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Graft polymerization of methyl methacrylate onto short leather fibers

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Summary

In this work, the graft polymerization of methyl methacrylate (MMA) monomer onto short leather fibers (SLF) was investigated as a function of the monomer/leather fiber ratio. This chemical modification was made by aqueous emulsion polymerization initiated by a redox system. The effect of' the monomer concentration on the grafting parameters (deposited and grafted polymer, as well as grafting efficiency) were determined. Composites formulated with SLF without chemical modification have showed lower tensile and impact properties in comparison with composites formulated with treated fibers. However, the elongation at break values for both systems remained similar as the MMA content changed. The morphology of SLF grafted with MMA was examined by both optical light microscopy (OLM) and scanning electron microscopy (SEM). Micrographs have shown polymer deposition on individual fibers and bundles of SLF. They have also revealed that PMMA may interpenetrate the SLF network and be deposited in large and coarse aggregates around individual fibers, but without occupation of the free space in the fiber net.

Introduction

Residues and wastes of organic fibers are used as fillers or reinforcements in thermosets and thermoplastic polymers, such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS), polymethyl metacrylate (PMMA), etc. The composites formulated offer significant weight advantages, a combination of good mechanical properties with a low specific mass, and provide the economic benefit of lower cost (1-5). Taking into account that organic fillers or fibers are derived from renewable natural resources; most of them show a common limitation in applications. The limitation is a poor compatibility between the hydrophilic filler (high level of moisture absorption by the fiber) and the hydrophobic thermoplastic polymer. However, a large number of attempts have been made to improve the adhesion between polymeric matrices and natural fibers such as coconut, wood, nutshell flour, hemp, jute, sisal, and cellulose (6-9). These attempts have included modifying the chemistry of the fiber surface or the polymer matrix.

Some investigations into chemical modification of leather fibers have been conducted on leather products (10-11). The aims of these investigations were to produce new leather products, such as leather boards, while retaining the natural appearance of leather. These investigations demonstrated that acrylic monomers, such as methyl methacrylate (MMA), butyl acrylate (BA) and others, can be grafted onto tanned or untanned leather fibers with an improvement in the mechanical properties (12). However, this system (acrylic-leather) has special characteristics, not all the polymer generated is grafted onto the leather fibers. Usually the efficiency of grafting reactions is a function of

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large number of variables e.g. the type of initiator, structure of the polymeric substrate, the monomer, the ratio of reactants and reaction conditions (13). In this work the system (acrylic-leather fibers) used different amounts of monomer in order to determine the optimum monomer/leather fiber ratio. The amount of monomer, which had reacted with the leather substrate, to produce a true graft copolymer was determined by solvent extraction. The reacted monomer is insoluble in chloroform. The percentage of polymer grafted was used to determine the grafting efficiency and to ensure the adhesion between the fiber-matrix (14).

The aim of this paper is focused to study graft polymerization of methyl methacrylate (MMA) onto SLF by emulsion polymerization. Consequently, aspects of deposition, efficiency and grafted polymer values are emphasized. The effect of chemical modification on SLF and the fiber content on the tensile and impact properties of SLF-PMMA composites were determined. This process of chemically modifying SLF could be considered as a useful technique for recycling thousands of different leather wastes.

Experimental

Materials

Wastes of chrome-tanned leather fibers from cattle skin (Nappa rojo) obtained from a tannery of León City, México were used. The pieces were milled using a rotary mill and sieved in a mesh of 1.5 mm diameter. The average fiber aspect ratio (L/D) was 60. The monomer used was methyl methacrylate (MMA) inhibited with 10 ppm of monomethyl ether of hydroquinone (MEHQ) from Aldrich Chemical Corp. It was purified by distillation. The potassium persulfate (KPS) and the sodium metabisulfite (MBS) were obtained from J.T. Baker S.A. The surfactant used was Triton X-45 (an alkyl phenoxy polyethoxy ethanol) from Aldrich Chemical Corp. Polymethyl methacrylate (PMMA) was used as the polymeric matrix of the composites formulated with treated and untreated SLF. This resin was provided by Plastiglass de México, S.A. The supplier reports the follow physical properties: density of 1.19 g/cm^3 and melt flow index of 6.41 g/10 min.

Graft copolymerization of acrylic monomer

Grafting reactions were carried out in a glass reactor (1 L) in a bath at constant temperature (30°C). The water, SLF, surfactant and the initiator (MBS) were added into the reactor under an inert atmosphere. These components were mixed with mechanical agitation for 15 min. The initiator KPS was added and mixed for 30 min. Afterwards, the monomer was added and the components were mixed for 4 h. An inert atmosphere of N_2 was used during the polymerization process. Approximately 100% polymerization was reached in all the experiments. The treated fibers were filtered and dried for 24 h at 60°C and the amount of deposited polymer was determined gravimetrically. To determine the amount of homopolymer in each system 5 g of modified SLF were subject to Soxhlet extraction with chloroform for 24 h. The percentage of homopolymer was calculated gravimetrically. The description of the general graft polymerization procedure is outlined in Table 1.

Preparation and characterization of composites

The composites were prepared by mixing the polymer matrix with the modified and unmodified SLF (0-40% wt) using a torque rheometer, Brabender model PLE-330 at 200°C. The mixing procedure received special attention in order to achieve a truly random fiber distribution (15,16). Specimens for tensile and impact tests were cut according with the ASTM standards from plates of 1.5 min thickness. These were prepared by thermal compression molding at 200°C and 2.8 MPa in a Carver Laboratory press. The mechanical properties of the composites were determined using the specimens described by the ASTM procedure D-638. The tests were performed in an Instron 1125 Universal testing machine at room temperature and at a crosshead speed of 5 mm/min. The impact strength was measured following the DIN 53453 norm, in a CEAST impact tester Resil 25 with a pendulum velocity of 3.46 m/sec.

Table 1 Grafting formulations experimented, (grams)

Components	**Treatments**			
	M0	**M1**	**M2**	**M3**
Leather (SLF)	26	26	26	26
Water	882	882	882	882
Surfactant solution, (Sol. 1%)	2.05	2.05	2.05	2.05
Initiator:Potassium persulfate (KPS, Sol 5%)	2.6	2.6	2.6	2.6
Sodium metabisulfite (SMBS, Sol.5%)	1.3	1.3	1.3	1.3
Monomer: Methyl methacrylate (MMA)	13	26	52	78

IR spectroscopy

Infrared spectroscopic measurements were done in a FTIR spectrophotometer Nicolet Protégé 460 with a resolution of 2 cm^{-1} and 100 scans. The KBr solid disk technique was employed to prepare samples with modified and unmodified SLF. The modified SLF used in this analysis were previously subjected to Soxhlet extraction with chloroform in order to remove the PMMA deposited over fiber surface.

Thermal analysis

The thermogravimetric (TG) and calorimetric measurements were performed using a thermogravimetric balance (TGS-2) and differential scanning calorimeter (DSC-7) Perkin Elmer, respectively. A heating rate of 10øC/min and a sample weight of 5-10 mg were used in an N_2 atmosphere (100 mL/min). During evaluation of differential thermogravimetric (DTG), the peak temperature and amount of char left at 550°C were determined.

Morphological analysis

A stereoscope microscope (Zeiss, German) model Wild M-400 was used at different magnifications (24x-75x) to observe the morphology of SLF samples after grafting emulsion polymerization with MMA. This provided a suitable resolution for morphological studies of the fiber surface. Scanning electron microscope (SEM) micrographs for treated and untreated SLF were obtained with a JEOL JSM 5400LV.

Results and discussions

To improve the properties of composites formulated with short tanned leather fibers it is necessary to carry out a chemical modification of the leather surface. The method used in this work was the grafting of PMMA by emulsion polymerization. Table 2 shows the grafting parameters of SLF subjected to chemical modification. It can be seen that all the grafting parameters increase as the monomer/leather fiber ratio is increased, some of them tend towards constant values when the monomer/leather fiber ratio is equal to 3. Therefore, the amount of MMA used in the reaction had a special effect on the grafting efficiency and the chain length of the PMMA formed (9). Meanwhile, the deposited polymer appears to increase continuously with the monomer/leather ratio, and it reaches values around 4 times, in comparison with the lowest ratio. The percentage of grafted polymer also showed dependence on the monomer concentration. This grafting parameter increased gradually because the amount of polymer formation in the reactor increased. It is well known that some radicals on the leather fiber can start the polymerization due to the cationic chromium complex in the tanned leather fibers (17). Therefore, the amount of deposited and grafted polymer increases as the monomer/leather ratio is augmented. On the other hand, the concentration of the redox initiator pair was kept constant, for all the experimental formulations. This was because the grafting parameters are strongly dependent on the complex processes involving the interactions of the leather microstructure, individual diffusion rates, relative initiator efficiency and other sources of viability.

Table 2 Grafting parameters

Reaction Variable: MMA/Leather ratio	**Deposited Polymer, %**	**Grafted Polymer, %**	**Grafting efficiency, %**	**Range Decomp. °C**	**Residual Mass, %**
0.5/1	11.61	3.38	10.62	331 and 422	17.4
1/1	23.12	8.87	15.07	322 and 412	16.2
2/1	35.97	16.02	30.81	321 and 408	12.6
3/1	48.27	29.80	38.205	323 and 413	10.4

The application of IR absorption spectroscopy has aided the identification of small organic molecules such as proteins, because they have similar spectra than the collagen (18). However, this analytical technique was used in this work to prove the production of a collagen-g-PMMA copolymer. All of the treated SLF were previously subjected to a solvent extraction, in order to remove the PMMA deposited on the fiber surface. The collagen spectra shows a wide band at 3400 cm^{-1} which is due to the hydroxyl group. The short peaks around 3060 and 2950 cm^{-1} are the asymmetrical stretching bands of -CH$_3$ and =NH bonds, respectively. Another characteristic shown in the spectra graphs by the leather without chemical treatment are amide and C=O bands at 1650 cm^{-1} and COO- at 1530 cm^{-1} A characteristic band of leather samples is observed at 1200 cm^{-1} which represents the chromium complexes. Due to their positions and intensities these could be related to a possible binding with a sulfate group. The bridging sulfate groups in chromium complexes have four absorption bands each in the range of 1300-900 cm^{-1} (19). Samples of leather after the extraction process of PMMA showed an intensive peak at 2950 and 1725 cm^{-1} corresponding to (CH$_3$) methylene and (C=O) carbonile ester groups. The intensification of this band is shown in Figure 1. Since other bands did not participate in the grafting reaction they were considered as references. This proved that MMA monomer had grafted onto the collagen chains of the leather fiber.

It was proved by thermogravimetic analysis (TGA) that the chemical modification of SLF was successful, this is shown in Figure 2. The leather samples have an initial weight loss of 10% around 100°C because the water absorbed by the leather fibers is released. After this process the leather fiber is stable up to 250°C where a gradual decomposition begins to take place and two inflections are observed. The last inflection occurs around 420°C and the temperature of ash formation is reached at 580°C. The leather-g-PMMA copolymers show a behavior quite similar to the leather and the homopolymer thermograms. The deposited or grafted polymer could be "coating" the fiber surface and reducing its capacity to absorb moisture. The main decomposition occurs between 310 to 450°C, after this decomposition the residues are about 12% of the initial weight. Using the first derivative curve for these samples, the temperature of decomposition is calculated at 390°C and 404°C for samples M1 and M3, respectively. The decomposition temperatures for the leather without treatment and the PMMA matrix are 360øC and 410°C, respectively

The chemical modification of grafting MMA onto leather fibers has improved the thermal stability of leather fibers.

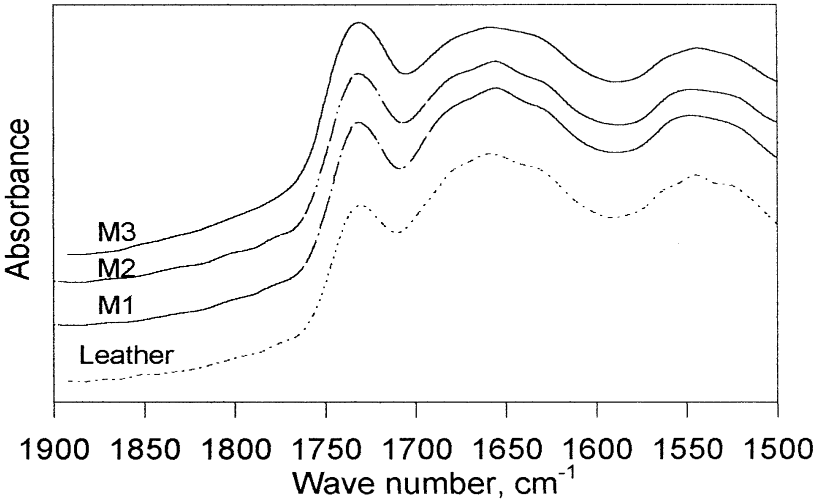

Figure 1 IR spectrum of SLF at different monomer concentrations

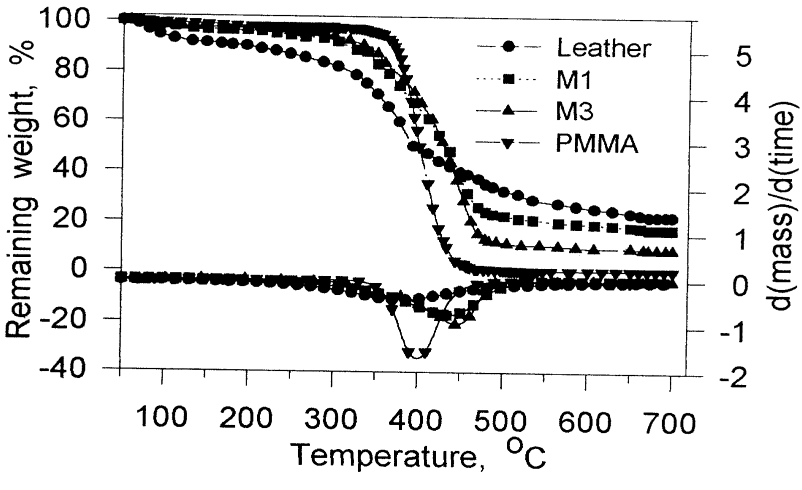

Figure 2 TG and DTG curves for PMMA, leather and treated leather samples

The mechanical properties of PMMA filled with modified and unmodified SLF are summarized in Table 3. From the results it can be observed that the grafting of PMMA produced moderate changes in the mechanical properties of the composites. The tensile strength values in some formulations were increased by about 35% over composites formulated with untreated SLF. A decreasing trend in the mechanical properties (tensile and impact strength) of the composites formulated with untreated SLF was observed as the fiber content increased. This is due to the fibers producing discontinuities in the matrix which act as stress concentrators during the tests. The mechanical parameters measured for the composites formulated with chemically modified SLF showed significant changes in strength values compared with the same untreated fiber concentration.

However, the strength values of composites formulated with treated SLF do not reach the strength of the PMMA matrix. The improvement in the tensile strength of the composites formulated with the chemically modified SLF may be due to the efficiency with which the applied load is transferred through the matrix material to the SLF. This is controlled by the adhesion at the fiber-matrix interface. PMMA-SLF composites filled with treated leather fibers retained similar elongation at break values compared with composites containing untreated fibers. For both types of fibers, the elastic modulus of the composite increased as the fiber content increased. A slight difference between the modulus of the untreated and treated leather-PMMA composites was observed.

Table 3 Mechanical properties of PMMA-leather fiber composites*

Treatment	Leather % wt	Tensile strength, MPa	Elastic modulus, MPa	Elongation at break, %	Impact strength, kJ/m^2
PMMA		56.3 (8.45)	2869 (614)	3.6 (0.51)	22.5 (2.8)
Untreated leather fibers	5	38.8 (3.35)	3361 (156)	1.4 (0.14)	11.8 (1.8)
	10	32.4 (1.39)	3370 (154)	1.1 (0.26)	3.5 (1.7)
	20	29.8 (3.29)	3571 (148)	1.0 (0.12)	3.4 (1.8)
	30	29.4 (3.67)	3647 (86)	0.9 (0.26)	2.9 (1.2)
	40	22.5 (1.75)	3624 (124)	0.7 (0.08)	2.7 (0.7)
Treatment M0	5	41.1 (1.41)	3386 (129)	1.4 (0.28)	9.8 (2.6)
	20	37.3 (3.89)	3444 (95)	1.3 (0.23)	3.6 (1.6)
	40	23.6 (2.10)	3794 (87)	0.7 (0.09)	2.9 (0.5)
Treatment M1	5	39.2 (2.30)	3339 (129)	1.4 (0.18)	8.4 (2.1)
	20	33.9 (3.60)	3331 (109)	1.2 (0.14)	3.7 (1.3)
	40	30.3 (1.23)	3648 (129)	1.0 (0.11)	2.8 (0.8)
Treatment M2	5	34.0 (3.82)	3243 (121)	1.2 (0.23)	11.0 (1.9)
	20	28.4 (2.29)	3448 (68)	1.0 (0.12)	3.8 (1.5)
	40	25.7 (1.18)	3535 (141)	0.8 (0.08)	3.7 (0.9)
Treatment M3	5	36.3 (3.25)	3222 (363)	1.3 (0.17)	9.6 (1.7)
	20	27.8 (2.09)	3344 (122)	1.0 (0.12)	4.3 (1.3)
	40	21.7 (1.93)	3389 (68)	0.7 (0.10)	3.9 (1.1)

The values in parentheses give the standard deviation

The optical and scannign electron micrographs of short leather fibers are shown in Figures 3 and 4. Figure 3 shows a group of leather fibers which are aggregated into bundles and constitute a fibrous matrix. Individual fibers have a diameter of 4 μm. In some cases, as shown in Figure 4, the deposited polymer around a microfibril (single fiber) produced domains of 20 μm thickness. As MMA monomer concentration increased the packed polymer (polymer aggregation) around the individual fiber increased. Although some features of the morphology of modified leather samples have been revealed an extremely complex morphology was caused by non-uniformity of the leather fibers. The SEM analysis has proved to be a suitable technique to follow the aggregation level of deposited polymer.

Conclusions

In this work it has been found that chemical modification by grafting MMA onto leather fiber (collagen chains) can improve the bonding forces between natural fiber and thermoplastic matrix, although tensile and impact strengths of such fiber composites have not been found to be superior to the unfilled thermoplastic. Considering that leather wastes are a cheap filler, the composites formulated have acceptable tensile and impact strengths, as well as other important properties. The grafting copolymerization was analyzed using different techniques. By FTIR spectra the leather fiber samples showed characteristic bands of methylene and amino acids, while the copolymer leather-g-PMMA samples have shown a gradual increase in the peak at 1730 cm^{-1}. This is due to the carbonile group as the monomer concentration is increased. On the other hand, an improvement in thermal stability of the leather fibers was observed. This could prove that grafting of PMMA onto the SLF had occurred. The effect of the monomer/leather ratio on the grafting parameters has shown that different percentage of deposited and grafted polymer can be reached, as the monomer/leather fiber ratio is increased. The PMMA grafted onto the leather fibers imparts polymeric characteristics; therefore the properties of the fibers are like those of a hybrid material. The morphology shown in the SEM micrographs revealed that little grafting could occur in systems with low monomer concentration. As this variable increases a coarse deposition of polymer is observed on the single fiber surfaces.

Figure 3 Microphotograph by optical microscope of untreated short leather fibers

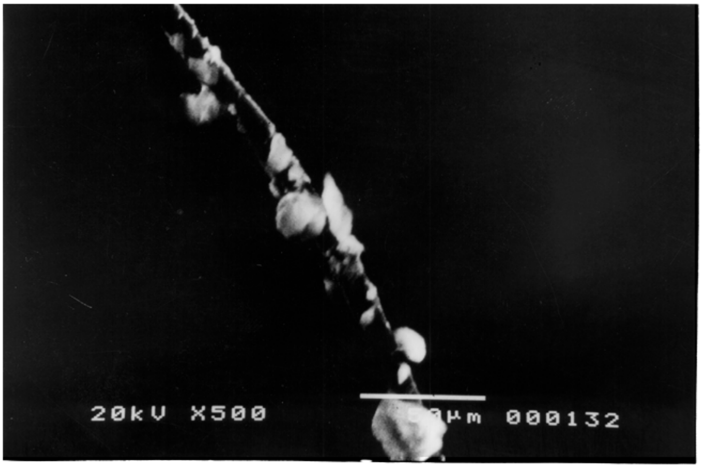

Figure 4 SEM microphotograph of treated SLF (Treatment M3)

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