Emulsion Polymerization Grafting of Methyl Methacrylate onto Short Leather Fibers

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SUMMARY : The graft polymerization of methyl methacrylate (MMA) monomer onto short leather fibers (SLF) was made by aqueous emulsion polymerization. The effect of the monomer /short leather fiber ratio on the grafting parameters (deposited and grafted polymer) were determined. From the results obtained with the monomer investigated in this study, it was found that the grafted polymer has modified the properties of the substrate, even when it is present in a relatively small amount .

In analogy with composites formulated with natural fibers subjected to chemical modification, the tensile and impact properties of composites formulated with untreated fibers are smaller than composites formulated with treated fibers. However, the elastic modulus for both kinds of systems has remained in similar values as the content changes.

Introduction

One of the most important problems of the tannery industries is the disposal of hundreds of tones of leather shavings and trimmings, which represent a very serious problem of environmental pollution. The fibers from these wastes could be used, however, as fillers in thermoplastics in various applications where a leather-like appearance is important (e.g. in the shoes or furrier industries). Madera[1-2)] has reported the properties of composites formulated with untreated short leather fibers (SLF) in a PVC matrix. Although, this material has a strong possibility to be used by the shoe industry, an improvement of the adhesion between the leather fibers and the polymeric matrix would be necessary to fulfil several industrial requirements. One alternative is the chemical modification by emulsion polymerization of an acrylic monomer[3-4)]. This treatment must contribute to improve the leather mechanical properties maintaining its natural appearance[2)].

The aim of this paper is focused to study the effect of the emulsion polymerization grafting of methyl methacrylate (MMA) onto SLF on the mechanical properties of composites

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formulated with SLF. Consequently, aspects of deposition, efficiency and grafted polymer values are emphasized. The effects of chemical modification and the fiber content on the tensile and impact properties of SLF-PMMA composites were determined. This process of chemical modification of SLF could be considered as a useful technique to recycle thousands of different leather wastes.

Experimental

Materials. Wastes of chrome-tanned leather fibers from cattle skin (red Nappa) obtained from a tannery of León, Mexico, were used. The pieces were ground into a rotary mill and sieved. The leather fibers were observed with a transmission optical microscope (American optical, model Phase-star). Micrographs obtained with this technique allowed to determine an average value of the fiber aspect ratio (L/D) of 60. Methyl methacrylate (MMA) from Aldrich Chemical Corp. was used as monomer. It was purified by distillation. The potassium persulfate (KPS) and the sodium metabisulfite (MBS) were obtained from J. T. Baker S.A. The surfactants used were Triton X-45 (an alkyl phenoxy polyethoxy ethanol) and sodium dodecylbenzensulfonate (DBS), both furnished by Aldrich Chemical Corp. Polymethyl methacrylate (PMMA, Plastiglass) was used as polymeric matrix in the composites formulated with treated and untreated SLF.

Grafting reactions were carried out in a 1 l glass reactor thermostated at 28 °C. SLF, distilled water, tensoactive and MBS were introduced into the reactor and mixed. The system was purged with nitrogen during 15 min. The initiator KPS was added and mixed for 30 min. Afterwards, the MMA was added and all the components were mixed during a reaction period of 4 h[6]. The percentage of polymerization conversion reached in all the experiments was almost 100%. The treated fibers were filtered and dried. The amounts of polymer in the aqueous phase and on the fibers were determined gravimetrically. Soxhlet extraction of samples of modified SLF allowed to calculate the percentage of deposited and grafted polymer.

The composites were prepared by mixing the polymer matrix and the modified and unmodified leather fibers (0-40% wt.), using a torque rheometer Brabender model PLE-330 at 200 °C. The procedure of mixing has received an especial attention, in order to achieve a truly random fiber distribution. Specimens for tensile and impact tests were cut according with the ASTM standards from plates of 1.5 mm thickness prepared by thermal compression molding. The mechanical properties of the composites were determined using the specimens described by the ASTM procedure D-638 with an Instron 1125 Universal testing machine. The impact strength was measured following the DIN 53453 norm, in a CEAST impact tester Resil 25.

Results and Discussion

The effects of the monomer/leather ratio and the type of surfactant on the fiber modification were studied for a series of systems containing the same fiber content. During the reaction, polymer particles are formed in the aqueous phase by conventional nucleation mechanisms. Afterwards, some particles precipitate directly on the fiber surface or coalesce in water and form polymer agglomerates. Simultaneously, monomer dissolved in water may react with active centers at the fiber –water interface and the graft copolymer of MMA and collagen is synthesized. The mechanism of the active center apparition is not clear, but it may be due to a free radical transmission from the redox pair in the aqueous phase to the biopolymer or by an activity of the chrome tied to the functional groups on the collagen chains.

The results of the chemical modification of the fibers are shown in Figures 1 and 2. It may be observed that, for both surfactant systems, the fiber modification parameters increase as the monomer/leather fiber ratio is augmented. 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 amount of grafted polymer has also showed dependence on the monomer concentration. This number of PMMA chains grafted onto the

Figure 1. Deposed and grafted polymer on modified SLF in presence of DBS.

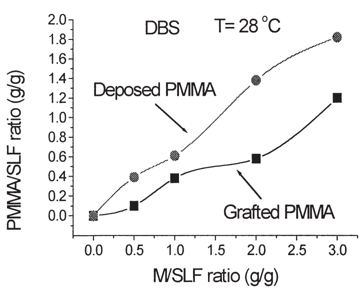
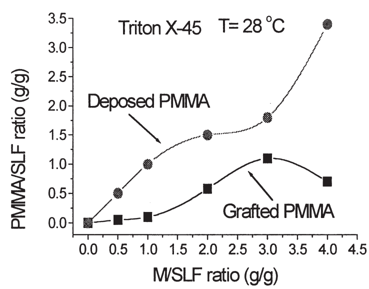


Figure 2. Deposed and grafted polymer on modified SLF in presence of Triton X-45.



fibers has increased gradually, due to a greater probability of monomer reaction. As it was mentioned previously, it is well known, that some radicals on the leather fiber can start the polymerization, due to cationic chromium complex of the tanned leather fibers[5]. Therefore, the amount of deposited and grafted polymer increases as the monomer/leather ratio is augmented. However, it was observed that the DBS allowed to obtain a greater number of polymer chains directly grafted to the collagen which constitute the fibers.

Scanning electron studies of the modified SLF an extremely complex morphology that was caused by non-uniform features of the leather fibers. The micrograph in Figure 3 allows to observe a group of leather microfibrils with a diameter of 4 μm and which are aggregated in bundles. These microfibrils constitute the fibrous matrix. Small polymer aggregates deposed on the fiber surface were observed. SEM studies revealed also that as the MMA monomer concentration is increased, the packed polymer (polymer aggregation) around individual fiber also increases.

A series of model blends of the modified SLF and PMMA were prepared and their mechanical properties measured (see Figure 4). In all the cases, it was observed that the elastic modulus was not sensibly affected by an increase of the PMMA grafted and deposited on the SLF. However, an improvement of the impact resistance of the blends with the amount of deposed and grafted PMMA was observed at different SLF contents. This improvement of

Figure 3. Micrograph of a modified SLF (MMA/SLF ratio: 20 g/g).

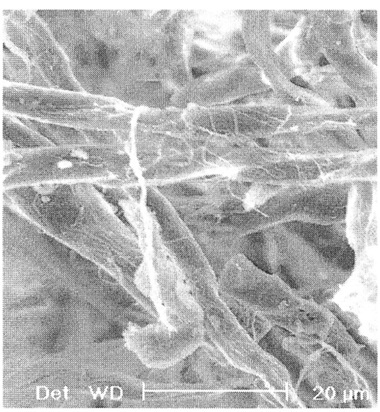
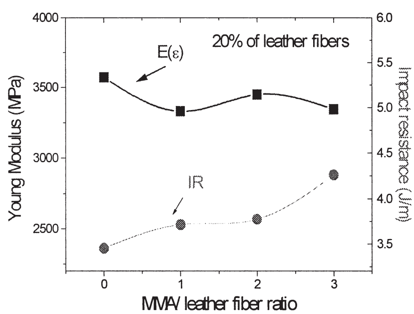


Figure 4. Elastic modulus and Impact resistance of PMMA filed with 20% of modified SLF.



the breakage resistance of the composites formulated with chemical modification, may be explained in terms of an applied load transferred through the matrix material to the fiber-matrix zone, which is controlled by the interfacial adhesion.

Conclusions

It was shown in this work the feasibility to prepare collagen-g-PMMA materials. DBS is a more efficient tensoactive in the grafting polymerization of MMA onto SLF than Triton X-45. The mechanical characterization of a series of PMMA filled with modified SLF showed an increment of the impact resistance with the amount of PMMA grafted onto the collagen fibers. Therefore, the chemical modification of the fibers allowed to improve the interfacial cohesion of the composite materials.

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