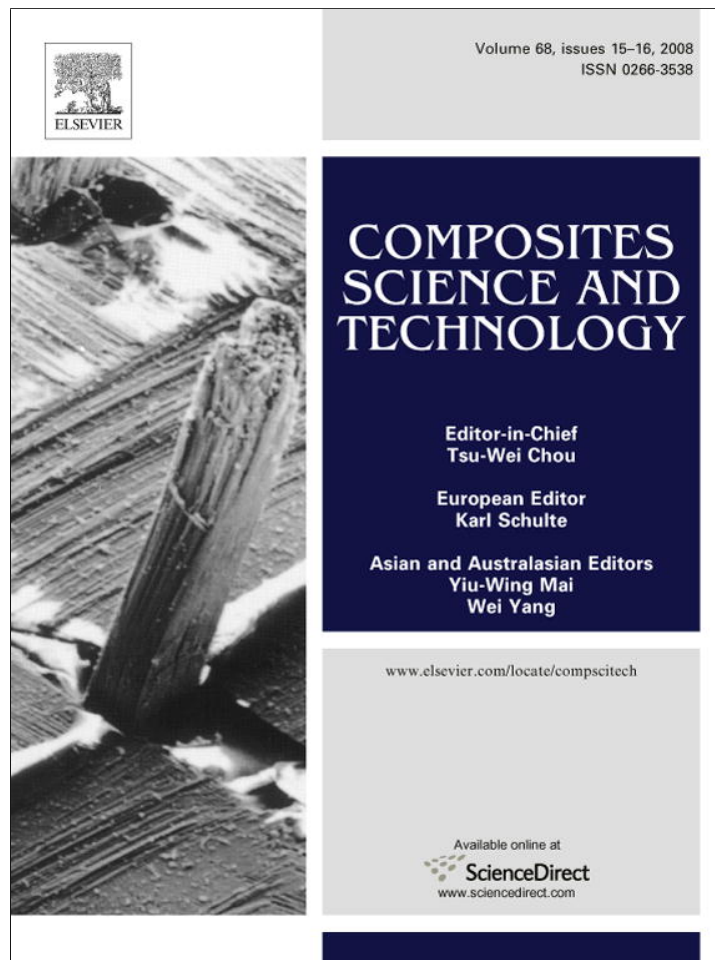


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Composites based on acylated cellulose fibers and low-density polyethylene: Effect of the fiber content, degree of substitution and fatty acid chain length on final properties

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ABSTRACT

Low-density polyethylene was filled with unmodified and fatty acid (hexanoic, dodecanoic, octadecanoic and docosanoic acids) esterified cellulose fibers. The thermal and mechanical properties, morphology and the water absorption behavior of the ensuing composites were investigated. The chemical modification of the cellulose fibers with fatty acids clearly improved the interfacial adhesion with the matrix and hence the mechanical properties of the composites and decreased their water uptake capacity. The performance of the composites was strongly affected by the degree of substitution (DS) and the fatty chain length as indicated by the fact that esterified cellulose fibers with low DS gave composites with better mechanical properties.

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1. Introduction

The remarkable properties of cellulose, the most abundant naturally available polymer, and also of its derivatives, have been exploited for centuries and new potential applications for this ubiquitous renewable resource are still being hunted, mainly in response to the predicted dwindling of fossil resources, their skyrocketing prices and to the increasing interest in the development of biodegradable materials based on renewable resources [1,2].

One of these ongoing investigations concerns the use of cellulose fibers as reinforcing elements in composite materials based on polymeric matrices [3]. The major problems faced by researchers in this field are mostly related with the highly polar surface of the cellulose fibers, which causes (i) a very low interfacial compatibility with non-polar matrices like polyolefins (ii) moisture uptake and (iii) inter-fiber aggregation by hydrogen bonding. Numerous strategies have been explored to overcome these drawbacks, mostly involving specific surface treatments of the fibers aimed at reducing its polar character, which include both physical and chemical modifications [3].

For example, the acylation of cellulose fibers with fatty acids [4–9] represents an interesting way to prepare reinforcing elements for composites with common thermoplastic matrices, such

as polyethylene (PE). This strategy is particularly relevant because of the renewable and biodegradable nature of fatty acids and, of course, of their predominantly non-polar nature. However, only a few studies on the preparation and characterization of composites with cellulose fibers esterified with fatty acids and PE have been published thus far [10–12]. These studies considered only fatty acid derivatives with C11/C18 and C12/C18 aliphatic chains, respectively, neglecting important parameters, such as the degree of substitution (DS), fibers morphology and the fatty chain length.

As part of a wider research project on the heterogeneous chemical modification of cellulose fibers [6,7,13–16] for new applications (composites, paper materials, etc) we have been studying the preparation and characterization of composite materials based on acylated cellulose fibers and low-density polyethylene (LDPE). In this investigation, cellulose fibers modified with different fatty acids (C6, C12, C18 and C22) and different DS were investigated. The thermal and mechanical properties, the morphology and the water absorption behavior of the ensuing composites were evaluated.

2. Experimental section

2.1. Materials

The cellulose fibers used in this study were in the form of industrial *Eucalyptus globulus* ECF (Elemental Chlorine Free) bleached

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kraft pulp, kindly provided by a Portuguese pulp mill. The fatty acids (hexanoic C6 99%, dodecanoic C12 99%, octadecanoic C18 95% and docosanoic C22 \geq 80%), low-density polyethylene (LDPE), thionyl chloride, pyridine, toluene and *N,N*-dimethylformamide (DMF), were supplied by Sigma–Aldrich. Toluene was dried with sodium wire. Pyridine and dimethylformamide (DMF) were purified by distillation over sodium hydroxide.

2.2. Fibers modification

The details related to the preparation of the acid chlorides by the standard reaction of the corresponding fatty acids with thionyl chloride, the heterogeneous esterification reactions in both media (toluene and dimethylformamide) and the determination of the degree of cellulose substitution (DS) have already been described [6,17]. The conditions associated with all the modifications are summarized in Table 1.

2.3. Compounding and processing

Composites were prepared by compounding the polymeric matrix with the unmodified and acylated cellulose fibers in a melting mixer (Haake Rheomix 600P) working at 170 °C. Firstly, LDPE pellets were charged and, after melting, dried fibers were added. The systems were mixed during 7 min at 100 rpm. In order to study the effect the fatty acid chain length, the reaction solvent and the DS on the composite properties, a 30 wt.% of fibers was used. The loading of modified fibers (C121hT) was also varied from 15 to 70 wt.% in order to study the effect of fiber loading.

Subsequently, the composites were molded, in an injection molding machine (Thermo-Haake Minijet II) for tensile (bar according to ISO 527-2-5A) and DMA analysis.

2.4. Composites characterization

The composites were characterized using Thermogravimetry (TGA), Differential Scanning Calorimetry (DSC), Dynamical Mechanical Analysis (DMA), Tensile tests, Scanning Electron Microscopy (SEM) and water absorption tests.

TGA essays were carried out with a Shimadzu TGA 50 analyzer equipped with a platinum cell. Samples were heated at a constant rate of 10 °C/min from room temperature to 800 °C, under a nitrogen flow of 20 mL/min. The thermal decomposition temperature

was taken as the onset of significant (\geq 0.5%) weight loss, after the initial moisture loss.

DSC thermograms were obtained in a Mettler-Toledo DSC822e apparatus calibrated with indium and equipped with a Haake EK90/MT intracooler system. The samples (5–10 mg) were analyzed by heating-cooling cycles between –60 and 150 °C, under nitrogen at a scan rate of 20 °C/min using 40 μ L aluminum standard pans.

DMA measurements were carried out with a Tritec 2000 DMA Triton equipment, in the bending (single cantilever) mode. Tests were performed at 1 Hz and the temperature was varied from 25 to 100 °C by 4 °C steps.

Mechanical analyses were performed at room temperature in an Instron Universal Tester, model 4206, according to ASTM D 638 for tensile tests, using a load cell of 1 kN. The data acquisition rate was 10.0 Hz and the deformation rate 5 mm/min.

SEM micrographs of the composite fractured surfaces were obtained with a SU-70 equipment operating at 4 kV.

2.5. Water uptake

Composite samples (dimensions 60 \times 10 \times 1 mm) were immersed in distilled water at room temperature to study their water uptake. A minimum of three samples were tested for each composite material. The weight increase due to water absorption was periodically assessed for \sim 3 months. Samples were taken out of the water, the wet surfaces were immediately wiped dry, weighted and then reimmersed in water. The water uptake at time t , W_{uptake} , was calculated as:

$$W_{\text{uptake}} = \left(\frac{W_t - W_0}{W_0} \right) \times 100\%$$

Where W_0 is the specimen initial weight and W_t the specimen weight after an immersion time t .

3. Results and discussion

The composites prepared in this study were in general homogeneous, except those with unmodified cellulose fibers, which showed some fiber agglomeration. All composites were characterized in terms of thermal and mechanical properties, morphology and water uptake capacity.

4. Thermal properties

The cellulose-based LDPE composites showed, in most cases, TGA profiles that were a combination of those of the corresponding cellulose fibers and matrix (Fig. 1) and were always less stable than the unfilled LDPE because of the presence of the natural fibers.

The composites with unmodified fibers gave a thermal degradation profile that was a perfect sum of those of the separated components, indicating that they degraded independently (Fig. 1). These results were a clearly evidence of the poor compatibility, i.e. bad interfacial adhesion, between the unmodified cellulose fibers and the PE matrix. Conversely, the composites with esterified cellulose fibers displayed an intermediate thermal behavior, which involved the expected different weight losses, associated with the two elements of the composite, but also a considerable increase in the thermal stability of the fibers, accompanied by a slightly decrease in the T_{dmax} (maximum decomposition temperature) of the PE matrix (Fig. 1). These results were a first indication of the good adhesion between the esterified cellulose fibers and PE matrix.

DSC thermograms of all the cellulose-based LDPE composites showed an endothermic peak ascribed to the melting of the crys-

Table 1

Degree of substitution (DS) of the acylated cellulose fibers (the abbreviations refer the fatty acyl chain lengths, the solvent used and the reaction time, e.g. C6T1h, refers the cellulose fibers esterified with hexanoyl chloride (C6) in Toluene (T) during 1 h (1h), in the case of fibers modified in DMF a constant reaction time of 6 h was used)

Cellulose fibers identification	FA	Solvent	Reaction time (h)	DS
Cellulose	–	–	–	–
C6T1h	C6	Toluene	1	0.42
C6T2h			2	0.79
C6T6h			6	0.53
C6DMF		DMF	6	1.26
C12T1h	C12	Toluene	1	0.61
C12T6h			6	1.17
C12DMF		DMF	6	1.28
C18T2h	C18	Toluene	2	0.07
C18T6h			6	0.24
C18DMF		DMF	6	1.23
C22T2h	C22	Toluene	2	0.01
C22T6h			6	0.07
C22DMF		DMF	6	1.01

talline domains of the matrix, with a maximum at about 109 °C (Table 2). The incorporation of both unmodified and acylated cellulose fibers did not significantly affect the melting temperature, regardless of the fiber content and fatty acyl chain length. This behavior had already been observed with other natural fiber-based composites [12,18,19].

As expected, the enthalpy of fusion (ΔH_m) decreased with the fiber loading (PEC12T1h series) due to the corresponding decrease in the amount of matrix. However, for composites with the same reinforcement content (30%), ΔH_m was poorly affected by the fatty acid chain length and by the DS. A slight decrease was only observed for composites with cellulose fibers bearing high DS values, namely all those modified in DMF and the C12/toluene sample.

Moreover, the degree of crystallinity of the composite materials was not detectably affected by the fiber content and properties.

5. Mechanical properties

The dynamic mechanical measurements were performed for LDPE composite materials filled with 30% of either unmodified or modified cellulose fibers, and with different fiber contents (15%, 30%, 50% and 70%) for the cellulose fibers modified with C12 (C12T1h). The curves of the $\log(E'/\text{Pa})$ (storage tensile modulus)

Table 2

Melting temperature (T_m), melting enthalpy (ΔH_m) and degree of crystallinity (X_c) of LDPE-based cellulose composites obtained from the DSC curves

	Fatty acid	Fiber loading	T_m (°C)	ΔH_m (J g ⁻¹)	X_c (%)
PE	–	–	109	94.0	33
PECellulose	–	30	109	69.7	35
PEC6T1h	C6	30	109	71.7	36
PEC6T2h		30	109	68.7	34
PEC6T6h		30	109	73.8	37
PEC6DMF		30	109	65.7	33
PEC12T1h	C12	30	109	68.5	34
PEC12T6h		30	109	69.6	35
PEC12DMF		30	110	65.0	33
PEC18T2h	C18	30	109	64.9	33
PEC18T6h		30	111	63.5	32
PEC18DMF		30	110	62.1	31
PEC22T2h	C22	30	110	66.1	33
PEC22T6h		30	109	64.7	32
PEC22DMF		30	109	52.8	27
PEC12T1h15	C12	15	109	80.6	33
PEC12T1h30		30	109	66.9	34
PEC12T1h50		50	109	47.7	33
PEC12T1h70		70	108	28.6	33

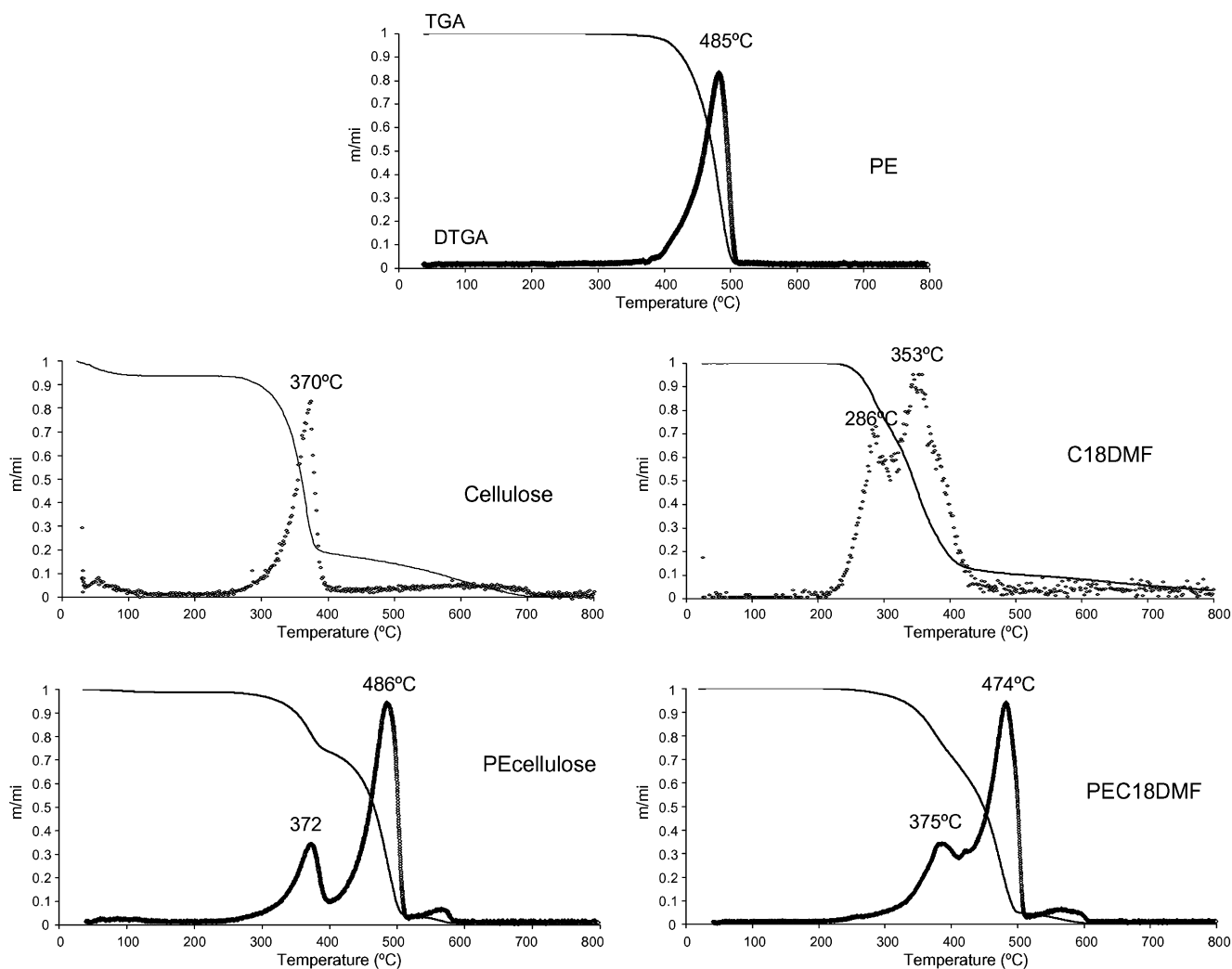


Fig. 1. Thermograms of unmodified and C18 esterified cellulose-based LDPE composites.

vs. temperature at 1 Hz are displayed in Fig. 2, which incorporates as reference that obtained with the unfilled matrix. DMA experiments were only performed in the temperature range 25–100 °C (rubbery plateau) [20].

At room temperature, the amorphous domains of the matrix were in the rubbery state, and their crystalline regions acted as physical crosslinks, resulting in a high storage modulus. This rubbery modulus is known to depend on the degree of crystallinity of the material. It was observed that the storage modulus decreased gradually with increasing temperature, due to the increasing movement of amorphous domains of PE. The experiments were ended just before the melting of the crystalline zones.

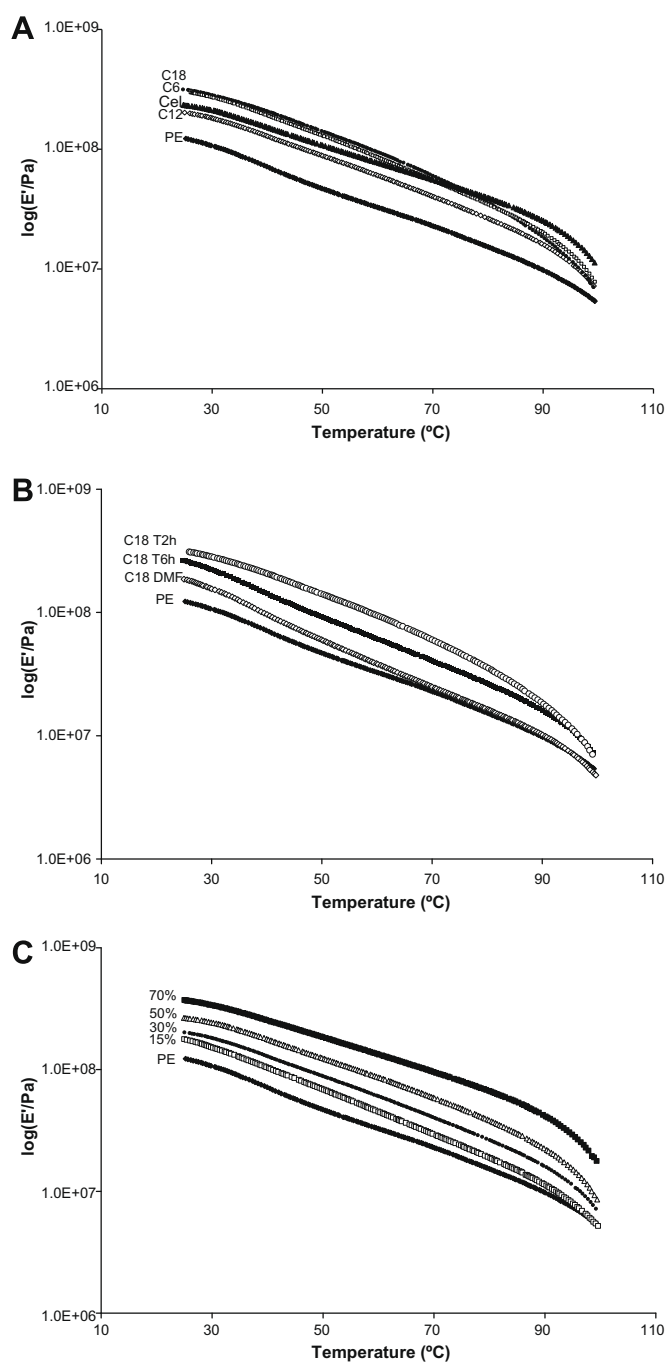


Fig. 2. Logarithm of the storage modulus E' vs. temperature (at 4 Hz) for cellulose fibers/LDPE composites: (A) effect of fatty acid chain length, (B) effect of the DS and (C) effect of fibers charge.

The addition of 30 wt.% of unmodified or acylated cellulose fibers to the LDPE matrix led in all cases to an increase in the storage modulus. However, this effect was strongly dependent on the fiber properties. The expected reinforcing effect depended on two main factors, viz (i) the quality of the adhesion between both components, which induces the efficiency of the stress transfer from the matrix to the fibers and (ii) the fiber aspect ratio (L/d , L being their average length and d their average diameter). Here, the composites filled with cellulose fibers modified in toluene, for 1 h, except those with C12, presented a higher dynamic mechanical modulus than their counterparts with unmodified fibers (Fig. 2A), which obviously arose from the better interfacial adhesion between the modified fibers and the matrix. In this case, the aspect ratio did not play an important role because, for the same fatty acid, the esterified fibers with a lower DS preserved essentially the features of the native fibers, such as crystallinity and fiber length. On the other hand, for composites filled with cellulose fibers modified in toluene for long reaction times (6 h) and in DMF, the increase in the storage modulus was, in most cases, lower than that observed with

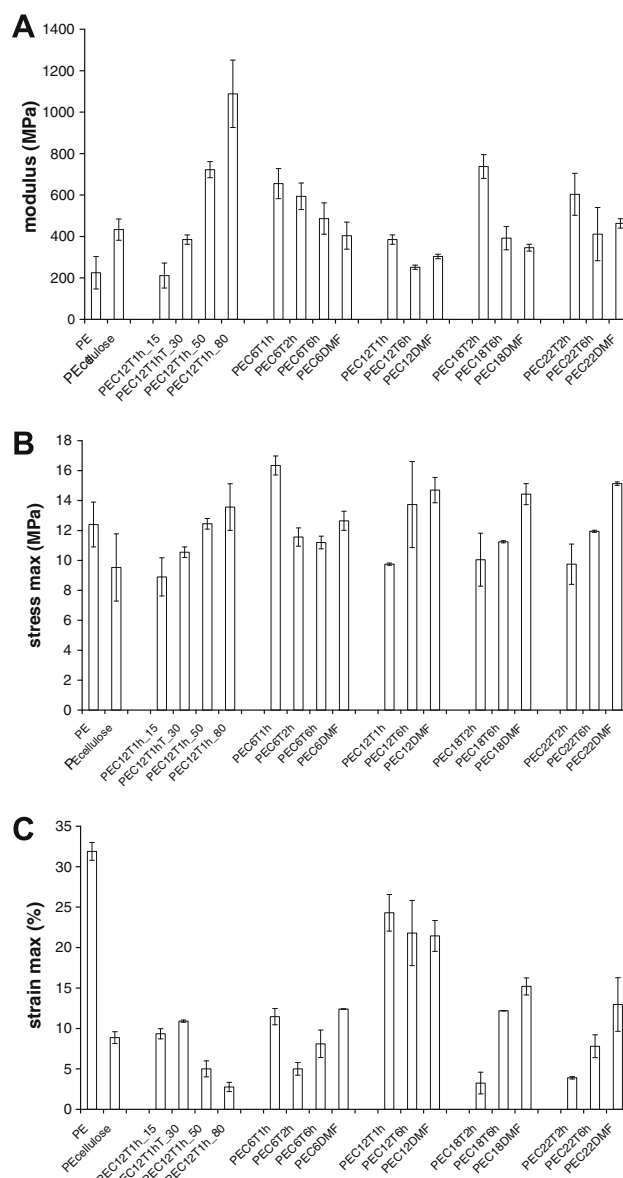


Fig. 3. Young's modulus (A), tensile strength (B) and elongation at break (C) of all cellulose-based LDPE composites studied.

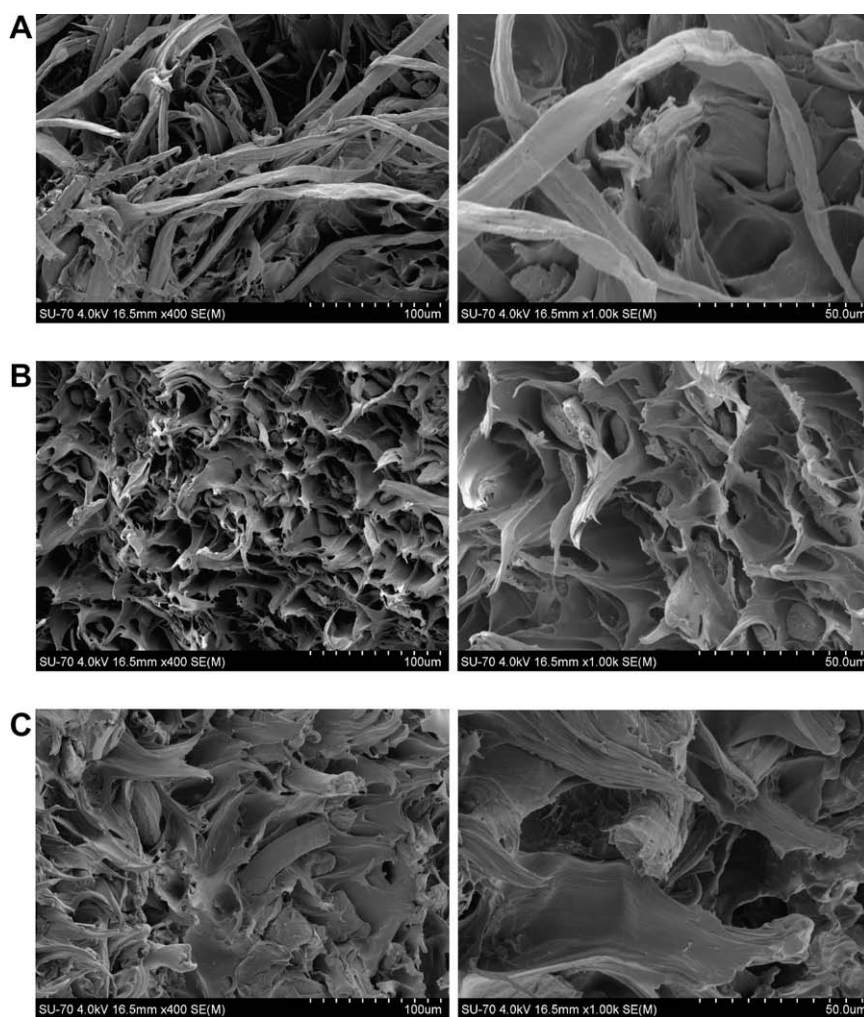


Fig. 4. Scanning electron micrographs of the fractured surfaces of cellulose fibers/LDPE composites, resulting from the tensile tests: (A) PECellulose, (B) PEC6T1h and (C) PEC18DMF.

the unmodified fiber counterparts (Fig. 2B). It seems that in this case, the aspect ratio played the major role on the mechanical properties of the PE-composites, since severe reaction conditions (time and the use of a swelling solvent) increased the DS, but led, in general, to a considerable decrease in the fiber length, as previously reported [6,7], and therefore in the aspect ratio. These results are in agreement with published data, where the LDPE composites with unmodified fibers presented better mechanical properties than those with fibers esterified for 4 h in toluene with dodecanoyl and octadecanoyl chloride [12].

Moreover, the storage modulus increased considerably with the filler content (Fig. 2C), as previously observed with other cellulose-based composites [12,21–23].

The effect of the fiber loading, DS and fatty acid chain length on the large strain behavior of cellulose fibers/LDPE composites was investigated up to their failure. The Young modulus, determined from the typical stress–strain curve, increased considerably with the fiber content and, for composites with the same fiber loading, the presence of modified fibers gave higher values than that associated with the unmodified counterparts (Fig. 3A). These results were in perfect agreement with the DMA essays.

Additionally, the presence of fibers caused a considerable decrease in the elongation at break (Fig. 3C). Composites filled with cellulose fibers modified in DMF, and with C12 in toluene, displayed higher elongations at break, some of them very close to that of unfilled LDPE, compared with those containing fibers modified

in toluene with C6, C18 and C22. These composites, even with lower mechanical performance, are also quite interesting because they could replace unfilled PE in applications where the mechanical performance is not an important requirement, but with the advantage that these materials contain a considerable proportion of a renewable and biodegradable component.

6. Morphology

SEM micrographs of the fractured surface of the composites resulting from tensile tests are shown in Fig. 4. For each material, two different magnifications were used to display both the fiber dispersion and the interfacial adhesion.

Fig. 4A corresponds to the unmodified fibers in a LDPE matrix and clearly shows that the interfacial adhesion between the cellulose fibers and the matrix was very poor. The fibers were pulled out from the matrix practically intact and therefore, fracturing the composite sample did not lead to any substantial fiber breakage. Moreover, the presence of cellulose fiber aggregates, some of them visible with the naked eyes, provided strong evidence of the poor dispersion of the reinforcement within the polymeric matrix and consequently of the non-homogeneity of the material.

Conversely, SEM images of all modified fiber-based composites (Fig. 4B–C) provided evidence of the strong interfacial adhesion between the two components, as shown by the cellulose fibers breaking during fracture and also by their good dispersion within

the matrix, without aggregates formation. This behavior is the result of the surface acylation that conferred a non-polar character to the cellulose fiber surface [6,7]. Similar results were observed for cellulose fibers with different fatty moieties and DS values, which corroborates the surface energy values previously reported [6,7].

Finally, the composites with cellulose fibers modified in DMF (higher DS), and with C12 in toluene for 6 h, showed a more uniform morphology (Fig. 4C), i.e. the fibers were less visible because they were buried more effectively in the LDPE. As previously reported, the cellulose modification with fatty acids in DMF (and with C12 in toluene for long reaction times) leads to extensive degradation of the fiber ultrastructure and morphology [6], which probably gives rise to a better compatibility of the fibers with the matrix during the composite processing.

7. Water uptake

The water absorption results are crucial for understanding the performance of cellulose-based composites, since the moisture pickup under immersion in water or exposure to high humidity, intimately relates to such composite properties as mechanical strength, dimensional stability and appearance.

Fig. 5 shows the water uptake evolution for unmodified and acylated cellulose-based composites as a function of time. All the composites absorbed water during the experiment, but following quite different profiles. Since PE only showed a very small amount of water uptake after 3 months owing to its hydrophobic nature, the water uptake of the composites was entirely due to the presence of the natural fibers.

Water uptake was considerably higher for unmodified cellulose-based composites, compared with that of their acylated cellulose counterparts. This behavior clearly reflected the presence of long chain aliphatic moieties onto the fibers surface, after esterification with the fatty acyl chlorides, resulting in a considerable increase in their hydrophobic character, as previously reported [6,7]. However, for the acylated cellulose-based composites, the water uptake was not influenced to a great extent by the fatty acid chain length and DS, except of course for very low DS values (i.e. PEC182hT and PEC22hT samples). These observations are in good agreement with previously reported water contact angle measurement and surface energy determinations, where it was observed that the surface energy decreased only slightly with the fatty acid chain length and the DS [6,7].

Moreover, after this ageing period, only the composites with modified fibers (except those with very low DS) had reached an equilibrium moisture level. These samples exhibited a water up-

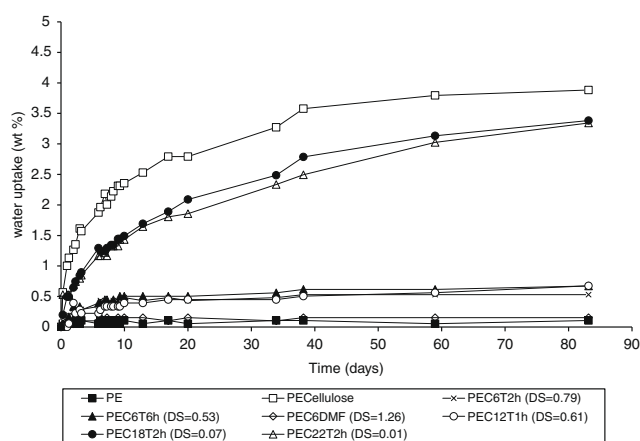


Fig. 5. Water uptake as a function of time for LDPE-cellulose-based composites when immersed in water at room temperature.

take pattern with two well-separated regions. Initially, the absorption was fast and followed a linear Fickian behavior before reaching an equilibrium plateau.

8. Conclusions

Composite materials were obtained by compounding unmodified and fatty acid-esterified cellulose fibers with low-density polyethylene. The surface chemical modification of the cellulose fibers resulted in improved interfacial adhesion between the fibers and the matrix and consequently in enhanced mechanical properties, as well as in a better water resistance. The results obtained clearly demonstrate the importance of a strict DS control in order to achieve better composite performances. Depending on the properties of the modified fibers (e.g. DS and morphology) these composites, incorporating a cheap and ubiquitous renewable resource, could have different potential applications, namely as structural materials (building or automotive) or packaging materials.

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