

Effect of Surface Modification of Glass Wool on the Mechanical and Electrical Properties of Polypropylene/Modified Glass-Wool Composites

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ABSTRACT: The surface of glass wool (GW) was modified by two different methods, either by grafting methyl acrylate (MA) onto GW in the presence of potassium persulfate (PPS) as initiator, or by adsorbing stearic acid (SA) as surface active agent onto the GW surface. It was found that conversion and grafting yield of poly(methyl acrylate) (PMA) onto the GW surface increased with increasing initiator concentration, whereas by modifying the GW surface by adsorption of SA, the adsorption of SA was found to be high at small values of equilibrium concentrations and two distinct plateau regions were observed. Mechanical and electrical properties of polypropylene (PP) sheets loaded with modified GW were measured. The obtained data showed that the presence of PMA as grafted polymer onto the GW surface has a plasticizing effect on the prepared PP composites. On the other hand, SA, as a surface modifier for GW, acts as a reinforcing agent for the formed PP composites, which have very good dielectric properties. From the obtained results, one can deduce that the prepared PP/GW composites have promising dielectric properties. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1061–1069, 2002

Key words: glass wool; polypropylene; permittivity; dielectric loss; grafting yield; surface modification

INTRODUCTION

In recent years, advances have been made with thermoplastics reinforced with short glass and other special fibers. These composites are very attractive commercially because they can be processed using rapid fabrication techniques such as compression molding. Apart from the necessity of ensuring that the fiber length and orientation are carefully controlled in the molded component, it is also well known that the nature of the fiber–matrix interface plays a vital role in influencing

composite properties.¹ Surface modification can be accomplished by surface polymerization, surface polymer grafting, or surface treatment by some surface-active agents.^{2–5} It is well known that the structure and properties of the three-component composites depend on component properties: the characteristics of each component, miscibility, and processing conditions. For three-component systems such as PP–elastomer–filler, mutual compatibility and adhesion of the components are the crucial factors influencing structure and properties.⁶ A designed microstructure can be obtained only by controlled processing conditions with well-controlled interfaces between the various components. Any modification changing this relationship will lead to a significant struc-

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Table I Glass-Wool Fiber Diameter Distribution

Grain Size (μm)	Weight Percentage
-1000 + 500	28.22
-500 + 250	20.46
-250 + 125	26.89
-125	24.43

ture, and consequently, a change in properties. Glass-wool (GW) fiber is an insulating fiber that is used primarily as raw material in the manufacture of acoustic ceiling tiles. The fiber has found popularity in thermal and electrical insulation. Processed glass-wool fiber is used as a filler reinforcer in phenolic molding and thermoplastic applications. The aim of the present work is to study the surface treatment of glass wool by grafting of methyl acrylate or by adsorption technique. Some polypropylene/modified glass-wool mixes were prepared. The effect of the presence of glass wool on the mechanical, physical, and electrical properties of the prepared composites was the focus of this investigation.

EXPERIMENTAL

Materials

Methyl acrylate (MA) monomer (stabilized with 14 ppm hydroquinone), redistilled before use and stored at -20°C . Benzene was a product of S.D. Fine Chemicals (UK). Cyclohexane was a product of Adwic, Prolabo Co. (France). Potassium persulfate (PPS), ethanol, and methanol were provided by Merck (Schuchardt, Germany). All water used was purified by distillation. Potassium hydroxide was a product of Aldrich Chemical Co. (Gillingham, Dorset, UK). Stearic acid used was supplied by Transporting and Engineering Company (TRANCo, Alexandria, Egypt). Polypropylene isotactic homopolymer was a product of Hyundai (Seoul, Korea) with melt-flow index = 8 g/10 min grade H3401.

The glass wool was supplied by the Iron and Steel Co. (Helwan, Egypt). Mesh size distribution is given in Table I.

Chemical analysis of two different batches of glass wool is given in Table II. Wet chemical methods were used for determination of the various constituents.

Grafting Polymerization of MA onto Glass Wool Using PPS as Initiator

MA monomer was polymerized in an aqueous medium in the presence of glass-wool fiber and PPS as initiator. The polymerization reactions were carried out at 70°C in a thermostatically controlled water bath. The amount of grafted polymers is usually taken as the increase in weight after solvent extraction of homopolymer and drying. The grafting yield (%) is defined as the ratio of the increase in weight to the initial fiber weight as follows:

Grafting yield(%)

$$= \frac{\text{Final GW fiber weight} - \text{Initial GW fiber weight}}{\text{Initial GW fiber weight}} \times 100$$

Surface Modification of GW with Stearic Acid

Using the method described previously,⁷ an adsorption isotherm can be drawn. From the isotherm, it is clear that the plateau at equilibrium concentration 0.018 mol/L is formed, which occurs at monolayer surface coverage. Glass wool was immersed in stearic acid solution (0.03 mol/L) for 48 h. The modified GW of known adsorbed amount (from the adsorption isotherm = 0.06×10^{-3} mol/g) was separated by filtration.

Mechanical Properties

Tensile strength (TS), which is defined as the applied force per unit area of the original cross-

Table II Chemical Analysis of Two Different Batches of Glass Wool

Constituent	First Batch	Second Batch
SiO ₂	30–35%	36.44%
CaO	34–38%	37.63%
Al ₂ O ₃	11–14%	10.92%
MgO	3.5%	4.55%
BaO	4.9%	—
FeO	0.7–1.2%	—
Mg	1.5–3%	—
S	1.23%	—
Na ₂ O	1–1.5%	0.82%
K ₂ O	0.2–0.5%	0.66%
SO ₃	—	1.92%
L.O.I.	—	0.16%
Moisture	—	0.04%
Cu ppm	—	86

Table III Grafting Polymerization of MA (19.08 g) onto Glass Wool (50 g) Using PPS of Different Concentrations as Initiator System at 70°C

Concentration of PPS ($\times 10^3$ mol/L)	Conversion (%)	Grafting Yield (%)
6.67	85	1.2
13.3	92	8
20.0	93	7
26.6	97	3
33.3	99	2

sectional area at the moment of the rupture of the specimen) and elongation at break, for the prepared PP/GW composites, were measured by a Zwick 1425 testing machine, speed at 50 mm/min. Hardness was measured by using an HT 2004 hardness tester as described in DIN 53 456.

Electrical Properties

Measurements of the permittivity (ϵ') and dielectric loss (ϵ'') for the investigated samples were carried out in the frequency range 100 Hz to 100 kHz using LCR-meter digital bridge-type AG-4311B (Ando, Japan). A Q-meter-type TF 1245A with an oscillator-type TF 1246 was used for the measurements at frequencies above 100 kHz.

RESULTS AND DISCUSSION

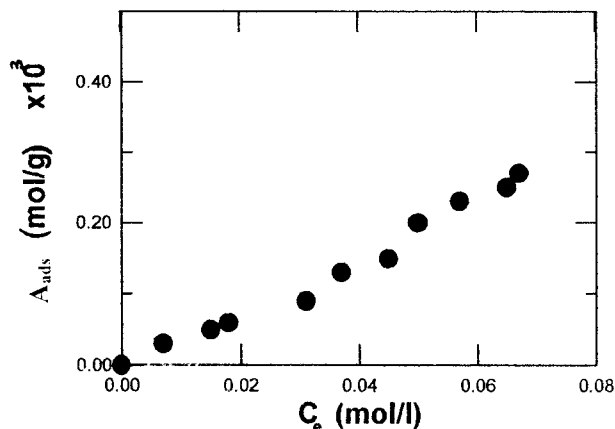
Surface Modification of GW Using Grafting Polymerization of Methyl Acrylate

The grafting polymerization of MA (19.08 g) in the presence of GW (50 g) using PPS of different concentrations as initiator, the conversion of monomer to polymer, and the grafting yields are given in Table III, from which it is obvious that the conversion of monomer to polymer increases by increasing initiator concentration. This agrees with the results obtained previously.^{8,9} Also, it is clear that the grafting percentage increases with increasing initiator concentrations up to 13.3×10^{-3} mol/L, then decreases (i.e., an optimum initiator concentration exists).

Surface Modification of GW Through Adsorption of Stearic Acid

Adsorption Isotherm

The adsorption isotherm was determined by calculation of the adsorbed amount (A_{ads}) with the

**Figure 1** Adsorption isotherm of stearic acid from cyclohexane on GW.

equilibrium concentrations C_e . The results are shown in Figure 1. From the figure it can be detected that the adsorption of stearic acid from cyclohexane on the glass-wool surface appears to increase with time up to 48 h, after which there is no change in the adsorbed amount with time.

The adsorption isotherm was determined at room temperature using an initial concentration C_0 in the range of $1-10 \times 10^{-2}$ mol/L. The adsorption of stearic acid on the GW surface is high at small amounts of equilibrium concentrations C_e , and two distinct plateau regions are observed on the isotherm; there is a small plateau at the low equilibrium concentration of 0.018 mol/L, and the second plateau starts at 0.057 mol/L C_e . Table IV

Table IV Adsorption Isotherm of Stearic Acid on GW Surface and Its Sedimentation Properties as a Function of Initial (C_0) and Equilibrium Concentrations (C_e) of Stearic Acid in mol/L

C_0 (mol/L)	C_e (mol/L)	Adsorbed Amount ($\times 10^3$ mol/g)	Sedimentation Volume (mL)
0.10	0.067	0.27	1.600
0.09	0.065	0.25	1.600
0.08	0.057	0.23	1.605
0.07	0.050	0.20	1.607
0.06	0.045	0.15	1.605
0.05	0.037	0.13	1.600
0.04	0.031	0.09	1.600
0.03	0.018	0.06	1.570
0.02	0.015	0.05	1.570
0.01	0.007	0.03	1.590
Blank	0.000	0.00	1.800

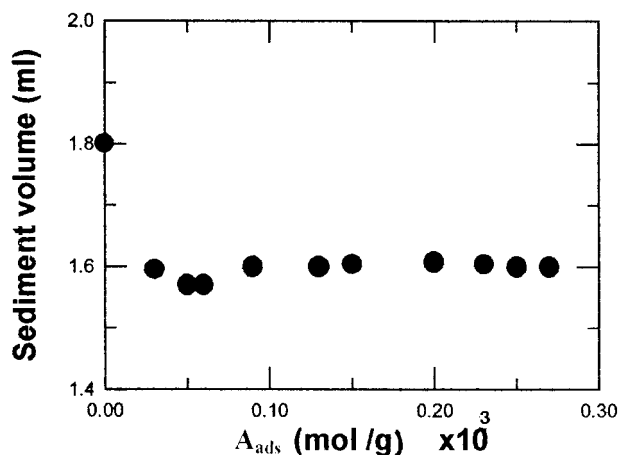


Figure 2 Sedimentation properties of GW in nonpolar medium (cyclohexane) in the presence of stearic acid.

shows C_0 , C_e , A_{ads} , and S_v (sedimentation volume) of stearic acid on the GW surface as a function of the equilibrium concentration.

The first plateau was observed at an adsorbed amount of 6×10^{-5} mol/g, then the adsorption increases with C_e up to 23×10^{-5} mol/g to form the second plateau, which means that the isotherm formed from two distinct steps.

Sedimentation Properties

The sedimentation properties of GW in nonpolar medium (cyclohexane) depend on the amount of water present; therefore, GW was oven-dried at 105°C. The change of S_v of GW in cyclohexane with A_{ads} is given in Table IV and shown graphically in Figure 2. From the figure, it is clear that the presence of 0.03 mol/L initial concentration of stearic acid is sufficient to reduce the sediment volume of GW from 1.8 to 1.59 mL. Generally, there is no change in the S_v with increasing A_{ads} . From the figure it can also be detected that the minimum S_v was obtained at an adsorbed amount of 6×10^{-5} mol/g, which is related to formation of the first layer in the adsorption isotherm; furthermore, this generates the formation of monolayer surface coverage from the stearic acid on the GW surface. Increasing the adsorption isotherm over that of the monolayer surface coverage has no influence on the sediment volume.

Mechanical Properties

Mechanical Properties of PP/Unmodified and PP/Modified GW Composites

Figure 3 shows the mechanical properties of PP filled with different weight percentages of unmod-

ified and modified GW. It is clear that both the PP/unmodified and PP/modified GW composites undergo a decrease in the tensile strength (TS) of PP sheets compared to that of the unfilled PP, as shown in Figure 3(a). Also, the TS decreases with increasing GW %, which is the same for PP filled with either unmodified or modified GW.

Figure 3(b) shows that elongation at break ($E\%$) clearly decreases in the case of PP sheets filled with modified GW than in the unfilled PP sheets. The values of $E\%$ are not affected by increasing the weight percentage of modified GW. Also, from this figure, one can see that, at small wt % values of unmodified GW (2.5 wt %), the $E\%$ of filled PP is smaller than that for the unfilled PP. At higher weight percentage, $E\%$ increases with increasing unmodified GW wt %.

The hardness H (in $\text{N/mm}^2 = \text{MPa}$) of PP, loaded with unmodified and modified GW, decreases by increasing glass wool wt %, as noticed in Figure 3(c). Also, it is clearly shown that the hardness values of PP/modified GW composites are relatively higher than those obtained for unmodified composites over the range of glass-wool concentrations under consideration. There is no detectable change in H values for PP/unmodified GW composites by increasing GW wt %.

Mechanical Properties of PP Sheets Loaded with GW Modified by Stearic Acid (PP/GWs)

Table V shows the mechanical properties of PP filled with GW modified at the monolayer surface coverage from the adsorption isotherm. From the table, it is clear that the presence of glass wool modified with stearic acid in PP sheet composites decreases the TS compared with that obtained for pure PP. This is because the existence of stearic acid in the composite will produce an interface between the matrix and the filler, which in turn reduces the TS. Moreover, TS is not affected by increasing the amount of modified GW in the prepared composites.

In addition, Table V shows that the TS of PP composites was found to be 288 (kg/cm^2) at 2.5 wt % for GWs and 310 (kg/cm^2) for composites containing 10 wt % GWs. The elongation values of the prepared PP sheets loaded with GWs are also given in Table IV. The presence of modified GWs increases the $E\%$ of PP sheets over that of the PP sheet alone, whereas by increasing the weight percentage of GWs in PP composites the $E\%$ increased only slightly.

The values of the hardness of the prepared PP sheets are also presented in Table V and Figure 3.

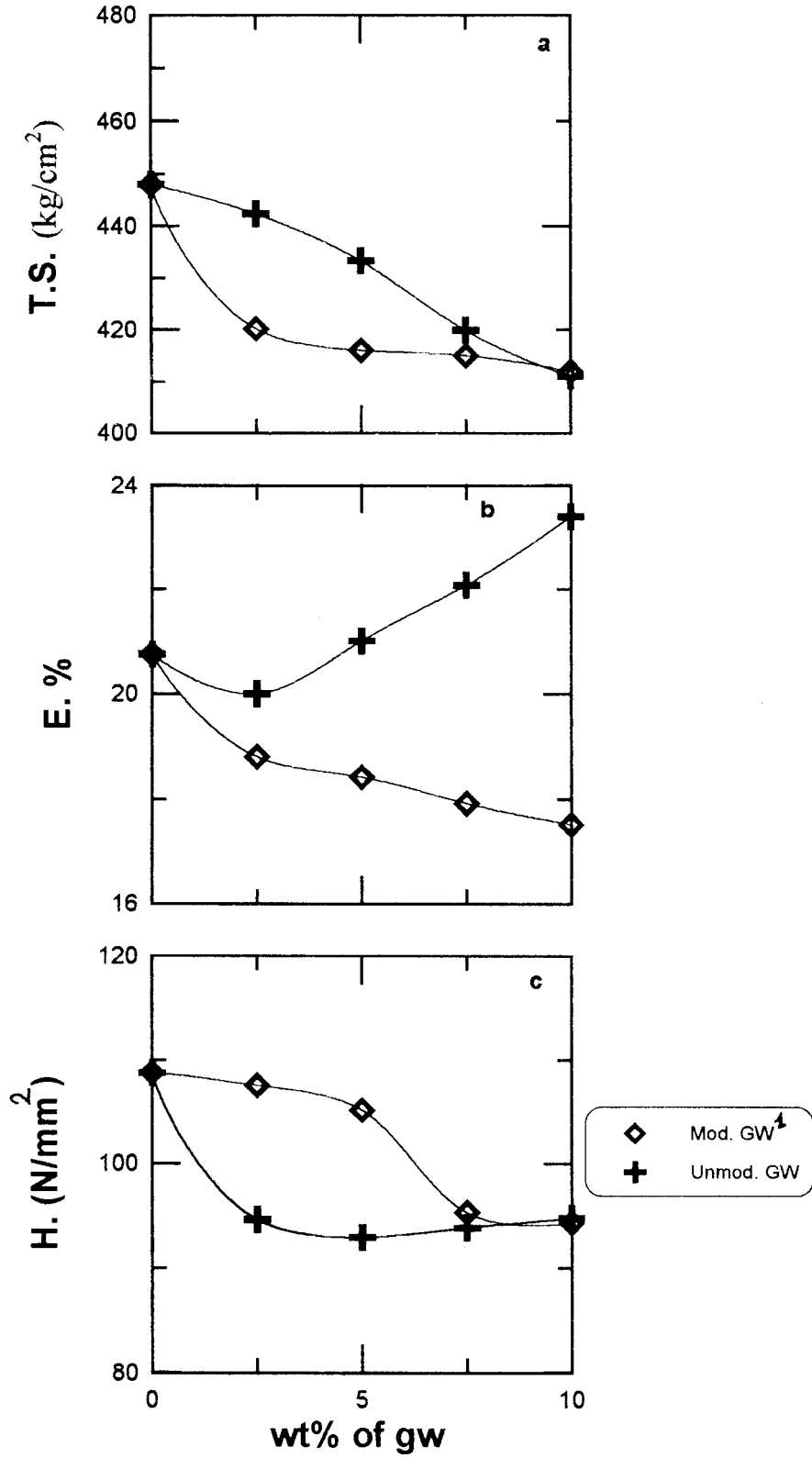


Figure 3 Mechanical properties of PP/GW composites versus unmodified and modified GW (different wt %).

Table V Mechanical Properties of PP Sheets Loaded with Glass Wool Modified by Stearic Acid

GW (wt %)	PP (wt %)	Mechanical Properties ^a		
		TS (kg/cm ²)	<i>E</i> (%)	<i>H</i> (N/mm ²)
0	100.0	450	21	108.7
2.5	97.5	288	27	479
5.0	95.0	290	29	450
7.5	92.5	306	38	436
10.0	90.0	310	40	408

^a TS, tensile strength; *E*, elongation at break; *H*, hardness.

It is obvious that the hardness of the PP composites containing GWs are higher than that of the pure PP sheets. Also, *H* decreased with increasing GW wt %.

Effect of Surface Treatment of GW on Mechanical Properties of PP Composites

Surface modification of fibers is widely used and thoroughly studied nowadays, whereas the effect of the modification of interfacial structure in the filler containing polymers has not yet been described.^{10–13} The effect of interfacial parameters and modified interphase on the mechanical properties has been demonstrated and even calculated, mainly in the case of unoriented filled polymers,^{14–16} but the orientation process modified by an interfacial layer has still not been studied thoroughly.

In the three-component PP–GW–modifier systems, the structure and properties depend on component properties, the characteristics of each component compatibility, and processing conditions. It should also be realized that the distribution of fillers is the key factor affecting microstructure. In the present work we have two systems: (1) PP–GW modified by stearic acid and (2) PP/PMA-*g*-GW. In both of these three-component systems we notice that the mechanical properties of PP/GWs composites are completely different from those of PP/PMA-*g*-GW. Tensile strength values of PP/GWs composites are lower than those of PP/PMA-*g*-GW, whereas *E*% values of PP/GWs were clearly higher than those of PP/PMA-*g*-GW. Although it is known that filler decreases *E*%, there are many examples of increasing *E*% when small amounts of rigid filler are used.¹⁷ In the case of higher filler content, above

5% by weight, the matrix is restricted in its ability to provide strength between packed particles and the particles that do not wet, and bond well to the matrix, causing cavitation. Smaller particles at lower concentrations are freer to move within the matrix and, correspondingly, the matrix is freer to provide strength around them. The viscous drag of small particles with good adhesion to the matrix can then produce an apparent strength and higher elongation.¹⁸ In the core-shell structure, the GW was covered by stearic acid and the interface between the filler and the matrix was improved. This will result in an increase in the *E*%.

The results show that the values of hardness of both PP composites are clearly higher in the case of PP loaded with GWs than in those of PP loaded with PMA-*g*-GW. This can be explained by the fact that the presence of a surface-active agent such as stearic acid increases wetting of filler particle surfaces by polymer molecules.¹⁹ Also, stearic acid with a polar group of –COOH can easily produce hydrogen bonding in PP matrices and can form ionic bonding with GW. This would reinforce the formed composite and hence increase the hardness.²⁰

Dielectric and Electrical Properties

Measurements of dielectric properties over a wide range of frequency characterize the electrical properties of a material in terms of: (1) the dispersion of the permittivity and (2) the loss factor frequency behavior, which may be further analyzed to give information on the dielectric and the dc conduction behavior.

Dc Resistivity

The dc resistivity for the investigated composites was measured using a high-impedance electrometer (Keithley 6517; Keithley Metrabyte, Taunton, MA). The values were too high to be detected, even at higher temperatures up to 180°C, given that the instrument measures only up to 10¹⁷ Ω cm⁻¹. This reflects the excellent electrical insulation properties for the prepared PP composites.

Dielectric Measurements

The dissipation factor tan δ was still too small to be detectable over the used frequency range (10²–10⁶ Hz). This means that there is perfect storage of the electric response. In that manner, there is

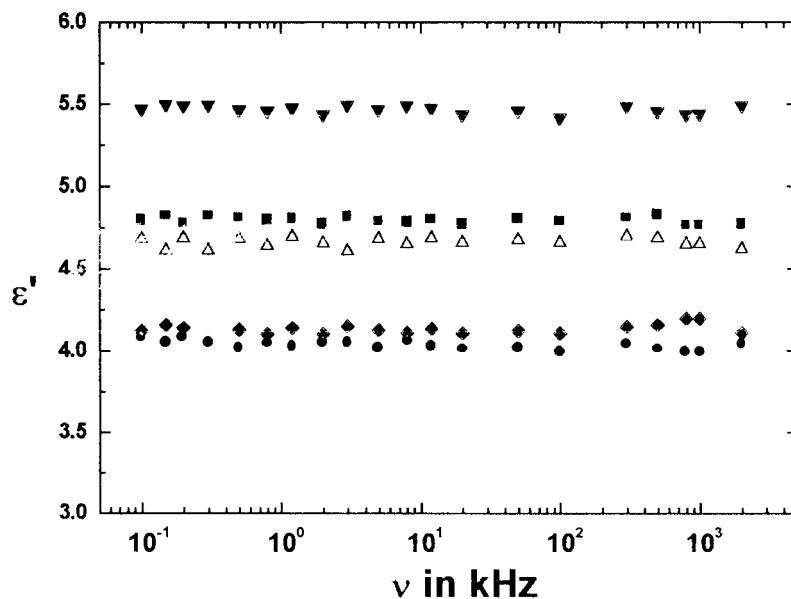


Figure 4 Permittivity ϵ' against frequency ν (in kHz) for some selected PP composite samples: ■, PP blank; ●, PP loaded with 5 wt % PMA-g-GW prepared by using 13.3×10^{-3} mol/L PPS as initiator; △, PP loaded with 7.5 wt % PMA-g-GW prepared by using 6.6×10^{-3} mol/L PPS as initiator; ▼, PP loaded with 10 wt % PMA-g-GW prepared by using 33.3×10^{-3} mol/L PPS as initiator; ◆, PP loaded with 2.5 wt % unmodified GW.

no detectable influence of the temperature, until about 180°C, on the dissipation factor. This means that the imaginary part of the complex permittivity ϵ'' equals zero over the whole range of frequency and temperature under consideration, given that $\tan \delta = \epsilon''/\epsilon'$. This finding is not unreasonable and is in good agreement with the electrical properties, given that $\epsilon'' = \sigma/\omega\epsilon_0$, where σ is

the conductivity and $\omega (=2\pi\nu)$ is the angular frequency.

Dielectric Properties of PP Loaded with PMA-g-GW

The measured dielectric constant ϵ' values of some randomly chosen PP composite sheets are

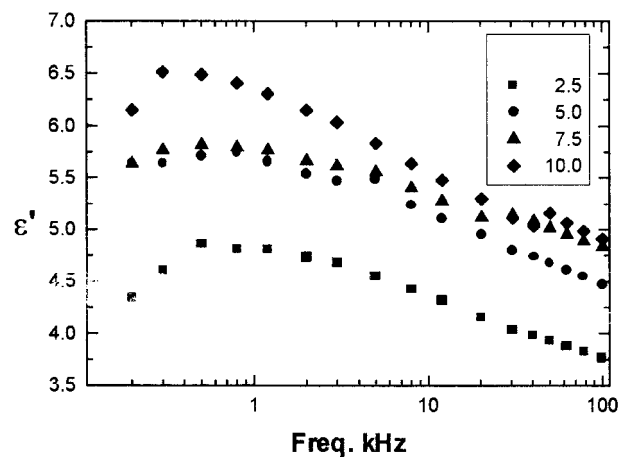


Figure 5 Permittivity ϵ' against frequency of PP/GWs composites at different weight percentages of GWs.

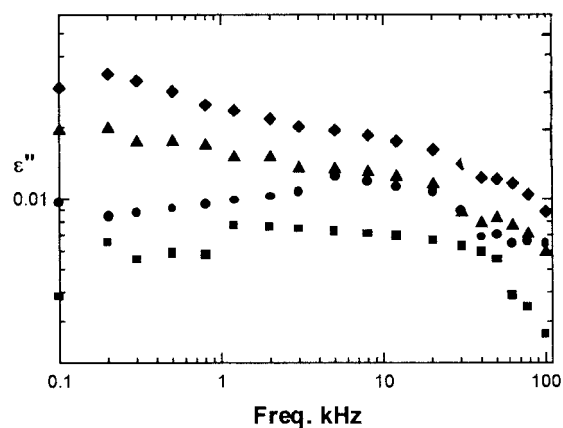


Figure 6 Dielectric loss ϵ'' against frequency of PP/GWs composites at different weight percentages of GWs (notations are the same as in Fig. 5).

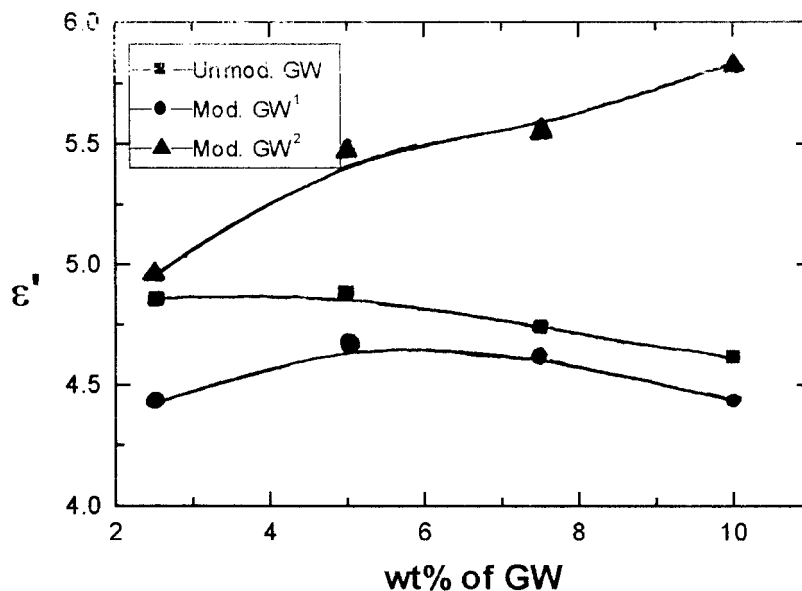


Figure 7 Permittivity ϵ' against GW wt % for PP composites loaded with unmodified GW, GW¹ (grafted with PMA), and GW² (modified with stearic acid).

illustrated graphically in Figure 4 as a function of frequency, in the range of 10^2 – 10^6 Hz. It could be concluded that permittivity of the composites under investigation is influenced by modification of the GW filler, or its amounts in the prepared composites, but not by frequency. This reflects the stability of the dielectric properties, which can be improved, over the range of frequency under consideration.

Dielectric Properties of PP Filled with GWs

Figure 5 shows the permittivity ϵ' as a function of frequency for the PP filled with GW, at different concentrations (wt %), modified with stearic acid as surface-active agent. It is clear from the figure that the polar group of stearic acid $-\text{COOH}$ plays a distinct role in the dielectric properties. There is a peak at about 300 Hz for all GW amounts. Its height increases with increasing the GW amount, whereas its position is not affected. Above the peak position frequency, a gradual decrease of ϵ' with increasing frequency is noticed, which could be associated with the polarization of the polar group.

The creation of polarity was followed by a detectable value of the dielectric loss ϵ'' . The dielectric spectra $\epsilon''(\nu)$, as shown in Figure 6, seem to be too complicated to be analyzed as a superposition of more than one microdynamic process. ϵ'' also

gradually increases with increasing GW concentration.

Effect of Using Different Types of Surface Modifiers

The dielectric constant ϵ' , at 1 kHz as spot frequency point, was measured for PP/unmodified and PP/modified glass-wool composites. Figure 7 shows that ϵ' increases gradually by increasing the amount of both unmodified and modified GW in PP sheets up to 4 wt %, after which it decreases again. This suggests that there is an optimum concentration of filler, either treated or untreated, at which ϵ' has its maximum value, which in turn reflects the best dielectric properties. Moreover, it is obvious from Figure 7 that the values of ϵ' for PP/modified GW composites are generally lower than those of PP/unmodified GW sheets. This may suggest the presence of unbound modifier.

The 1-kHz permittivity values of the PP samples filled with GW modified by stearic acid (GWs) were added in Figure 7. It is clear from the figure that by increasing the amount of GWs (from 2.5 to 10 wt %) in the PP matrix, there is an increase of ϵ' . This reflects the presence of a higher number of polar groups with increasing the amount of GWs in the PP matrix. Furthermore, it can be noticed that the ϵ' values of PP/GWs composites

are generally higher than those in PP filled with unmodified GW or PP/grafted GW.

CONCLUSIONS

- Modifications of the glass-wool surface can be carried out, either by monomer grafting onto it or by adsorption of a surface-active agent onto its surface.
- Results showed that conversion of monomer into polymer increases by increasing initiator concentration, whereas the trend is not the same in the case of graft yield.
- By using stearic acid as surface modifier, from the adsorption isotherm, two distinct plateau regions can be noticed, which means that there is more than monolayer surface coverage.
- Results of mechanical properties of the prepared polypropylene composites showed that the tensile strength of PP loaded with GWs is lower than that loaded with unmodified or grafted GW, whereas both elongation and hardness values of PP/GWs composites are remarkably higher than those obtained in the case of the other PP composites.
- Dielectric measurements showed that PP/GWs composites have higher ϵ' values than those in PP/unmodified or grafted GW composites. This was attributed to the presence of polar groups in those composites.

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