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Synthesis and Characterization of Bagasse Poly(methyl methacrylate) Graft Copolymer

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Summary: Graft copolymerization of methyl methacrylate (MMA) was carried out on bagasse fibers in an aqueous medium using ceric ammonium nitrate (CAN) as initiator under a neutral atmosphere. In order to obtain the optimum condition for graft copolymerization, the effects of initiator concentration, temperature, time of reaction, and monomer concentration were studied. The maximum grafting percent was found to be 122%. The bagasse grafted poly(methyl methacrylate) was characterized by FTIR and its thermal behavior was characterized by TGA.

Keywords: bagasse; ceric ammonium nitrate; copolymerization; methyl methacrylate; renewable resources

Introduction

In the last two decades the importance of natural based polymers as renewable resources increased significantly because of the growing environmental awareness of society and the depletion of natural oil reserves.[1–3] More and more attempts are made to produce such materials and they are used in increasingly amounts in several areas including packaging, agriculture, health care and etc.[4–9] Lignocellulosic materials represent the most important renewable sources of raw materials in the world. Sugarcane bagasse is one of those derivatives. Bagasse is an abundant, inexpensive, renewable, and biodegradable natural raw material. However, bagasse by itself is unsuitable for most uses because of its poor physical properties. Chemical modification of bagasse is a way to introduce many different properties such as elasticity, sorbancy, ion exchange capabilities, thermal resistance, and so forth.[10,11] The chemical modification of natural polymers by grafting has received considerable attention in recent years due to the wide variety of monomers available.[12–18] This method requires that the surface be modified, by bonding reactive sites of substrate either by initiator or reactive functional groups. Bagasse can be modified and tailored to useful forms by graft copolymerization by vinyl monomers under controlled condition. Selection of the initiator system for graft copolymerization on bagasse fiber is a critical consideration due to its lignocellulosic nature. Ceric ammonium nitrate (CAN) due to its unique properties has gained considerable importance as an initiator for graft copolymerization of vinyl monomers onto natural polymers at low temperature.[19–22]

This work presents a detailed study on the grafting of methyl methacrylate onto bagasse using ceric ammonium nitrate. The effects of various experimental conditions such as initiator and monomer concentrations, polymerization time, and temperature were also investigated.

Experimental Part

Materials

Raw bagasse short fibers, obtained from Sugarcane Development & Byproducts Co., Iran, were de-waxed by extracting

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with ethanol:toluene mixture (1:2) in a Soxhlet apparatus for 6 h. The fibers were then washed successively with ethanol and distilled water and dried under vacuum at 40 °C. Methyl methacrylate (MMA) was washed with 5% NaOH three times, dried over $CaCl_2$, and distilled under a vacuum at 46 °C. Ceric ammonium nitrate (CAN) and other reagents (analytical grades) were used as received.

Graft Copolymerization

Graft copolymerization reactions were carried out at given temperatures in a Pyrex vessel equipped with a propeller-type mechanical stirrer, gas inlet and outlet tubes. A mixture of 2.00 g of 40-mesh size bagasse and 100 ml degassed-deionized water was stirred under N_2 atmosphere. Then, methyl methacrylate was added and well dispersed. Five minutes later, a desired amount of CAN initiator (as 0.1 M solution prepared in 0.1 M HNO_3) was added. After the polymerization reaction for specified period, the reaction was quenched by transferring to a beaker containing methanol under stirring for 10 min. It was filtered, washed successively with distilled water, methanol and petroleum ether, dried in vacuum at 40 °C and then it was weighed. Finally, the fibers were extracted with acetone in a soxhlet apparatus for 12–15 h to dissolve all the homopolymers until a constant weight of grafted copolymers was obtained. The percentage graft yield was calculated as follows:

$$\%\text{Graft yield} = \frac{(\text{dry wt of graft copolymer} - \text{dry wt of bagasse})}{\text{dry wt of bagasse}} \times 100$$

Results and Discussion

Graft copolymerization of methyl methacrylate onto bagasse was done with a view to optimization of grafting parameters. In order to establish the optimum condition for graft copolymerization of methyl methacrylate on bagasse, the reaction variables, the initiator concentration, time and temperature associated with polymerization and the monomer concentration were studied.

Figure 1 shows that initiator concentration profoundly influences grafting percent. The increase of CAN concentration from 0.005 to 0.050 M increases grafting percent. This variation in grafting percent is clearly due to amount of free radical generation by initiator, and greater number of grafting site created by initiator. But at higher initiator concentration, the excessive

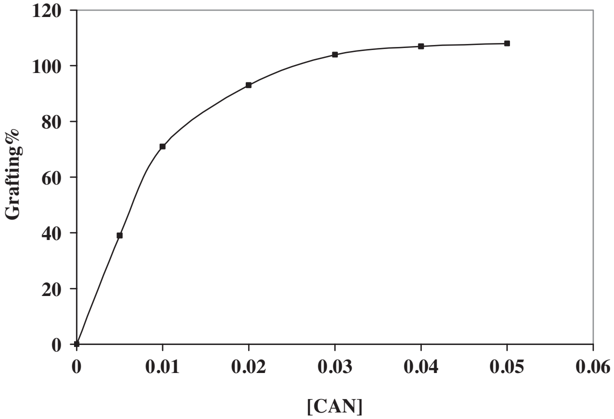

Figure 1.
Effect of CAN concentration on grafting percent.

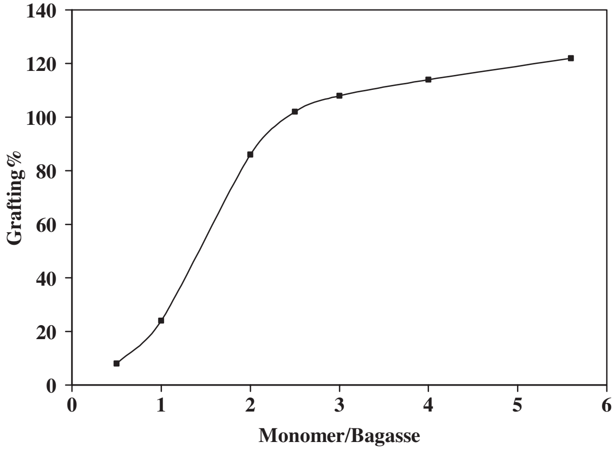

Figure 2.
Effect of MMA to bagasse ratio on grafting percent.

radical concentration in the medium causing increase in the rate of termination reactions and decrease in graft percent.

The effect of monomer to bagasse weight ratio on grafting percent is shown in Figure 2. To promote a favorable grafting, the monomer/bagasse weight ratio ranging 0.5–5.0 were studied. Grafting percent increased with increase amount of monomer, it is obviously due to more availability of monomer. Relevant data shows that there is decrease in trend above the 3:1 monomer to bagasse ratios; it is probably resulted from an increasing in homopolymerization of MMA in high concentration.

The polymerization reactions were carried out at several temperatures from 30 to 70 °C. The Figure 3 shows grafting percent increased with increasing of temperature (from 30 to 50 °C) and then decreased. The grafting enhancement is related to increase in number of free radial on trunk polymer with increase in temperature. In addition, some surface characters of bagasse act as physical barrier to limit the penetration of monomer into the fiber structure, and there is an enhanced diffusion of monomer and

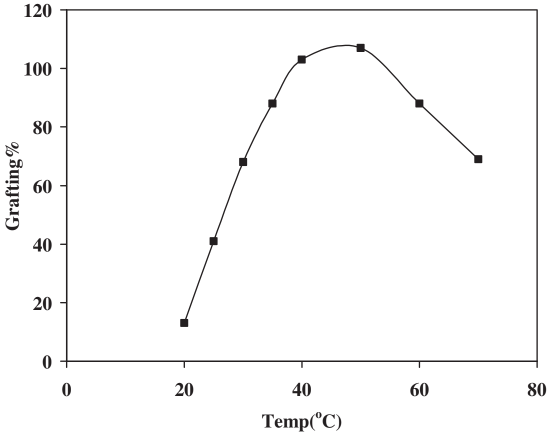

Figure 3.
Effect of reaction temperature on grafting percent.

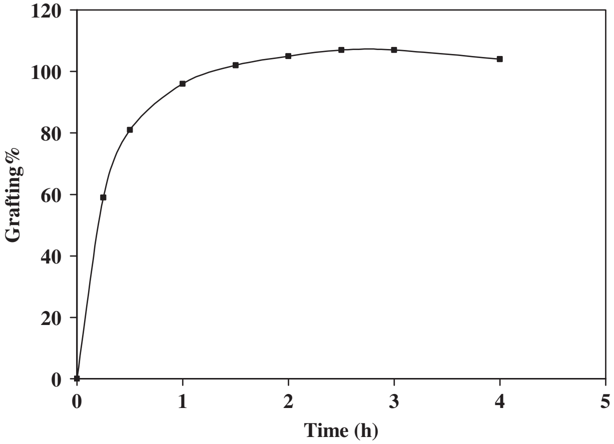

Figure 4.
Effect of time of reaction on grafting percent.

initiator in fiber structure caused by temperature increasing. Nevertheless, at temperature higher than a certain value, the faster rate of chain radical termination and factors such as formation of the homopolymer also appears to be a function of temperature. Therefore, grafting percentages are affected by combinations of the mentioned factors.

Figure 4 illustrates effect of reaction time on grafting percent. It was found grafting percent to be increased steadily with increase of time up to 30 min, after which very little change was observed in trend. This phenomenon was explained on the basis of the availability of the monomer and free radicals on substrate backbone which decreased with time. In reaction times more than 4 h, negligible weight loss was observed. It may be correspond to acidic hydrolysis of substrate.

Infrared Spectroscopy

Characterizations of bagasse and bagasse-g-PMMA constitute another important part of our investigation. Gravimetric analysis,

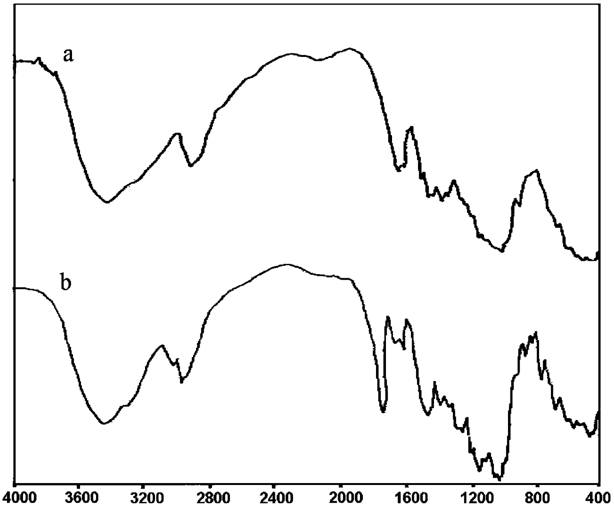

Figure 5.
IR spectra of a) bagasse and b) MMA grafted bagasse.

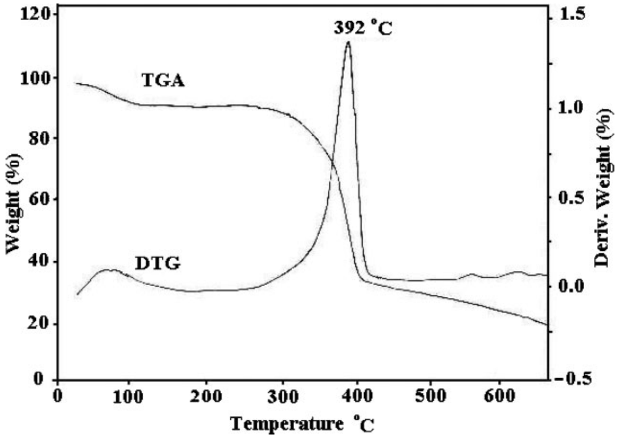

Figure 6.
TGA and DTG curves of bagasse.

weight growth and grafting percents in grafting process caused by grafting of MMA but it could be confirmed by some evidence. Figure 5 illustrates the FTIR spectra of bagasse and bagasse-g-PMMA. A broad absorption band in the region ~430 cm^{-1}, characteristic of hydrogen bond O–H stretching vibration and absorption bands observed in 2930 cm^{-1} to 3400 cm^{-1} and absorption bands observed in 1024 cm^{-1} are respectively related to stretching vibration and bending vibration of C–H, are common to all spectra. In case of MMA grafted bagasse (Figure 5b) it's shown an additional peak of an ester group at 1731cm^{-1}. This indicates the presence of MMA unit in the grafted bagasse and provides strong evidence of grafting.

Thermal Analysis

The thermal behavior of bagasse and MMA grafted bagasse are examined through TGA curves. In case of ungrafted sample, thermal degradation peak from DTG is at 392 °C and TGA shows the maximum decomposition temperature was 401 °C, but with grafted bagasse it's shown that thermal degradation peak from DTG is at

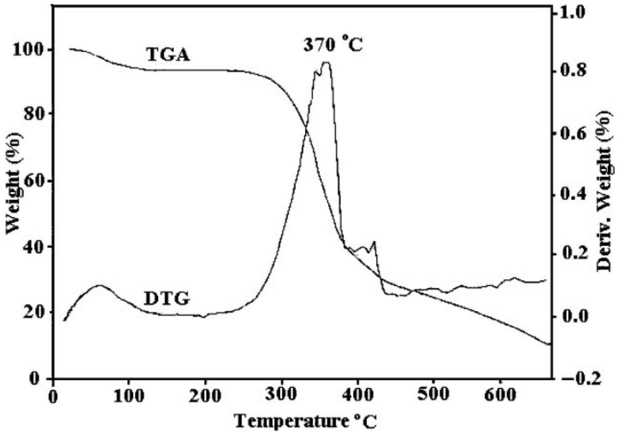

Figure 7.
TGA and DTG curves of MMA grafted bagasse.

370 °C, however TGA shows for 71, 96, 109 and 113% gross yield, the maximum decomposition temperatures of 430, 450, 458, and 462 °C were noted. It is evident from this analysis that the thermal stability of grafted bagasse is more than that of nongrafted. Figure 6 is the continuos weight loss curve for thermal degradation of 12.924 mg of nongrafted bagasse from 20 to 650 °C. Decomposition was observed to begin at 40 °C and become very rapid at 300 °C and the maximum weight loss occurred at 401 °C.

Figure 7 shows the thermal degradation of 11.618 mg of MMA-grafted bagasse sample from 30 to 650 °C. Decomposition begins slowly at 40 °C and becomes rapid at 250 °C. The reaction was complete at 462 °C and resulted in the maximum weight loss.

Conclusion

Grafting of methyl methacrylate onto bagasse in an aqueous medium is a process which is far from simple in view of the heterogeneity of the system and multi constituent nature of fabrics. Ceric ammonium nitrate can effectively initiate graft copolymerization of MMA onto bagasse at ambient temperature. Grafting percent can be adjusted by varying reaction parameters. The spectroscopic data confirm that the grafting of MMA onto bagasse has occurred. Thermal analysis data show that the grafted samples are more thermally stable than nongrafted samples, considering the maximum decomposition temperature. It may be ascribed to additional chemical bonds introduced into the molecule during the grafting process.

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