

Preparation, Characterization, and Some Physical Properties of Polypropylene/Poly(methyl acrylate)-Grafted Glass Wool Composites

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ABSTRACT: Polypropylene/poly(methyl acrylate)-grafted glass wool (PMA-g-GW) mixes were prepared. The polymerization process was carried out using potassium persulfate (PPS) and PPS/acetone sodium bisulfite (ASBS) as a redox-pair initiation system at 60 and 70°C. The effect of using PPS or PPS/ASBS on the grafting percent and conversion percent reveals that the conversion percent values on using PPS as an initiator are higher than those of PPS/ASBS, while in the case of grafting, the inverse is true, that is, using PPS as an initiator gives grafting percent values lower than

those that can be obtained using PPS/ASBS. The dielectric properties, thermal diffusivity, specific heat capacity, and thermal conductivity of PP loaded with modified glass wool as a function of different types and concentrations of initiators—used in the grafting polymerization process, namely, PPS and the redox initiating system—were also studied. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 723–732, 2003

Key words: glass wool; composites; permittivity; conversion; grafting

INTRODUCTION

It is well known that the mechanical, thermal, and electrical properties of composite materials containing glass fiber are lowered when the cohesion between the glass fiber and the matrix is incomplete.¹ To enhance the particle compatibility, surface modification of these particles can be carried out. This can be achieved in many ways: Among them is grafting a monomer onto glass fiber. With these grafted glass fibers, it may be possible to correct defects of the composite materials and also to improve the mechanical properties.² Generally, the surface properties are the most important in determining the quality of the finished material.³ It is known, for example, that a solid formed from a liquid can engulf or reject the fine dispersed particles depending on the surface energy of the particles and the matrix.⁴

There is, nowadays, an increasing demand for polymeric materials with high thermal and electrical insulation properties. This has been done through filling polymers with some inorganic fillers of high thermal and electrical insulation properties such as long or short glass fibers or using glass spheres as in the work

of Donald and Chen.⁵ Glass wool (GW) fiber has found popularity in thermal and electrical insulation and, also, in processed glass wool fiber is used as a filler in thermoplastic applications.

Recently,⁶ it was found that the mechanical properties of some prepared polypropylene (PP) composites showed that the tensile strength of PP loaded with GWs is lower than that loaded with unmodified or grafted GW, while both the elongation percent and the hardness values of PP/GWs are remarkably higher than those obtained in the case of the other PP composites. Also, it was found that the conversion percent and the grafting percent of poly(methyl acrylate) (PMA) onto the GW surface increase with an increasing initiator concentration. While modifying the GW surface by adsorption of stearic acid, it was found that the adsorption of stearic acid is high at small values of equilibrium concentrations and two distinct plateau regions were observed.

In this study, GW fibers were grafted with methyl acrylate (MA) using emulsifier-free emulsion polymerization. The effects of the grafting reaction conditions, such as the type of initiator and its concentration, temperature, and presence of different amounts of GW in the reaction mixture, were studied. PP/PMA-grafted GW (PMA-g-GW) mixes were prepared. The thermal and electrical properties of the prepared PP composites were studied.

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EXPERIMENTAL

GW and reagents

GW is a product of the Iron and Steel Co. (Helwan, Egypt). Its fiber size distribution and chemical analysis were given elsewhere.⁶ The MA monomer (stabilized with 14 ppm hydroquinone) and potassium persulfate (PPS), ethanol, and methanol were provided by Merck (Schuchardt, Germany). MA was redistilled before use and stored at -20°C . Sodium bisulfite and acetone were products of the El-Naser Pharmaceutical Chemical Co. (Cairo, Egypt). Benzene was a product of S.D. Fine Chem. Ltd. (England). Acetone sodium bisulfite (ASBS) was prepared as described previously.⁷

Washing of GW

GW was ground using a mortar and washed thoroughly with distilled water several times, filtered, and dried in an electric oven at 105°C .

Grafting polymerization of MA onto GW

The following ingredients were mixed in a 500-mL flask: water, the initiator, GW, and, finally, the MA monomer. The polymerization reactions were carried out at the required temperature ($\pm 1^{\circ}\text{C}$) in an automatically controlled water bath. To study the effect of the initiator concentration on the physical properties, different amounts of the initiator, 6.67, 13.3, 20.0, 26.6, and 33.3×10^{-3} mol/L of PPS, and of the redox initiator system (PPS/ASBS), 6.67/13.3, 13.3/26.6, 20.0/40.0, 26.6/53.3, and $33.3/66.6 \times 10^{-3}$ mol/L, were used. To study the influence of the GW concentrations on the polymerization process of MA, different weights of GW, 1, 5, 10, 30, and 50 g, were added. The amount of the grafted polymer is usually taken as the increase in weight after solvent-extraction of the homopolymer and drying. The percent grafting is defined as the ratio of the increase in weight to the initial fiber weight as follows:

$$\% \text{ Grafting} = \left[\frac{\text{final fiber composite weight} - \text{initial fiber weight}}{\text{initial fiber weight}} \right] \times 100$$

All experiments were run with mechanical stirring at 500 rpm. This speed is in the range where the agitation has no noticeable effect on the rate of polymerization.⁸ Since the composition of the materials in the reaction vessel is known, the conversion percentage of the monomer to the polymer is easily calculated. The purification and precipitation of the polymer were done by the method described by Grassie.⁹

Extraction of homopolymer (PMA) by Soxhlet technique

The prepared PMA composite was incompletely dissolved in its good solvent (benzene). This is due to the

grafting reaction which occurred for PMA onto GW. For this reason, the Soxhlet-extraction experiments were carried out to separate the homopolymer (MA) from the grafted one.

Morphology investigations

Samples were sputtered with gold film and investigated with a scanning electron microscope type JSMK.20 SEM from JEOP.

Preparation of polypropylene/PMA-g-GW composites

PP was melted first in a plasticorder (C.W. Brabender Model 0426/PE) at 180°C for 3 min. Before the addition of the filler (either PMA-g-GW or GW modified with stearic acid), a rotating speed was maintained at 70 rpm for 8 min for a well-blended composite. Each compounding was compressed at 300 kg/cm^2 for 5 min at a temperature of 190°C . It was then cooled under compression for another 5 min. Sheets of 1-mm thickness were made in this way and were used for measuring the electrical and thermal properties.

Thermal properties

For measurements of the thermal diffusivity and specific heat capacity and deducing the thermal conductivity of the solids, the flash method was used:

$$\lambda = \alpha \rho C_p$$

where λ is the thermal conductivity; α , the thermal diffusivity; C_p , the specific heat; and ρ , a constant.

RESULTS AND DISCUSSION

The MA monomer was polymerized in an aqueous medium in the presence of GW. The polymerization process was carried out using PPS and PPS/ASBS as the redox-pair initiation system at 60 and 70°C .

Grafting polymerization of MA using PPS as initiator

The grafting polymerization of MA in the presence of GW using PPS of different concentrations as an initiator, the conversion percent of the monomer to the polymer, and the grafting percent are illustrated graphically in Figures 1 and 2. From the figures, it is obvious that the conversion of the monomer to polymer increases by increasing the initiator concentration. This agrees well with the results obtained previously.^{10,11} Also, it is clear that the grafting percentage increases with increasing initiator concentrations to

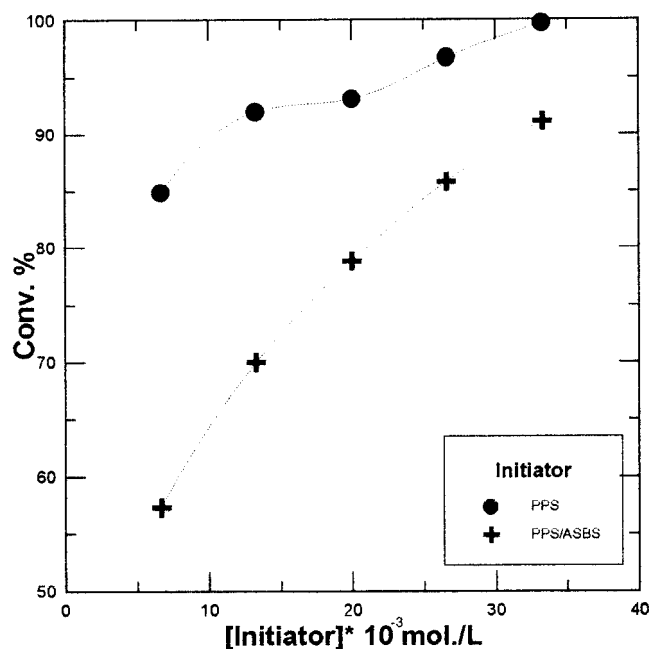


Figure 1 Conversion % of MA versus initiator concentrations.

13.3 × 10⁻³ mol/L, then decreases, that is, an optimum initiator concentration exists.

Grafting polymerization of MA onto GW using PPS/ASBS as redox initiation system

The effect of using PPS/ASBS as the redox initiation system on the grafting polymerization process of MA onto GW at 70°C was investigated and the values of the grafting percent and conversion percent are given in Figures 1 and 2. From Figure 1, it is clear that the conversion percent increases by increasing the concentration of the redox initiation system, while the grafting percent is decreased.

The effect of using PPS or PPS/ASBS on the grafting percent and conversion percent is illustrated in Figures 1 and 2, which reveal that the conversion percent values on using PPS as an initiator are higher than those of PPS/ASBS, while in the case of grafting, the inverse is true, that is, using PPS as an initiator gives grafting percent values lower than those that can be obtained using PPS/ASBS.

Effect of temperature

The grafting polymerization of MA was carried out using PPS/ASBS as a redox-pair initiation system in the presence of GW at different temperatures. From Figures 3 and 4, the conversion of the monomer to polymer increased by increasing the redox initiation system at both 60 and 70°C. Also, the grafting percent increased to an initiator concentration of 13.3/26.6 × 10⁻³ mol/L then decreased. By matching the values

of the conversion percent obtained at both 60 and 70°C, it was found that the conversions obtained at 60°C are higher than are those obtained at 70°C. This may be due to the hosting effect of GW to the cations of the redox initiator at higher temperatures, which, in turn, decreases the generation of free radicals.¹¹

On the other hand, from Figure 4, it is obvious that, with increasing temperature from 60 to 70°C, the percentage of grafting increases and this is in accordance with the work of Stannett et al.¹² and Dzedziela and Wiesielowska.¹³ This may be due to several reasons: First, this may be due to the increased activity of the initiating free radicals at high temperatures. Second, this may be due to the increase in the activation energy at high temperature. As a result of the increase in the activation energy, the swellability of the fibers, the solubility of the monomer, and its diffusion rate from the solution phase to the fiber phase increases, thus increasing the grafting yield. Generally, the same behavior of the grafting percent as a function of the initiator concentration can be seen. This assures the suggestion of the presence of an optimum initiator concentration.

Effect of GW amount

The effect of the GW amount on the polymerization of MA was investigated at 70°C using different concentrations of PPS/ASBS as the redox-pair initiation system. The results of the grafting percent and the conversion percent are illustrated graphically in Figures 5 and 6.

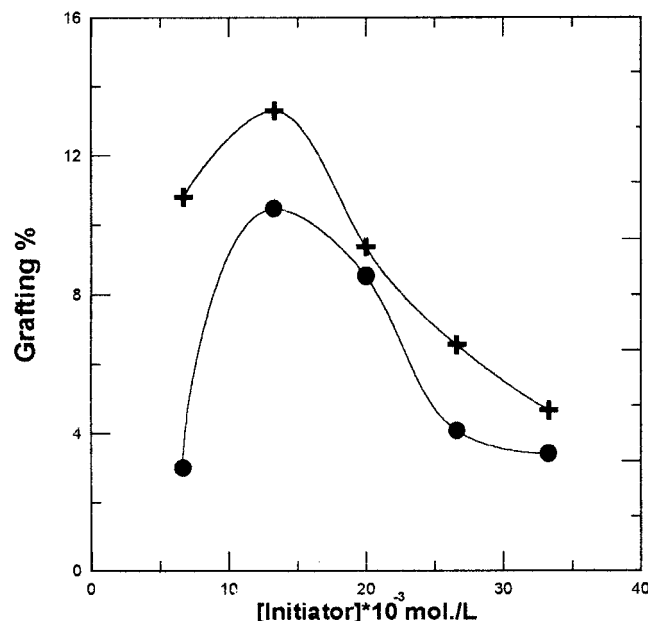


Figure 2 Grafting % of MA onto GW versus initiator concentrations.

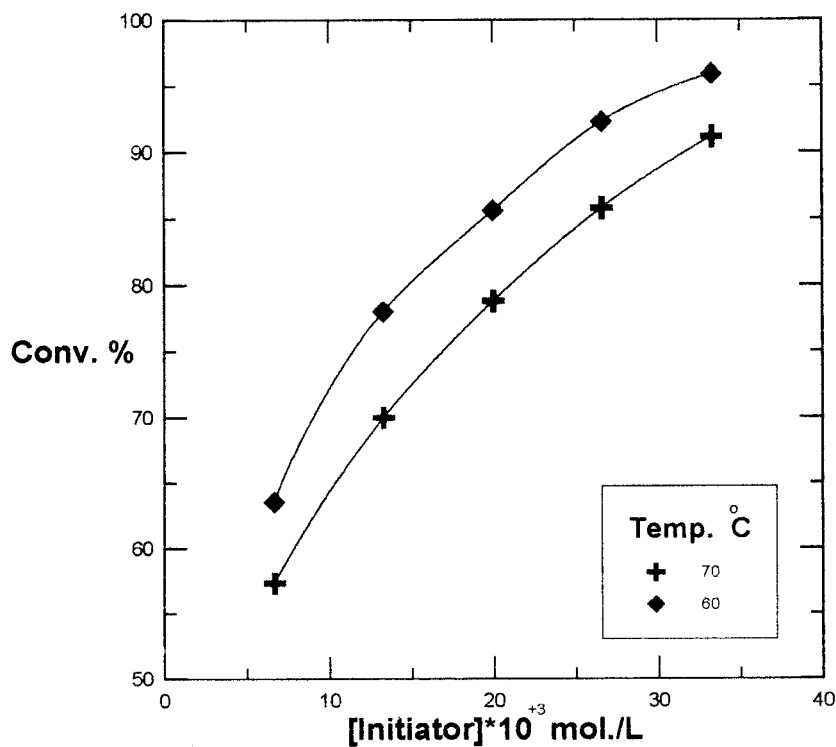


Figure 3 Conversion % versus initiator concentrations at different temperatures.

From Figure 5, it is clear that, at a very low amount of GW (1 g), the grafting percent and conversion percent (Fig. 6) are very high due to the catalytic effect of

GW at low amounts. It could be concluded that the high amounts of GW reduces both the grafting percent and the conversion percent. This could be attributed to

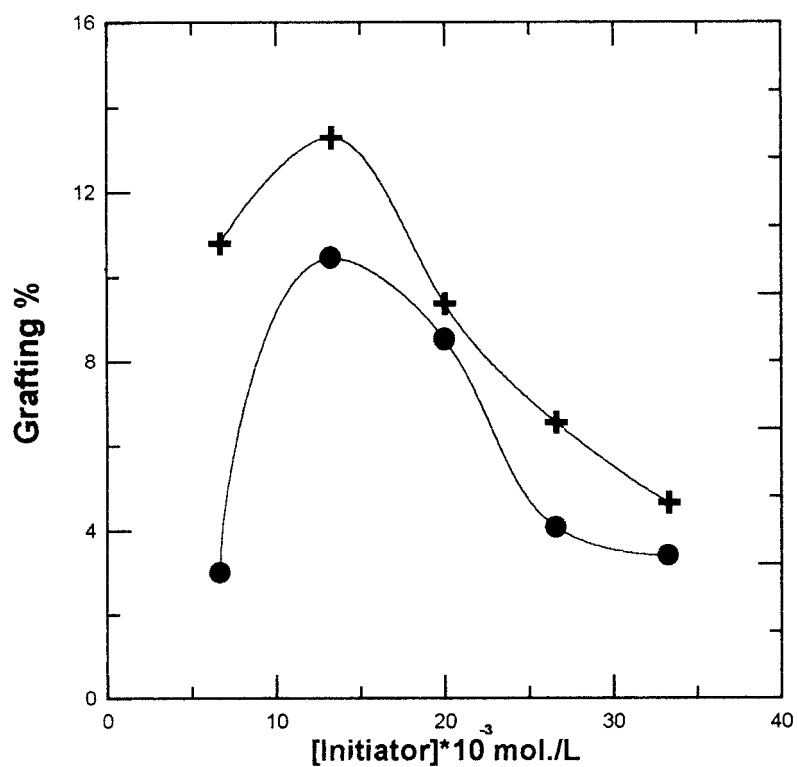


Figure 4 Grafting % versus initiator concentrations at different temperatures.

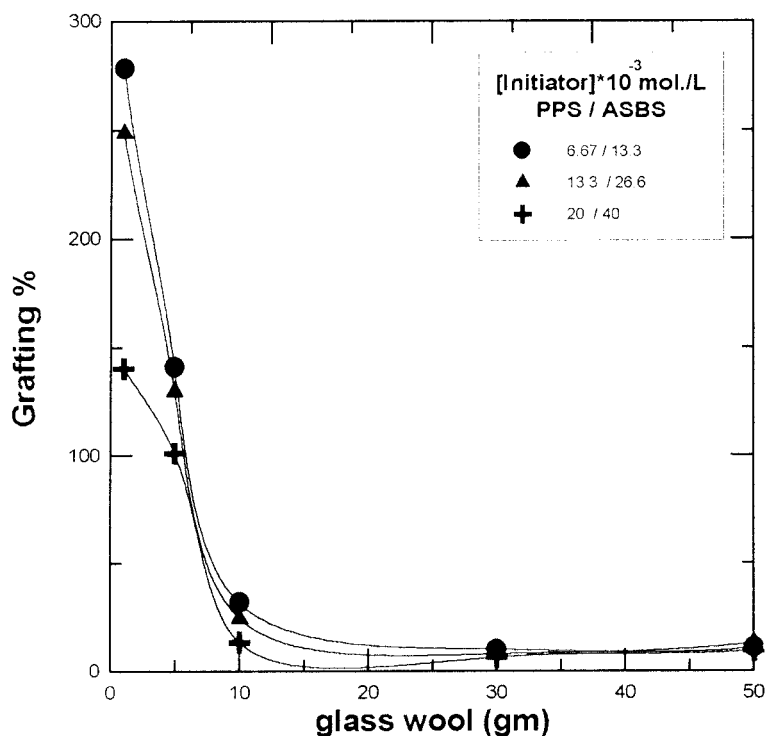


Figure 5 Grafting % of MA onto GW versus GW amount at different redox initiator concentrations.

the poisoning effect offered by GW to the formed radicals, which are responsible for producing monomeric growing radicals.

The effect of the redox initiation system concentration was studied on both the grafting percent of MA onto GW of different amounts and the conversion

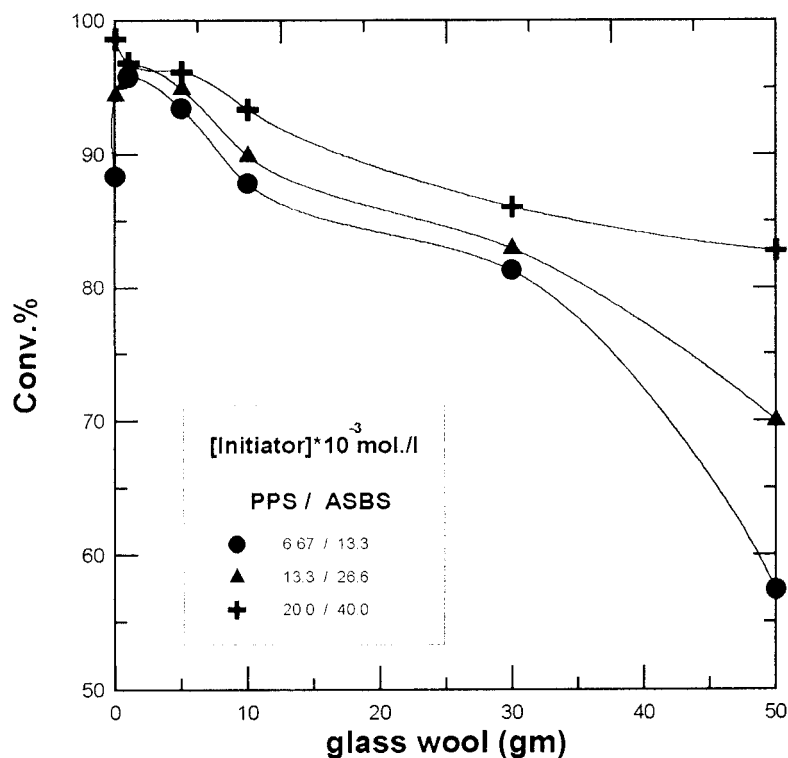


Figure 6 Conversion % of MA obtained at different GW amounts using different redox initiator concentrations.

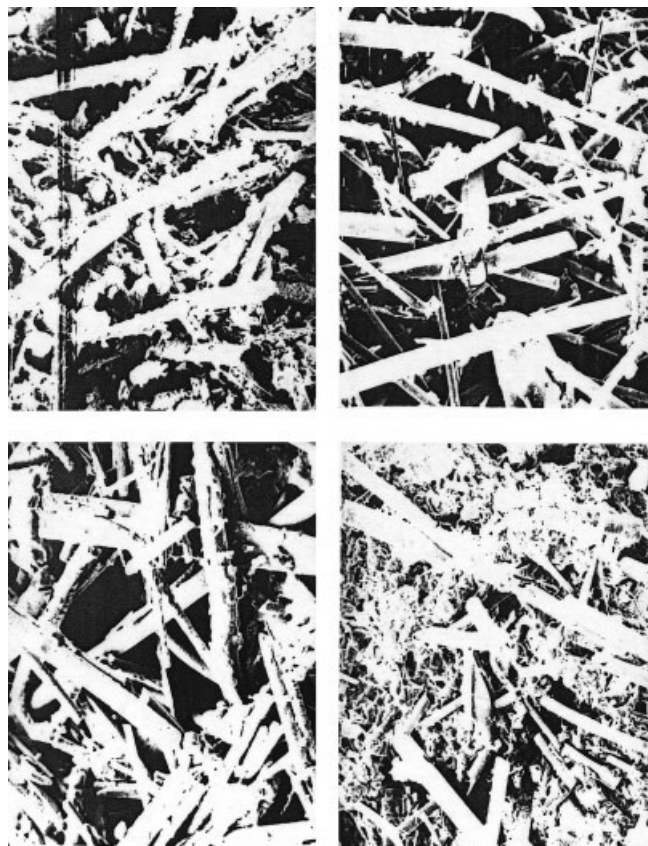


Figure 7 Scanning electron micrographs ($\times 150$) of (a) pure GW-grafted with PMA, (b) grafting % = 32, (c) grafting % = 10, and (d) grafting % = 11.

percent of the monomer to polymer. The previously mentioned figures reveal that the grafting percent decreases with increasing of the redox initiation system, while the conversion increases.

Morphological study of GW grafted with PMA

The morphological study was carried out for some selected samples of GW grafted with PMA. The micrographs presented show the change of the grafting percentage with an increasing amount of GW. Figure 7 shows scanning electron micrographs of GW with different grafting percentages. It is clear that the untreated GW fibers are completely separate from each other; otherwise, in the case of the GW-grafted fibers, aggregates of PMA can be noticed on the GW fibers, which is good evidence for the formation of grafts of PMA onto the GW surface. The observed aggregates in the micrographs depend on the grafting percentage and, consequently, on the amount of the GW present.

Thermal properties

Effect of modification process and amount of GW

Figures 8 and 9 represent the dependence of the thermal properties, such as the thermal diffusivity, α , the

specific heat, C_p , and thermal conductivity, λ , on the amounts of unmodified and modified GW. It is clear; from Figures 8(a) and 9(a), that the incorporation of GW (unmodified or modified) into the polymer matrix increases the thermal diffusivity of the polymer at all percentages over the blank one (without filler). Also, the thermal diffusivity increases with an increasing GW content. The increase in the α values was not a simple arithmetic average of the thermal diffusivity of GW ($\alpha_{\text{exp}} = 22.6 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$) and that for the PP matrix ($7.2 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$). In such cases, at all concentrations, the polymer matrix apparently isolates the GW particles and maintains an appreciable temperature resistance. In addition, the α of PP films loaded with unmodified GW almost have higher values.¹⁴ This may be attributed to the noncoating surface particles rather than to the modified ones.

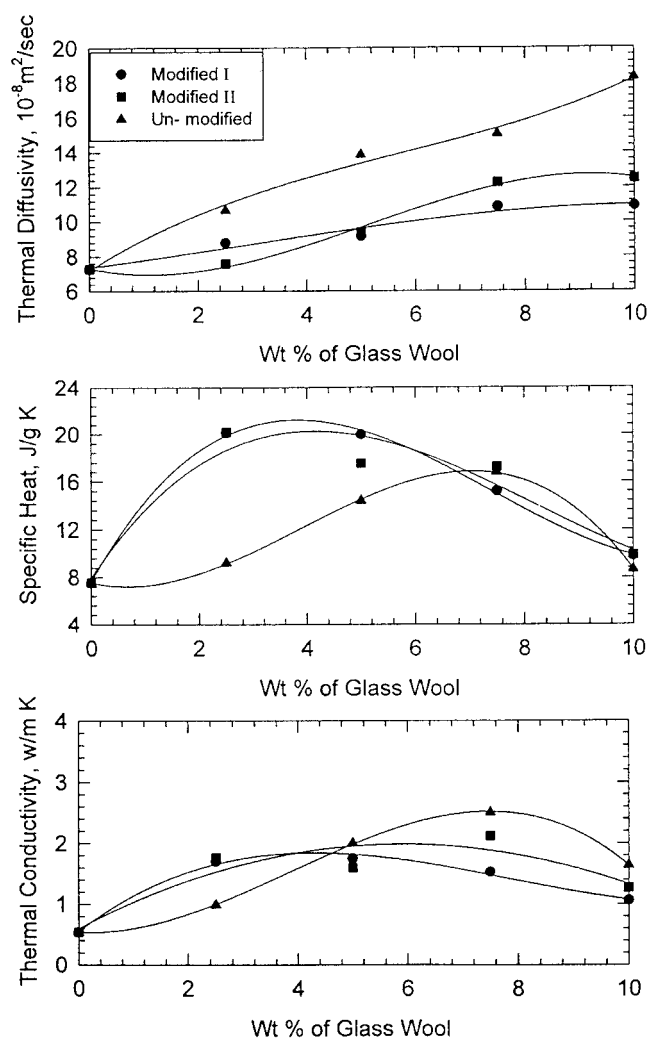


Figure 8 Thermal properties of PP composites versus weight percent of GW: (●) PP filled with grafted GW prepared using $6.6 \times 10^{-3} \text{ mol/L}$ PPS as initiator; (■) PP filled with grafted GW prepared using $13.3 \times 10^{-3} \text{ mol/L}$ PPS as initiator; (▲) PP filled with unmodified GW.

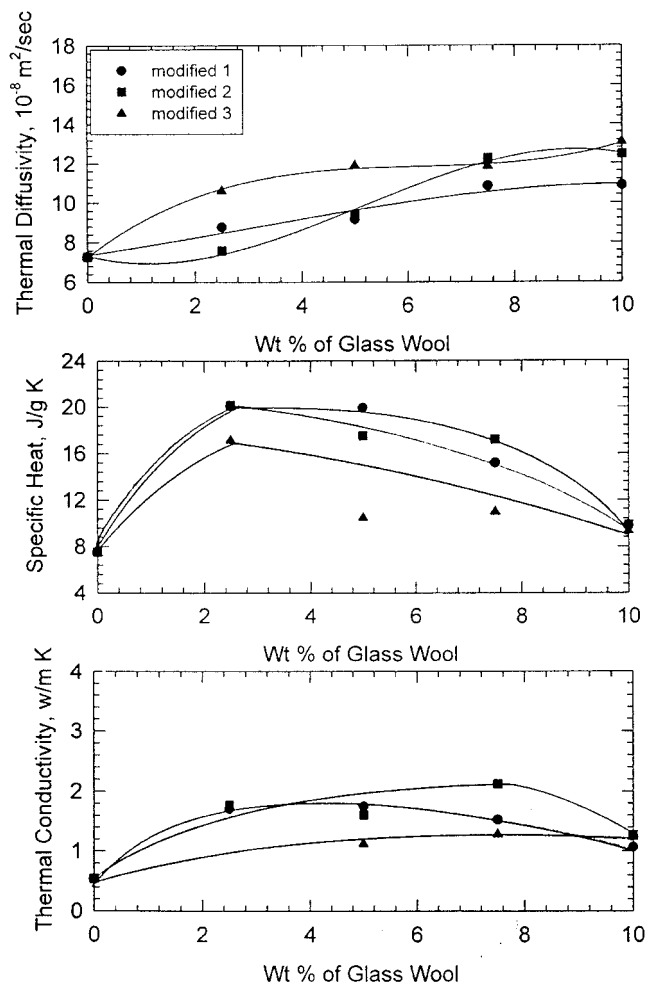


Figure 9 Thermal properties of PP composite sheets loaded with modified GW against weight percent of GW: (●) PP loaded with PMA-g-GW prepared using 6.6×10^{-3} mol/L PPS as initiator; (■) PP loaded with PMA-g-GW prepared using 13.3×10^{-3} mol/L PPS as initiator; (▲) PP loaded with PMA-g-GW using $6.6/13.3 \times 10^{-3}$ mol/L PPS/ASBS as redox initiator.

The heat capacity, C_p , is one of the most basic characteristics of matter. The information obtained from C_p is fundamental to the overall thermodynamics description of matter.¹⁵ From the C_p , one can derive other thermodynamic functions such as the entropy and thus obtain information on the flexibility and conformational ordering of polymers. The ability to reliably predict C_p plays an important role in heat insulation.

Figures 8(b) and 9(b) show the specific C_p of PP, loaded with different amounts of unmodified and modified GW. It is obvious that C_p first increases by increasing GW up to 5 wt % for modified GW and 7.5 wt % for unmodified GW and then decreases. The thermal conductivity, as a function of GW content curves, Figures 8(c) and 9(c), has the same undulatory behavior.

Debye¹⁶ postulated that thermal excitation products quantized elastic waves or lattice vibrations called

phonons. Resistance to heat flow is explained by phonon scattering at lattice imperfections or other inhomogeneties. Intramolecular energy transfer is more efficient than is intermolecular transfer since less phonon scattering is expected through covalent bonds than in the van der Waals type. Tightness of the bonds or arrangement of the molecules thus promotes λ .¹⁷ The increase in λ at low concentrations of GW is because the materials with higher thermal diffusivity usually have a higher thermal conductivity.¹⁸

Effect of the type and concentration of initiator

Figure 10 illustrates the thermal diffusivity, specific heat capacity, and thermal conductivity of PP loaded with 10% GW as a function of different types and concentrations of the initiators, namely, PPS and the redox initiating system. It is clear from this figure that the thermal properties slightly decrease by increasing the PPS concentration, while there is no detectable

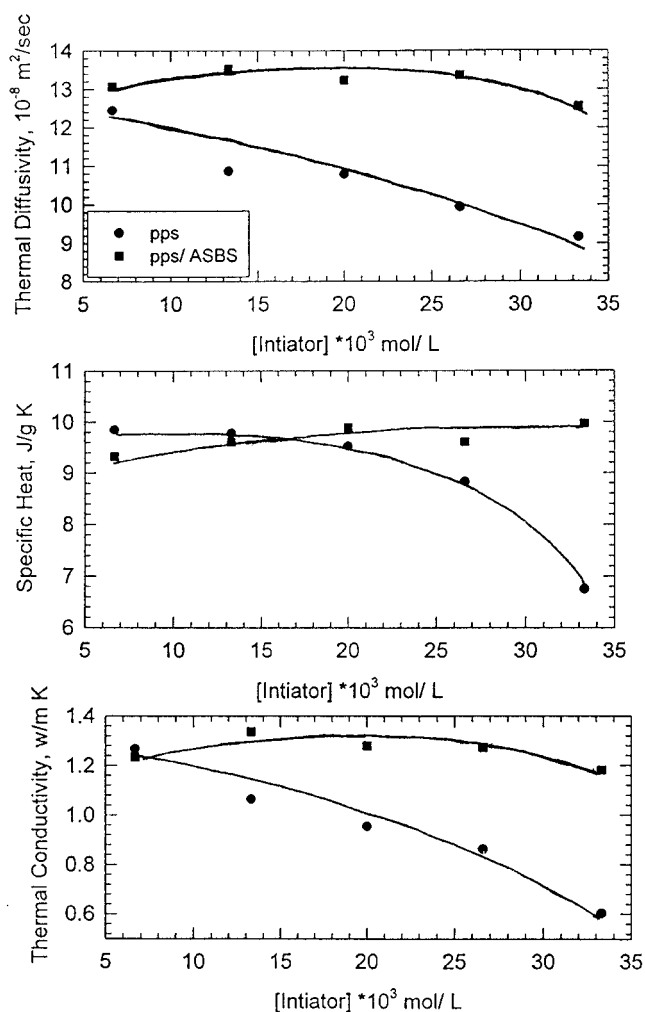
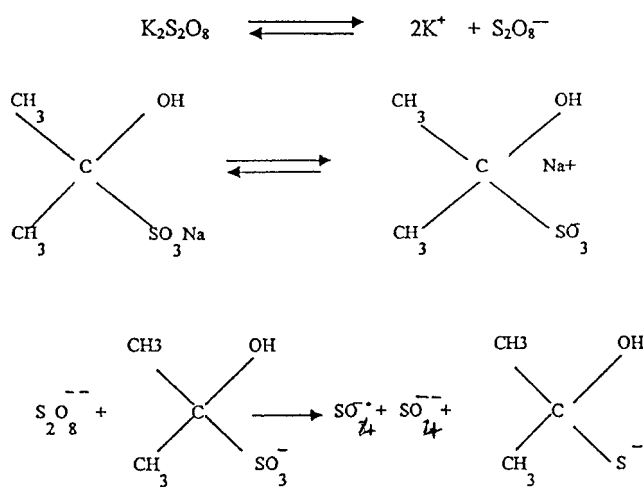


Figure 10 Thermal properties of PP composite sheets loaded with grafted GW using different types and initiator concentrations.



Scheme 1

effect of an increasing redox concentration. This may be due to the adsorbing effect of PMA to the SO_4 and SO_4 ions, which were generated from the initiation step as shown in the equations in Scheme 1. Consequently, phonon scattering takes place at the particle interface more than in the other samples (i.e., initiated by PPS); thus, a larger number of particles for the same volume in the case of those prepared by using PPS would bring about lower a thermal diffusivity α and heat capacitance C_p , and, consequently, affect the thermal conductivity λ , since $\lambda = \rho\alpha C_p$.

Effect of γ -radiation on the thermal properties

Organic compounds are sensitive to radiation by virtue of the irreversible chemical processes which take place when covalent bonds, in this case, C—C and C—H bonds, are excited or ionized by irradiation. The effect of radiation on polymers depends on whether irradiation is carried out in open air or in a vacuum, in the solid or in the liquid state, as well as in the presence or in the absence of additives. The most important chemical changes that irradiation produces in polymers are crosslinking, degradation, gas formation, changes in unsaturation (the formation of various types of double bonds between carbon atoms), crystallization, and oxidation. As a rule, crosslinking and degradation occur simultaneously. However, the ratio of their rates depends on the chemical structure of the polymer, its physical state, and the irradiation conditions.¹⁹ Polymers are generally divided into those that, predominately crosslink and those that predominately degrade.²⁰

The PP composites, which are loaded with 10 wt % unmodified and modified GW with MA using PPS and PPS/ASBS as different initiation systems, were selected according to their good thermal insulation, to study the effect of γ -radiation on the thermal insula-

tion of the irradiated composites. Figure 11 illustrates the dependence of the thermal conductivity for the previously mentioned samples on the γ -dose in the range 0–300 kGy. It is clear that the crosslinking process takes place for all samples loaded with modified GW to 200 kGy and to 100 kGy for composites loaded with unmodified GW. Consequently, the values of thermal conductivity (λ) for these composites increases in this range of γ -doses. Moreover, at γ -doses greater than 200 kGy, degradation takes place.

In regard to PP composites loaded with modified GW, the change in the initiating systems has a clear effect on the thermal conductivity of the irradiated samples. From Figure 11, it is obvious that samples loaded with modified GW prepared using PPS/ASBS as the initiator have a thermal conductivity higher than those prepared using PPS as the initiator at the same irradiation dose (200 kGy). This can be attributed to the presence of free ions and radicals in the terminated polymer chains ($\text{SO}_4^{\cdot-}$, SO_4 , and HSO_3), which are responsible for the thermal conductivity. The amount of these free ions are high in the case of using the redox initiation system rather than using PPS as the initiator.

The irradiation process increases the crosslinking density, which, in turn, increases the transmittance of the thermal vibration owing to the initial decrease in the distance between the molecular lattices. This conclusion is also supported by studying the effect of

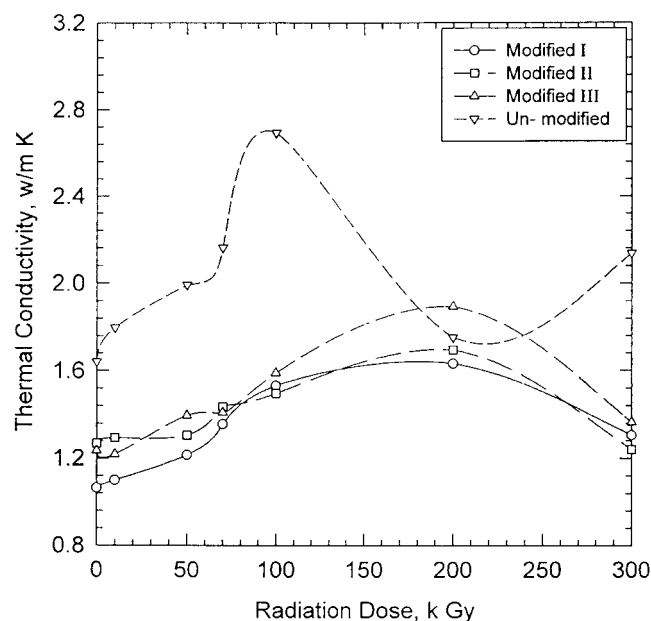


Figure 11 Thermal conductivity (w/mk) of some selected PP composite sheets versus radiation dose (kGy): (—○—) PP loaded with PMA-g-GW prepared using 6.6×10^{-3} mol/L PPS as initiator; (—□—) PP loaded with PMA-g-GW prepared using 13.3×10^{-3} mol/L PPS as initiator; (—△—) PP loaded with PMA-g-GW using $6.6/13.3 \times 10^{-3}$ mol/L PPS/ASBS as redox initiator; (—▽—) PP loaded with unmodified GW.

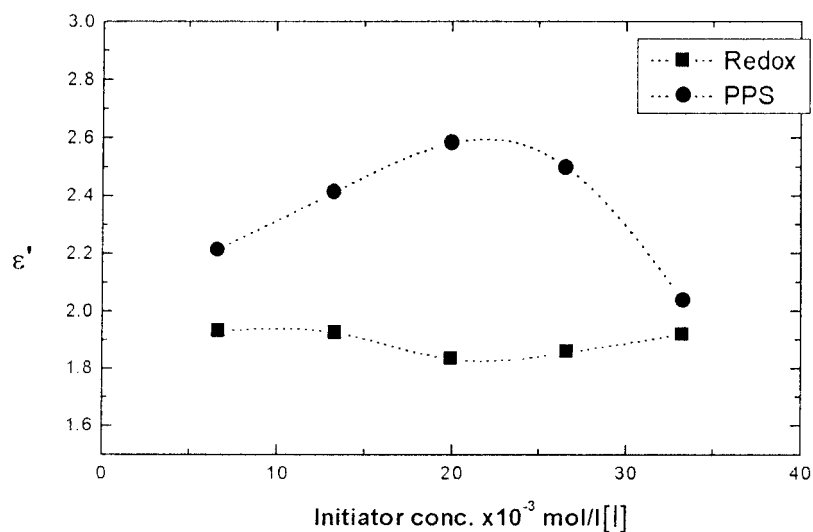


Figure 12 Permittivity ϵ' of PP/grafted GW using different types and initiator concentrations: (■) PPS/ASBA as redox system; (●) PPS as initiator.

irradiation on the thermal properties of polymer composites.²¹

Dielectric properties

Effect of the type and concentration of initiator

Figure 12 illustrates the permittivity, at 1 kHz of PP sheets loaded with 10% modified GW, against the concentrations of the types of two different types of initiator systems, PPS and the redox initiator. It is clear from the figure that there is a peaklike behavior in the case of composites prepared using PPS as the initiator. The permittivity values in the case of using PPS are higher than those obtained in the case of using the redox initiator system for all concentrations. On the

other hand, there is no detectable effect of the redox initiation system concentration on the permittivity values of the PP composites.

Effect of grafting

ϵ' values of PP sheets loaded with 10% by weight of modified GW as a function of the PMA grafting percent are shown in Figure 13. It is clear that ϵ' increases gradually by increasing the grafting percent. There is a maximum at 32%, then, the curve decreases again. The lowest value is at 141% grafting.

CONCLUSIONS

It can be concluded that using the PP/ASBS as the redox-pair initiation system gives a grafting percent

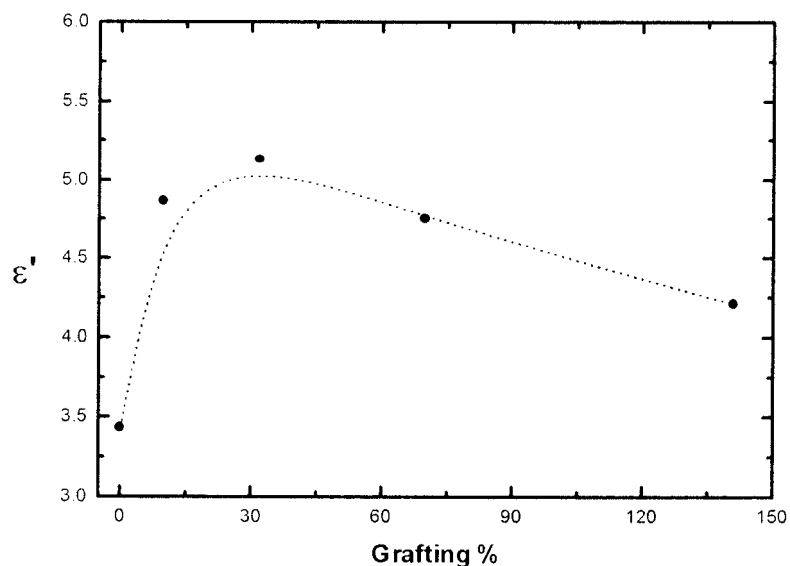


Figure 13 Permittivity ϵ' of PP/grafted GW composites versus grafting percent.

higher than that obtained using PPS alone as an initiator in the grafting polymerization process of MA. Also, increasing the temperature from 60 to 70°C increases the percentage of grafting. The presence of high amounts of GW decreases both grafting percent and conversion percent of MA into PMA. The thermal and electrical conductivity measurements of the investigated PP composites showed that using PPS as an initiator in the grafting polymerization process of MA onto GW decreases both the thermal and electrical conductivity more than in the use of PPS/ASBS as redox initiation system.

On studying the effect of γ radiation on the thermal conductivity of the PP composites, which are loaded with 10 wt % of unmodified and modified GW with PMA using PPS and PPS/ASBS as different initiation systems, the results showed that thermal conductivity of PP/unmodified GW increases with an increasing dose radiation up to 100 kGy and then decreases, while the thermal conductivity of PP/modified GW increases up to 200 kGy.

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