester resin and vegetable particles (oak sawdust and milled hazelnut shells) were prepared. The influence of the particle's chemical treatment on the final properties of the materials was investigated. The fillers were modified by a simple alkaline treatment or by further addition of acrylic acid to the hydroxyl groups of the lignocellulosic materials. The modification changed the chemistry of the particles as determined by infrared spectroscopy. Three-point bending tests were performed on the composites filled with the different sawdust batches and with untreated milled hazelnut shells. The modulus was maximum for the composite made with alkaline treated sawdust. However, the ultimate strength as well as the displacement were best if the fibers were acrylic acid treated. Composites made with milled shells showed the lowest ultimate properties.

Sägespäne von Eichenholz und Haselnußschalen als Füller für Polyester-Thermoplasten

Diese Arbeit beschreibt die Herstellung von Komposit-materialen aus ungesättigtem Polyesterharz, quervernetzt mit Styrol, und pflanzlichen Abfallprodukten (Sägespäne von Eichenholz und Haselnußschalen). Der Einfluß einer chemischen Vorbehandlung der Füller wurde untersucht. Die chemische Modifizierung erfolgte durch Alkalibehandlung oder Ankoppelung von Acrylsäure an die OH-Gruppen der Lignocellulosen. Die chemischen Veränderungen wurden mittels Infrarotspektroskopie (FTIR) verfolgt. Die Festigkeit der Werkstoffe mit unterschiedlichem Fülleranteil wurde mit einer Drei-Punkt-Biegeprüfung bestimmt. Maximale MOE-Werte wiesen die Werkstoffe mit alkalibehandelten Sägespänen auf. Die besten Werte in Bezug auf Festigkeit und Verformung erzielten die mit Acrylsäure modifizierten Materialien. Die Werkstoffe mit gemahlenen Haselnußschalen als Füller zeigten die niedrigsten Eigenschaftswerte.

1
Introduction

Wastes from agricultural and forestry industries are renewable, abundant natural materials that have been historically used as fillers of phenolic and ureic resins. The benefits are improved impact resistance, stiffness and lower costs.

In recent years, renewed efforts have been devoted to incorporate these fillers into other polymeric matrices. Wood fibers present good mechanical properties, high Young's modulus (10–80 GPa), and tensile strength (0.5–1.5 GPa) and at the same time a relatively low density (Chtourou, 1992). Thus, composites prepared with these fibers should compare favorably with those prepared with inorganic high density fillers.

However, some important drawbacks have prevented a more extended use of these fillers. The hydroxyl groups of the wood form strong hydrogen bonds that maintain cellulose fibrils attached into bundles forming larger fibers rendering difficult the dispersion of vegetable particles in most polymeric matrices. Recent research work has been concentrated on improving the adhesion between polymer and filler to favor the particle dispersion and increase the strength of the interface.

Based on this consideration, different authors have worked on chemical modifications of sawdust or wood flour to improve the mechanical properties of composites prepared with different thermoplastic matrices (Raj, 1989; Maldas, 1989). Felix and Gatenholm (1991) esterified cellulose with a polypropylene-maleic anhydride copolymer to improve the dispersion of the fibers in polypropylene. Using the same modifier, Sanadi et al. (1994, 1995) obtained improved mechanical properties in Kenaf fiber-polypropylene composites. The treatments are also used to reduce the attrition of the short fibers during mixing with the matrices (Gatenholm, 1993). Also, some studies on the reinforcement of rubbers using cellulose fibers have been published with remarkable reinforcement results, due to the lower modulus of pure rubbers (Yano, 1988).

Less work has been published on the incorporation of the fibers into thermoset matrices other than phenolics,

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which have been traditionally used as binders for wood by-products. Han et al. (1991) have published results on polyester composites which are of interest because of the ubiquitous matrix and because of the advantages of replacing the usual inorganic fillers (carbonates, glass fibers) by inexpensive agro/forest wastes. However, the fibers were not treated before being incorporated into the resin. The coupling agent was added to the mixture during compounding and no further study to determine the interface nature were performed. The coupling agent was homogeneously distributed throughout the composite and thus affected the properties of the interface as well as those of the matrix.

In the present work, the goal has been to determine the influence of the filler chemical treatment on the mechanical properties of the composites made from unsaturated polyester and sawdust. Milled hazelnut shells were also used as fillers to observe the effect of the different particle morphologies.

Dynamic scanning calorimetry (DSC) and infrared spectroscopy (FTIR) of the fibers before and after treatment allowed to identify the changes occurred during the modification. Flexural properties of the materials were measured in all cases.

2
Experimental

2.1
Materials

A commercial unsaturated polyester resin recommended for extrusion and compression molding processes (Synolite 591 A 1, DSM Resins, Italy) was used in this work. The resin was crosslinked with styrene at 80 °C for one hour, using benzoyl peroxide initiator (1.5% by weight). Additives to control cure-shrinkage were not used. Filled samples were molded under 90 bars pressure.

As filler-reinforcement, sawdust from oak (*Quercus petrea*) was used. Particles were sieved, and those larger than 2 mm were discarded. Milled hazelnut shells were
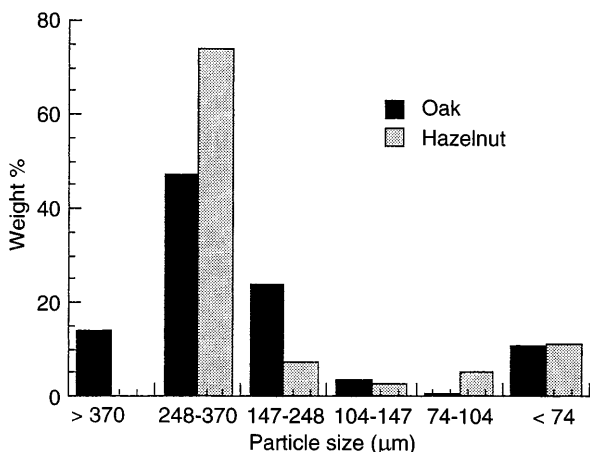

Fig. 1. Size distribution of the oak sawdust and milled hazelnut shells used as fillers in this study
Bild 1. Größenverteilung der Sägespäne und der gemahlenen Haselnußschalen, die als Füller verwendet wurden

also used as an alternative filler. Figure 1 shows the size distributions of the oak fraction used in the study and that obtained from the hazelnut shells. The last one is composed mainly of particles between 248 and 370 μm, while oak sawdust shows a broader distribution.

In the rest of the work, sawdust will also be mentioned as wood particles, because of their small size. However, sawdust is a fibrous material, as it can be deduced from the cell wall structure of the original wood formed by bundles of cellulose fibrils surrounded by lignin and hemicellulose. Milled hazelnut shells have a totally different aspect lacking of fibrous appearance.

2.2
Experimental techniques

Chemical treatment of the particles
The chemical modification of the particles was done following the procedure indicated by Hon and San Luis for the reaction of pine wood and acrylonitrile (1989). It consisted in a pretreatment of the sample with alkali followed by the reaction with the modifier as detailed below:

(a) 50 g of sawdust were immersed in 400 ml of an aqueous solution of sodium hydroxide (10% by weight) with constant stirring for 30 min at room temperature. Solids were recovered by centrifugation (7000 rpm, 15 min) and separation from the supernatant.

(b) The particles were immediately washed with a water-ethanol solution (50:50 by volume); solids were recovered by centrifugation and elimination of the supernatant. Washing was repeated until the supernatant was uncolored. Finally they were washed twice with ethanol (95%).

(c) The filler modified with acrylic acid, initially received the treatment described in (a). Then, the particles were preheated at 50 °C before being immersed in 400 ml of acrylic acid (99%, Aldrich). They were continuously stirred at 50 °C under reflux, during one hour. The solids were recovered after centrifugation and washed with a water/ethanol solution and then with ethanol as described in (b).

A small amount of milled shells was also treated with alkali and acrylic acid as described above.

The modification occurs through the nucleophilic addition of the wood-OH to the acrylic acid double bond, which is catalized by a strong alkali, such as NaOH. The reaction is shown schematically as:

$$wood\text{-}OH + CH_2\!\!=\!\!CH\text{---}COOH$$

$$\xrightarrow{OH^-} wood\text{-}OCH_2\text{---}CH_2\text{---}COOH$$
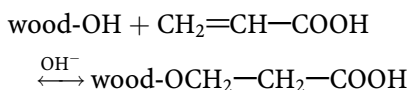
Acrylic acid homopolymerization can be neglected under the conditions of the treatment. Regarding this aspect, Breitenbach and Kauffman (1974) studied the bulk polymerization of acrylic acid. In their work, the formation of the homopolymer was carried out in the presence of an initiator (7×10^{-4} molar of 2,2′azobisisobutyronitrile) at 50 °C during 48 hours. In the present study, the addition of acrylic acid to the sawdust was carried out at 50 °C during only one hour, and the acid was originally supplied with 200 ppm of hydroquinone monoethyl ether as inhibitor in order to assure its thermal stability during handling and storage.

Thermal analysis

Dynamic scanning calorimetry (DSC) was used for the characterization of the particles (DSC Mettler). Runs were performed at 20 °C/min on samples of 5–12 mg. Also, thermogravimetric analyses were run on the unmodified particles (TGA Mettler TA 4000). TG runs were performed on samples of 20–30 mg at 20 °C/min.

Infrared spectroscopy

Fourier transformed infrared spectroscopy (FTIR) was used for the characterization of the lignocellulosic materials before and after treatment. Transmission spectra were obtained from pellets made from 1% (by weight) of particles in KBr.

Compounding

Mixing of the fibers with the bulk resin was carried out in a mixer Rheomix 60 controlled by a Rheocord 900. The free volume of the mixing chamber is 70 cm³. Kneading of the sample was carried out at 40 °C and 40 rpm during 20 min. After that time, the initiator was added and the mixing continued for 10 more minutes. All samples were prepared with 20% by weight of filler.

Molding of mechanical test specimens

A stainless steel rectangular mold of 7×14 cm² was used to prepare plaques. The mold was closed with a piston in a hydraulic press (P7-34, Campana Ing. Benedetto). A pressure of 90 bars was used, and the mold wall temperature was 80 °C. The pure resin was cured under identical temperature conditions, but without applying pressure. The thicknesses of the plaques varied between 2 and 3.5 mm, depending on the mass of mixture loaded. The densities of the different materials varied in a narrow range, between 1.12 and 1.24 g/cm³, as measured by pycnometry (Table 1).

Rectangular specimens 1×7 cm² in size were cut from the plaques with a diamond saw. Three-point bending tests were performed on at least six specimens for each sample and according to norm ASTM D 790M using a servohydraulic universal testing machine INSTRON 8501.

3
Results and discussion

3.1
Particle characterization

Thermal analysis showed that treated as well as nontreated particles strongly absorb ambient moisture. The thermogram obtained for untreated oak particles (Fig. 2, continuous line) shows an endothermic peak that appears

**Table 1.** Densities of the neat cured resin (UP) and composites (g/cm³)
Tabelle 1. Dichte des reinen Harzes (UP) und der Werkstoffe nach dem Aushärten (g/cm³)

Matrix (UP)	UP+untreated oak	UP+alkaline treated oak	UP+acrylic ac. treated oak	UP+untreated hazelnut
1.223	1.146	1.124	1.180	1.238
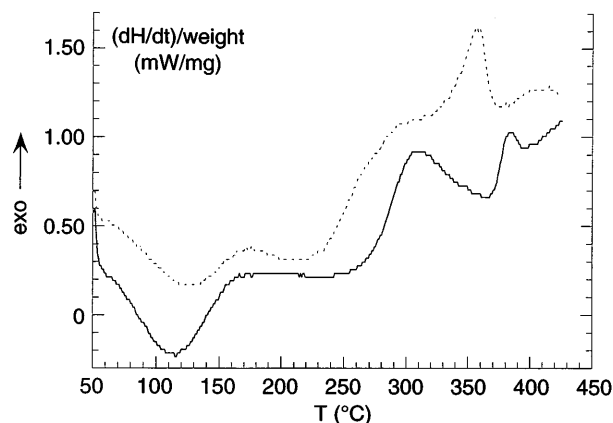
Fig. 2. DSC thermograms of the untreated and acrylic acid-modified oak particles (continuous and broken lines, respectively). The curve for the modified sawdust has been displaced vertically to better display the thermogram features
Bild 2. DSC-Thermogramme der unbehandelten (durchgezogene Linie) und mit Acrylsäure modifizierten (gestrichelt) Eichenspäne
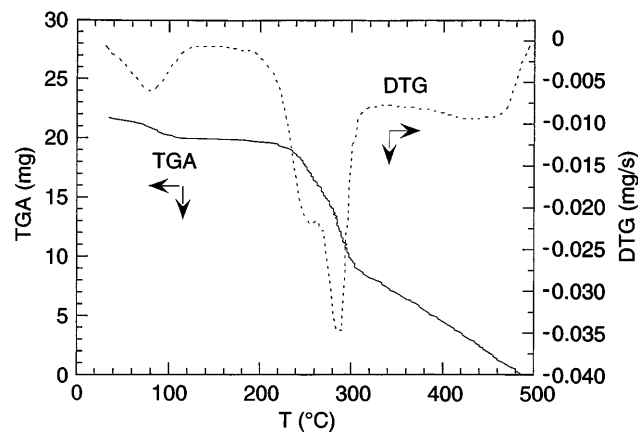
Fig. 3. Thermogravimetric (TGA) results obtained from untreated oak sawdust and derivative signal (DTG)
Bild 3. Thermogravimetrische Ergebnisse (TGA) an unbehandelten Eichenspänen und differentielle Thermoanalyse (DTG)

between 60 and 180 °C with a maximum at 113 °C, corresponding to the vaporization of water in the sample. The accompanying thermogravimetric analysis (TGA and derivative signal, DTG, in Fig. 3) showed a 8.15% decrease of the sample weight in that region (maximum at 81 °C) due to water desorption. Differences appear in the thermogram of the acrylic acid-treated sawdust. The water desorption peak is located at 126 °C (Fig. 2, broken line) with a comparatively lower area (less absorbed water than for the untreated sawdust). Similar changes in hygroscopicity have been reported previously in treated wood flour (Marcovich, 1997).

Differences due to the chemical modification are also seen in the high temperature range. Between 180 and 220 °C, there is a small change in the baseline of the DSC thermograms which corresponds to a thermal transition of the wood (shifted to lower temperatures in the treated sample). This transition has also been observed by other researchers using DSC or dynamic mechanical tests on

different woods and has been assigned to the α transition in wood (Hon, 1989; Mathias, 1991; Nakano, 1990).

Towards the end of the previous transition, degradation of the material begins with the maximum loss rate at 284 °C and resulting in a 57% reduction of the original mass, according to TGA results (Fig. 3). The corresponding change in the DSC curve is observed at 260 °C for the untreated sawdust, but appears about 20 °C below that temperature in the acrylic acid treated particles (Fig. 2).

At still higher temperatures, differences in the thermograms may be due to DSC instabilities and partial degradation of the material. Finally, at about 450 °C, the final carbonization of the material takes place (TGA results).

Similarly, DSC runs on milled hazelnut shells show very small differences, indicating that the chemical treatment was not as effective as in the case of sawdust, probably because of the different morphology and chemistry of the particles.

Infrared spectroscopy was used to study changes in the particle chemistry. Figure 4 shows the spectra of untreated oak sawdust and milled hazelnut shells: untreated (A), alkali treated (B), and acrylic acid treated (C). Peak assignment was done according to previous publications (Marcovich, 1996; Roy, 1991).

Comparison of spectra A and B shows that the treatment with NaOH solution produces a change in the 900 cm^{-1} peak, which corresponds to the β-linkage in cellulose. The increased intensity of this band after alkaline modification has already been reported by Reddy et al. (1990).

In spectrum A, a band appears at 1240 cm^{-1} and was assigned to the C—O bond of the acetyl group in xylan. After treatment with NaOH, the band splits into two, one at 1240–1265 cm^{-1} and the other at 1225 cm^{-1}. The first band is caused by vibrations in the structure of the guaiacyl structure of the lignin and the second one is due to vibrations of the syringyl structure (Roy, 1991).This band split is characteristic of the alkaline treatment of ligno-
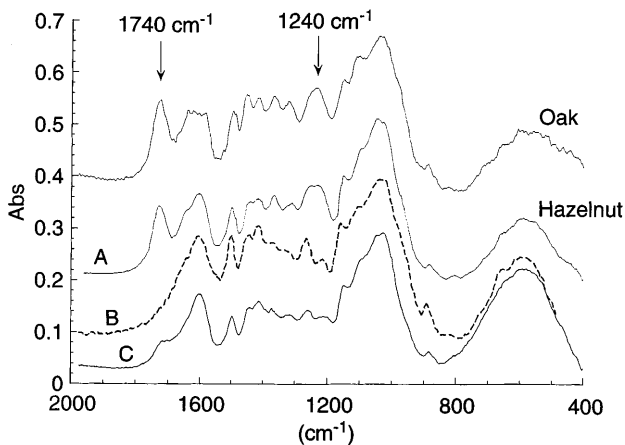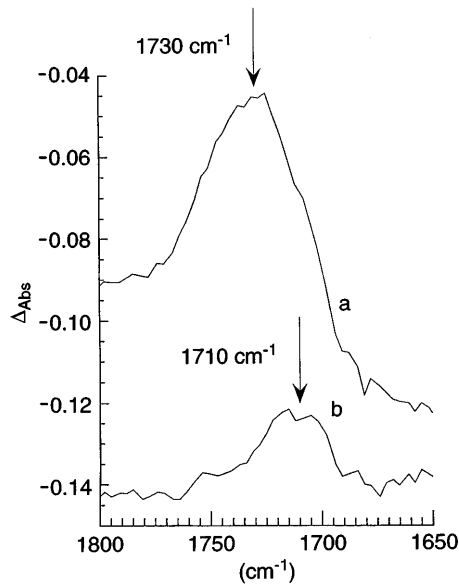

Fig. 5. FTIR difference spectra: *a* untreated oak sawdust – alkali treated sawdust; *b* acrylic acid modified oak sawdust – alkali treated sawdust
Bild 5. FTIR_Differenzspektren von Eichenspänen: *a* unbehandelte – alkalibehandelte; *b* acrylsäuremodifiziert – akalibehandelt

cellulosic materials, as has been reported previously (Roy, 1991; Reddy, 1990).

In the spectra of the untreated samples (oak and hazelnut-A), the peak at 1730 cm^{-1} is due to the carbonyl vibration in ester groups, but disappears after treatment in NaOH (spectrum B). When carboxylates are formed, the two C—O bonds become equivalent and the corresponding band should appear between 1550–1610 cm^{-1}. In this region other groups also absorb and thus, differences are not observable. Roy et al. (1991) found a similar occurrence for alkali treated jute.

Spectrum C (acrylic acid treated-hazelnut) shows a small peak with a maximum at 1704–1710 cm^{-1}. This is the region of absorption of the carbonyl groups of acids. The presence of this peak which was not present either in the original sample or in the alkali treated sample, indicates that the acrylic acid has been attached to the wood surface. Further indication of this result is presented in Fig. 5 which shows the difference spectra of (a) untreated – alkaline treated oak sawdust and (b) acrylic acid treated – alkaline treated oak sawdust. In that figure, the different positions of the carbonyl bands corresponding to ester in the original sawdust and to acids in the acrylic treated sawdust can be observed.

FTIR spectra made it possible to detect differences due to the chemical treatment of the fillers, with similar behavior being observed for the oak and hazelnut particles.

Fig. 4. FTIR spectra of the untreated oak sawdust and the milled hazelnut shells: *A* – untreated; *B* – NaOH treated; *C* – acrylic acid modified
Bild 4. FTIR-Spektren von unbehandelten Eichenspänen und gemahlenen Haselnußschalen: *A* – unbehandelt; *B* – NaOH-benadelt; *C* – mit Acrylsäure modifiziert

3.2
Compounding and mechanical tests
Figure 6 shows the torque signal for one of the samples during mixing. The behavior is similar to that found by other researchers during the incorporation and dispersion
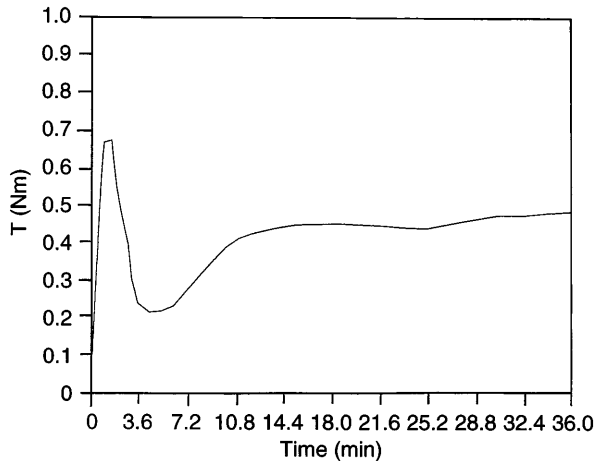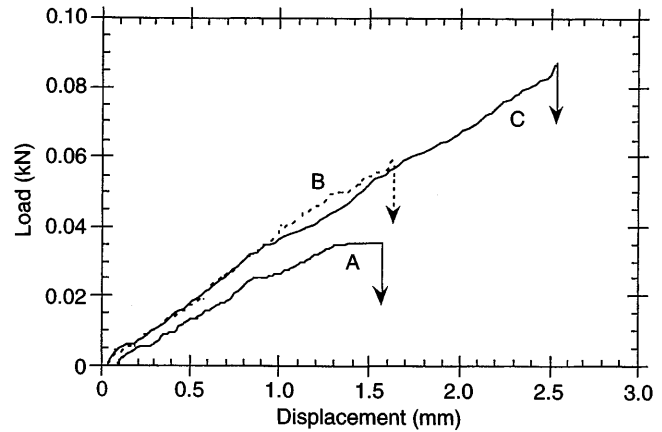
Fig. 6. Torque signal measured during the compounding step. The noise accompanying the signal was eliminated to better observe the main features described in the text
Bild 6. Drehmoment während des Mischens. Das Rauschsignal wurde entfernt, um die grundsätzlichen Verlauf besser darzustellen (s. Text)

Fig. 7. Typical load vs. displacement curves for the composites obtained from oak sawdust (20:80 weight ratio of filler:matrix): A – untreated; B – NaOH treated; C – acrylic acid modified
Bild 7. Typische Last/Verformungs-Kurve der Werkstoffe mit Eichenspänen als Füller (Füller:Matrix 20:80 w/w): A – unbehandelte Späne; B – NaOH-behandelt; C – mit Acrylsäure modifiziert

of carbon black fillers into rubbers (Nakajima, 1984; Cotten, 1985). The signal goes through a maximum immediately after the addition of the filler. The peak is related to the energy spent for incorporating the particles into the polymer, it coincides with the end of the ingestion of the batch into the mixing chamber. During that step, macroscopic wetting of the fibers occurs. After a short period in which the signal drops, a second increase in the torque occurs. An almost constant value was achieved during this step, during which kneading of the sample took place. The energy input is spent in dispersing the particles, producing a more intimate contact with matrix. The final constant value of the torque is very low (0.3–0.4 Nm), due to the low viscosity of the resin.

The addition of fillers resulted in an easier processing of the samples, because it reduced the sample shrinkage during crosslinking. Since no low profile additives were included in the formulations of the cured neat resin or the composites, the beneficial effect of loading the polyester resin was rather evident. The plaques of neat resin required a very careful preparation to obtain pieces large enough to cut the specimens to be tested. The shrinkage that occurs during curing provoked the formation of large cracks. Filled samples, by contrast, were easily prepared and no cracks appeared as the result of the crosslinking.

Typical load-deformation curves obtained from three point bending tests are shown in Fig. 7 for composites loaded with different types of sawdust. The behavior is linear up to rupture in all the samples tested.

Table 2 summarizes the average results. All the composites showed poorer mechanical properties than the cured neat resin, with the exception of a slight improvement of the bending modulus of the composites. These results differ from those reported in a previous work done with a low modulus-polyester resin for which the properties were improved with the addition of a similar load of sawdust (Reboredo, 1994). However, they are in agreement with the results obtained from a polyester matrix of similar bending properties (Marcovich, 1996).

Taking sample A as the reference composite, one can observe that the modulus increases with sample treatment and is maximum for composites loaded with NaOH treated sawdust. On the other hand, ultimate strength and deformation are maxima for composite C, which was prepared with acrylic acid modified fibers.

Sawdust used to prepare composites B and C have both undergone alkaline treatment and thus, the two type of particles should have a similar morphology. However, C-type composites have better ultimate properties, due to the improved compatibility between polymer and particles, while the modulus is reduced with respect to B composites. It is probable that the acrylic acid modification produces permanent changes in the sawdust properties, much in the same way that cyanoethylation produces plastification of wood (Hon, 1989; Kiguchi, 1991).

Untreated hazelnut shells used as fillers produced specimens with a similar modulus as sawdust composites, but with much lower ultimate properties. The different

Table 2. Bending properties of the matrix and composites
Tabelle 2. Biege-Eigenschaften der Matrix und der Werkstoffe

	E_b (GPa)	(MPa)	ε (mm/mm)
Matrix (UP)	3.33 ± 0.44	132 ± 12.7	0.046 ± 0.008
UP + untreated oak (A)	3.16 ± 0.27	49.77 ± 6.28	0.0163 ± 0.0013
UP + alkaline treated oak (B)	4.08 ± 0.31	55.26 ± 6.9	0.0154 ± 0.0019
UP + acrylic ac. treat. oak (C)	3.60 ± 0.24	60.01 ± 2.7	0.0179 ± 0.0011
UP + untreated hazelnut	3.72 ± 0.35	33.08 ± 0.27	0.0089 ± 0.00076

behavior is due to the different particle size distribution, but mainly to the different morphology of the hazelnut shell particles, which lack the fibrous structure of sawdust (Seymour, 1984).

4
Summary and conclusions

A commercial unsaturated polyester resin (styrene cross-linked) containing no additives was loaded with oak sawdust or with milled hazelnut shells. The sawdust particles were modified with two different chemical treatments and the bending performance of the final composites were compared.

The addition of any of the fillers facilitated the production of samples because of the reduced shrinkage during the curing step.

All the composites behaved poorly in the mechanical tests if compared with the behavior observed for the neat cured resin. On the other hand, the modulus of the filled polymer was highest for the alkaline treated sawdust, but the ultimate properties were slightly better in composites prepared with the acrylic acid-treated sawdust, due to the improved compatibility between matrix and filler.

The use of untreated milled hazelnut shells produced materials with a relatively higher modulus, but very poor ultimate properties (low σ and ε). The different behavior of shell and sawdust composites is thought to be due to the different particle morphology.

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