

FUNȚIONALIZAREA FIBRELOR DE STICLĂ PENTRU OBTINEREA DE COMPOZITE PE BAZĂ DE POLIPROPILENĂ

FUNCTIONALIZATION OF GLASS FIBERS FOR OBTAINING POLYPROPYLENE BASED COMPOSITE MATERIALS

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In this paper, the technology for obtaining polypropylene (PP) based composite materials reinforced with functionalized glass fibers (GF) is described. In the first step, glass fibers were functionalized by hydrolysis/condensation with (3-aminopropyl) trimethoxysilane as functionalization agent and in the second step, these materials were compounded at 180°C in a Brabender mixer with isotactic polypropylene. The obtained composites were morphologically and structurally characterized by X ray diffraction (XRD), infrared spectroscopy (FT-IR), and scanning electron microscopy (SEM). Based on the obtained results it can be concluded that GF functionalization leads to a better glass fiber - polymer interaction, GF being covered by an intimate PP film.

În această lucrare, este descrisă tehnologia de obținere a unor compozite pe bază de polipropilenă armate cu fibre de sticlă (FS) funcționalizate. În prima etapă, fibrele de sticlă au fost funcționalizate prin hidroliză / condensare cu (3-aminopropil) trimetoxisilan ca agent de funcționalizare și apoi, în etapa a doua, aceste materiale au fost amestecate într-un malaxor Brabender la 180°C cu polipropilena izotactică. Compozitele obținute au fost caracterizate din punct de vedere morfologic și structural prin difracție de raze X, spectroscopie în infraroșu și microscopie electronică de baleiaj. Pe baza rezultatelor obținute se poate concluziona că funcționalizarea fibrelor de sticlă duce la o mai bună interacțiune fibră de sticlă - polimer, fibrele de sticlă fiind acoperite de un film de polipropilenă - PP.

Keywords: glass fibers, polymer composites, glass fibers functionalization

1. Introduction

Polymer composites reinforced with glass fibers are extensively used in many industrial applications because of their very good ratio between properties and costs [1]. The adhesion of the GF and polymer is usually poor, especially when aliphatic polymers are used. In order to improve the properties of the composite materials (especially the mechanical properties) the adhesion between the two phases must be improved. Based on the literature data, there are two chemical ways to improve the adhesion of the phases. In the first one, the surface of the GF can be modified with an organic agent that has a better compatibility with the polymer. In the second one, the polymer can be modified with proper agents. Table 1 present the most used agents used for GF functionalization.

Usually, the polymeric substrates are functionalized by grafting them with isocyanides, anhydrides and silanes [4,5] while the compatibilizing agents used for some of the most important polymers (PP, PE and PVC) are presented in Table 2. The silanisation is often used for the functionalization of a wide range of material

surfaces, from glass to ceramics such as GF, silica, alumina, hydroxyapatite, etc [6-14].

The compatibility of the two phases can be done by functionalizing at least one component, the introduced groups being responsible for the better interaction. The aim of this work was to modify the surface of glass fibers in order to improve their compatibility with isotactic polypropylene. For this purpose, glass fibers were functionalized with (3-aminopropyl)trimethoxysilane and further compounded with isotactic polypropylene.

2. Experimental

(3-Aminopropyl)trimethoxysilane (APTMS 97%, Sigma-Aldrich), isotactic polypropylene (PP Impact copolymer TIPPLEN K 948, Tiszai Vegyi Kombinat RT (TVK), Hungary) and borosilicate glass fibers E (L=4.5mm, d=13μm, Camelyaf Glass Fiber, Turkey) were used without any more purification.

The functionalization was done by spraying an acidic aqueous solution of APTMS (5%) onto the glass fibers and drying them at room temperature for 24h followed by drying at 80°C, overnight. The amount of used APTMS was 5% (w/w) relative to glass fibers.

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Table 1

Functionalization agents for GF / Agenți de funcționalizare pentru FS		Ref.
Non-functional Simple Silane	Alkyltrimethoxysilane (methyl, ethyl, propyl, ...) Phenyltrimethoxysilane Dimethyldichlorosilane Phenyltrichlorosilane	[2]
Functional Simple Silane	Vinyltrimethoxysilane Cyanoethyltrimethoxysilane 3-aminopropyl triethoxy silane - APTES 3-aminopropyl trimethoxy silane - APTMS Chloropropyltrimethoxysilane Mercaptopropyltrimethoxysilane Glycidoxypropyltrimethoxysilane γ-methacryloxypropyltrimethoxysilane	[2,3]
Functional Dipodal Silane	<div style="display: flex; justify-content: space-around;"> <div style="text-align: center;"> $\begin{array}{c} \text{NH} \\ / \quad \backslash \\ \text{CH}_2 \quad \text{CH}_2 \\ \quad \\ \text{CH}_2 \quad \text{CH}_2 \\ \quad \\ \text{CH}_2 \quad \text{CH}_2 \\ \quad \\ (\text{CH}_3\text{O})_3\text{Si} \quad \text{Si}(\text{OCH}_3)_3 \end{array}$ <p>SIB1833.0</p> </div> <div style="text-align: center;"> $\begin{array}{c} \text{NH}-\text{CH}_2-\text{CH}_2-\text{NH} \\ \quad \quad \quad \\ \text{CH}_2 \quad \quad \quad \text{CH}_2 \\ \quad \quad \quad \\ \text{CH}_2 \quad \quad \quad \text{CH}_2 \\ \quad \quad \quad \\ \text{CH}_2 \quad \quad \quad \text{CH}_2 \\ \quad \quad \quad \\ (\text{CH}_3\text{O})_3\text{Si} \quad \quad \quad \text{Si}(\text{OCH}_3)_3 \end{array}$ <p>SIB1834.0</p> </div> </div> <div style="display: flex; justify-content: space-around;"> <div style="text-align: center;"> $\begin{array}{c} \text{S}-\text{S} \\ / \quad \backslash \\ \text{CH}_2 \quad \text{CH}_2 \\ \quad \\ \text{CH}_2 \quad \text{CH}_2 \\ \quad \\ \text{CH}_2 \quad \text{CH}_2 \\ \quad \\ (\text{CH}_3\text{O})_3\text{Si} \quad \quad \quad \text{Si}(\text{OCH}_3)_3 \end{array}$ <p>SIB1824.6</p> </div> <div style="text-align: center;"> $\begin{array}{c} \text{H} \\ \backslash \\ (\text{EtO})_3\text{Si}-\text{C}=\text{C} \\ / \quad \quad \quad \backslash \\ \text{H} \quad \quad \quad \text{Si}(\text{OEt})_3 \end{array}$ <p>SB1820.0</p> </div> </div>	[3]
Non-Functional Dipodal Silane	<div style="display: flex; justify-content: space-around;"> <div style="text-align: center;"> $(\text{CH}_3\text{O})_3\text{Si}-\text{CH}_2-\text{CH}_2-\text{Si}(\text{OCH}_3)_3$ <p>SIB1817.0</p> </div> <div style="text-align: center;"> $(\text{CH}_3\text{O})_3\text{Si}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}(\text{OCH}_3)_3$ <p>SIB1824.0</p> </div> <div style="text-align: center;"> $(\text{CH}_3\text{O})_3\text{Si}-\text{CH}_2-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{CH}_2-\text{Si}(\text{OCH}_3)_3$ <p>SIB1831.0</p> </div> <div style="text-align: center;"> $\begin{array}{c} \text{C}_6\text{H}_{13} \\ \\ \text{Si}(\text{OMe})_3 \\ \\ \text{Si}(\text{OMe})_3 \end{array}$ <p>SIB1829.0</p> </div> </div>	[3]

Table 2

Most common polymers and their compatibilizer agent / Cei mai utilizați polimeri și agenții lor de compatibilizare

Polymer	Compatibilizer agent (examples)
Polypropylene	polypropylene grafted with maleic anhydride [15] polypropylene grafted with itaconic acid derivatives [16] maleic anhydride grafted polyethylene-octene elastomer [17]
Polyethylene	maleic anhydride - <i>grafted polyethylene</i> [18,19] acrylic acid - <i>grafted polyethylene</i> [19] glycidyl methacrylate - <i>grafted polyethylene</i> [19] itaconic acid - <i>grafted polyethylene</i> [19] oxazoline <i>grafted polyethylene</i> [20]
PVC	poly[methylene (polyphenyl isocyanate)] [4] toluene 2,4-diisocyanate [4] hexamethylene diisocyanate [4] ethyl isocyanate [4]

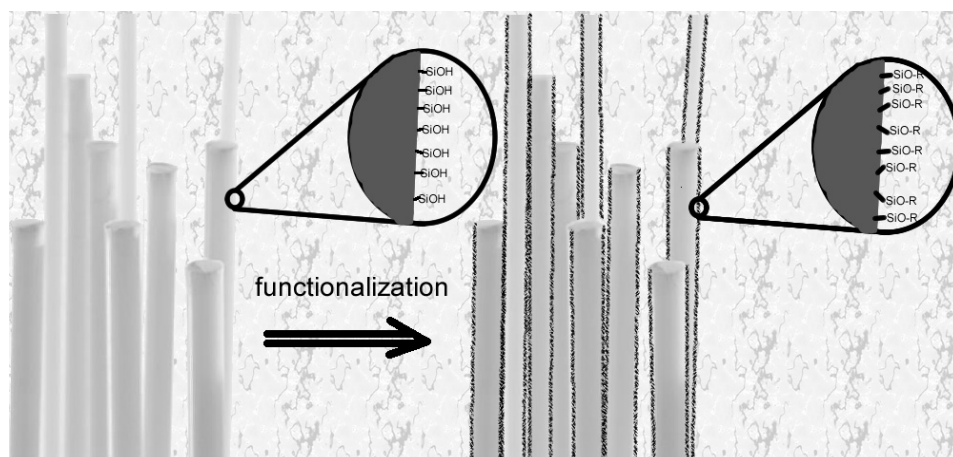


Fig.1 - Glass fiber functionalization by using siloxanes/Fibre de sticlă funcționalizată cu siloxani.

Schematically, the glass fiber functionalization is represented in Figure 1 and consists in partial or full transformation of Si-OH groups in Si-OR etheric groups [21].

Polymer composites reinforced with functionalized glass fibers were obtained in a Plasti-corder Brabender by compounding 30g GF, 100g PP, 1g dioctyl phthalate and 5g CaCO₃ and then further pressing the mixture at 175°C and 300kN. Once obtained, the samples were morphologically and structurally characterized by X-ray diffraction, Fourier transformed infrared spectroscopy, and scanning electron microscopy.

The functionalization of GF was studied with FTIR microscopy by using a Thermo iN10 MX FT-IR microscope operated in reflection mode. All the spectra were obtained in reflection mode, using a cooled imaging detector (MCT Array), and by co-adding 16 spectra at a spectral resolution of 8cm⁻¹ while the time of acquisition was 3 second/scan.

X-ray diffraction analysis was performed using a Shimadzu XRD 6000 diffractometer at room temperature. In all the cases, Cu-K_α radiation from a Cu X-ray tube (ran at 15mA and 30 kV) was used. The samples were scanned in the Bragg angle, 2θ range of 10 – 80°, with a sampling interval of 0.02.

SEM images were recorded on a HITACHI S2600N electron microscope coupled with an EDS detector, on samples covered with a very thin silver layer.

3. Results and discussion

3.1. X-ray diffraction

The XRD patterns of the obtained samples (PP/GF and PP/GF-APTMS) are similar as shown in Figure 2.

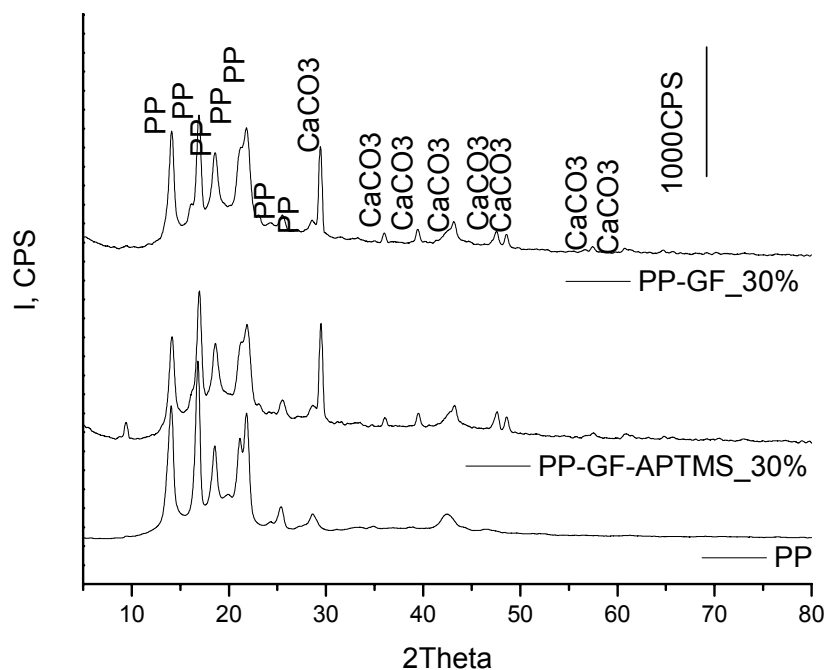


Fig. 2 - XRD patterns of PP/GF and PP/GF-APTMS / Difractogramele de raze X a materialelor PP/FS și PP/FS-APTMS.

As expected all the samples exhibit the main Roentgen interferences of isotactic PP ($2\theta \sim 14, 16.8, 18.5, 21.1, 21.8, 24.3, 25.4, 28.6^\circ$) [22] while the two samples containing calcium carbonate exhibit also the main diffraction peaks of calcite (ASTM 83-0578; $2\theta \sim 29.4, 30.4, 39.4, 43.2, 47.6, 48.5^\circ$). We can expect three side reactions that can lead to a modification of the XRD pattern but, due to the low processing temperature, in default of catalyst and the short processing time, neither the isomerisation or oxidation of PP, nor the calcite decomposition is identifiable. The crystallinity of the two samples seem not to be influenced by the functionalization process.

The XRD pattern of PP is not altered due to the compounding with GF or functionalized GF, even at high content of GF ($\sim 30\%$). This can be explained based on two facts: the low surface content of GF (due to the large difference in density between the GF and PP, the surface has a low content of GF) and especially due to the vitreous nature of GF (which induce low intensity diffraction peaks).

3.2. Infrared spectroscopy

FTIR spectroscopy was done in order to monitor the linkage of the coupling agent onto the surface of glass fibers. The FTIR spectra of glass fibers before and after the functionalization are shown in Figure 3.

It can be clearly stated that the two bands from ~ 2928 and 2857cm^{-1} increase in intensity due to the linkage of the aminopropyl group. This bonding can be also proved based on the bands from $1350\text{-}1460\text{cm}^{-1}$ corresponding to the scissoring and bending vibrations of the same group. It is also worth to mention that the GF functionalization can be also visualized in the region corresponding to the stretching vibrations of

Si-O-Si and especially based on the intensified band from $1080, 1114$ and 1174cm^{-1} . These bands were revealed by subtracting the spectrum of the GF from that of the GF-APTMS over the region of interest. The broad band from $\sim 3400\text{cm}^{-1}$ is assigned to the hydrogen bonds from GF-APTMS [23]. The water absorption can be explained especially due to the surface functionalization, the presence of amino groups increasing the hydrophilicity of the surface and consequently leads to higher water content.

In the case of composite materials (Figure 4) the characteristic bands of PP and can be easily identified. The main absorption bands of PP as well as their assignments are: 2950 (asymmetric CH_3 stretching vibration), 2918 (asymmetric CH_2 stretching vibration), 2867 (symmetric CH_3 stretching vibration), 2840 (symmetric CH_2 stretching vibration), 1455 (CH_2 scissor vibration), 1375 (symmetric CH_3 deformation) and 716cm^{-1} (rocking vibrations of methylene groups). The presence of the vibration from 1166cm^{-1} is an indication of the presence of the isopropyl group. The bands of GF and GF-APTMS are difficult to identify, because these bands are of low intensity and the composite contain only 30% GF and GF-APTMS, respectively. However, a more detailed analysis of the spectra allows the identification of the main characteristic absorption bands of GF: such as asymmetric Si-O-Si stretching vibrations ($\sim 1100\text{cm}^{-1}$), symmetric Si-O-Si stretching vibrations ($\sim 800\text{cm}^{-1}$) or bending vibrations of O-Si-O group ($\sim 470\text{cm}^{-1}$) [24].

FTIR spectra are also important because they can be used to analyse the stability of the polypropylene. The lack of the main bands of vibration of C-OH (especially the band from $\sim 1110\text{cm}^{-1}$) and COOH ($\sim 1715\text{cm}^{-1}$) is a proof of the fact that, no oxidation process occurred during the preparation.

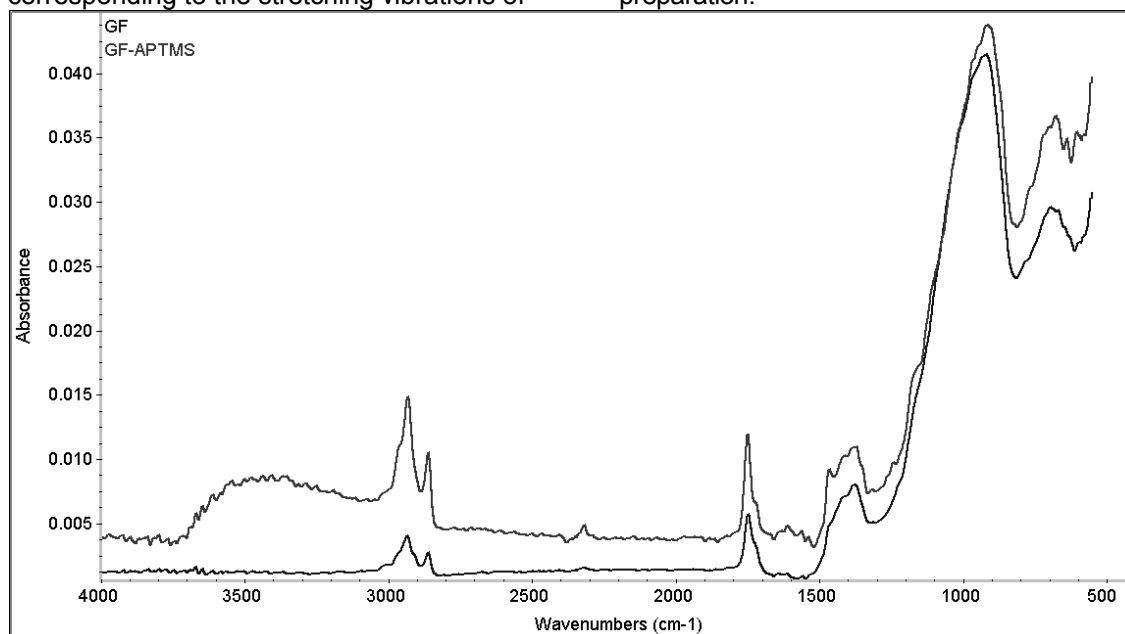


Fig.3 - FTIR spectra of GF and GF-APTMS / Spectrele FTIR ale FS și FS-APTMS

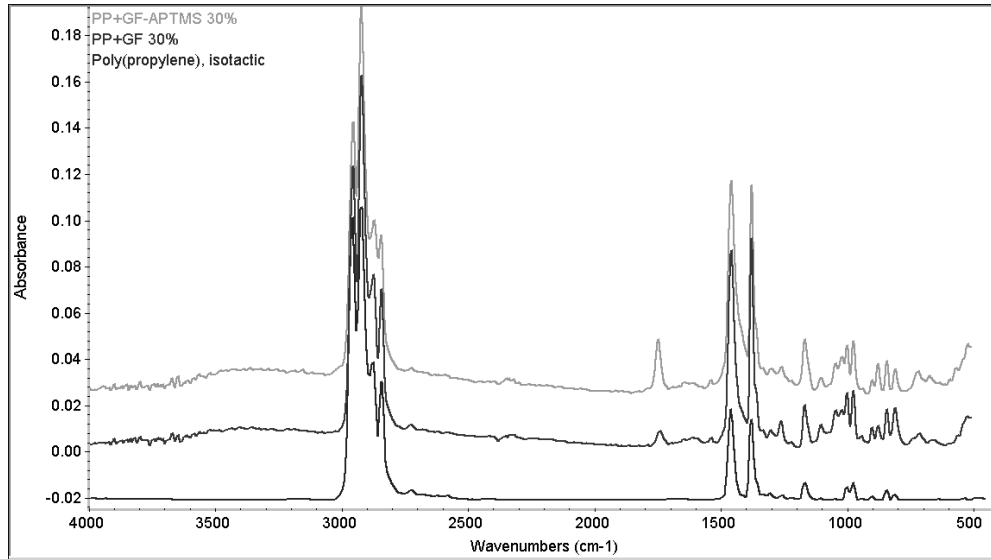


Fig. 4 - FTIR spectra of PP, PP/GF and PP/GF-APTMS / Spectrele FTIR ale PP, PP/FS și PP/FS-APTMS.

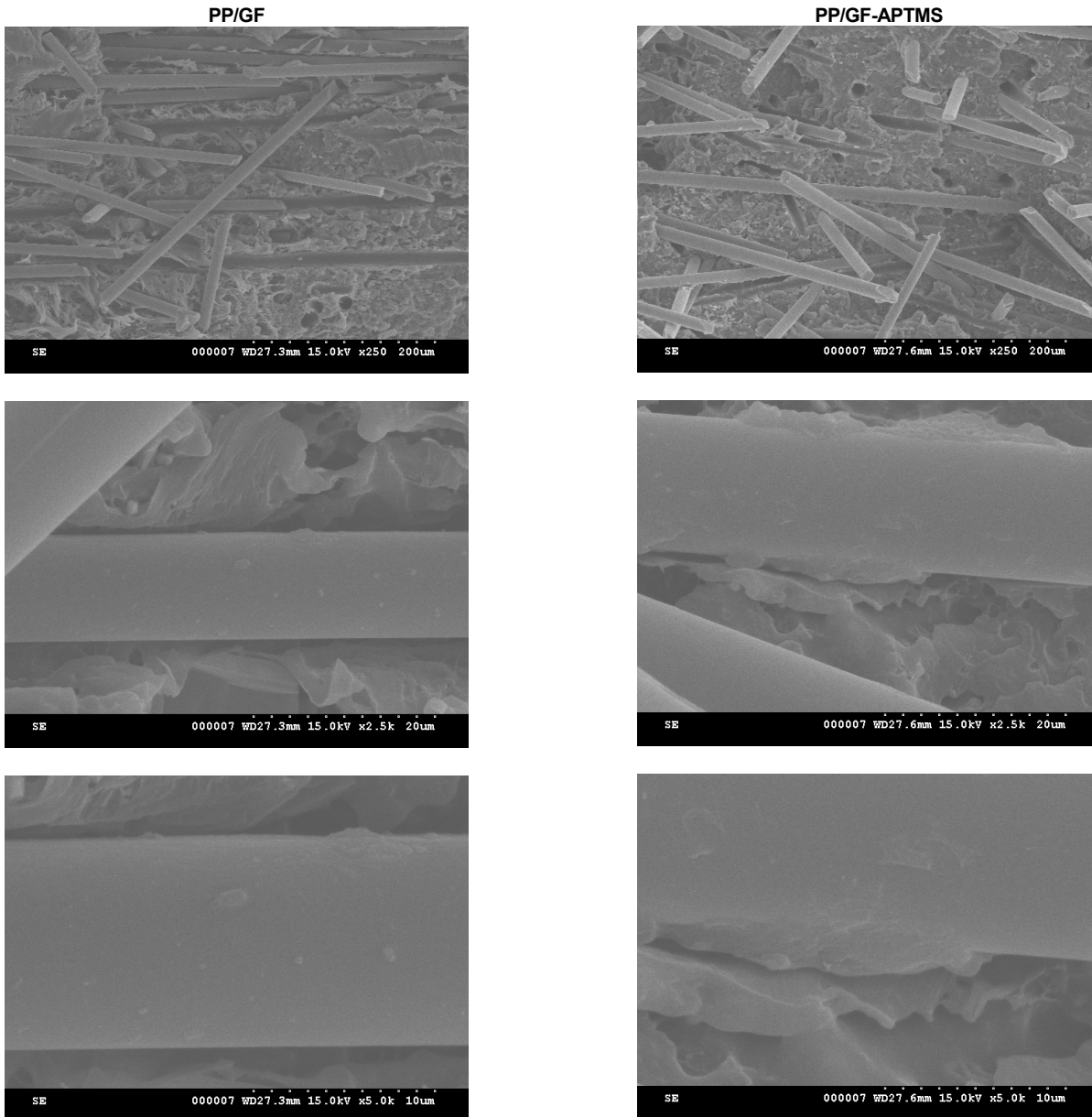


Fig. 5 - SEM images of the PP/GF and PP/GF-APTMS samples (cross-section) / Imagini SEM (in secțiune) a probelor PP/FS și PP/FS-APTMS.

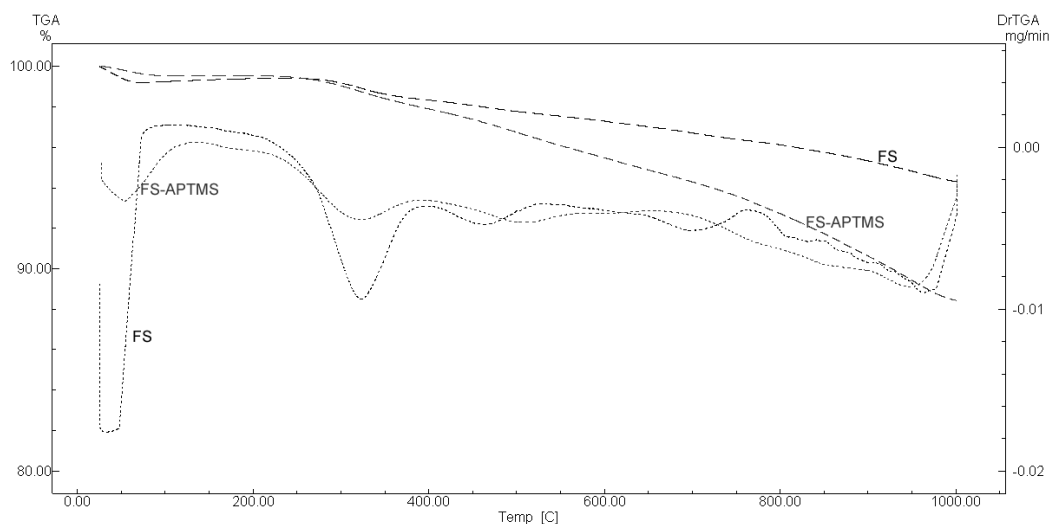


Fig.6- ATD-TG curves of GF and GF-APTMS / Analizele ATD-TG a FS și FS-APTMS.

3.3. Scanning electron microscopy

SEM images were recorded in the fracture region of the samples that were previously tested from the mechanical point of view and are shown in Figure 5.

At low magnification practically there are no differences between the two SEM images. At higher magnification, the different adhesion between the GF and PP could be observed. At 2500 or 5000x magnification, even after the mechanical testing the GF is still partially covered with PP which means a better adherence between the phases.

3.4. Complex thermal analysis

Complex thermal analysis (Figure 6) was recorded on both raw GF as well as on the APTMS functionalised GF (GF-APTMS). Analysing the thermo-gravimetric loss of the two samples it can be concluded that the functionalization process led to aminopropylsilane fixation on the GF, the weight loss associated with the aminopropyl degradation being ~5.8%.

4. Conclusion

The present work presents the preliminary results in the field of polypropylene - glass fibers compatibilization by using APTMS. The synthesis of polypropylene based composites reinforced with functionalized glass fibers was made in two steps. In the first step, glass fibers were functionalized through hydrolysis/condensation with (3-aminopropyl) trimethoxysilane as a functionalization agent and in the second step, the fibers were compounded with isotactic polypropylene. Polymer composites reinforced with functionalized and un-functionalized glass fibers (GF) were characterized by X-ray diffraction (XRD), infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and thermal analysis (ATD-TG). Based on the thermo-gravimetric losses the functionalization degree can be estimated at

~5.8%. SEM images reveal that the functionalization of the glass fibers allows a better interaction between the phases, the fibers being better covered with PP. Further works will be devoted to determining the best compatibilization way (perhaps both GF silanisation and PP grafting with maleic anhydride will be studied). The obtained materials are expected to exhibit higher chemical and mechanical properties and will be tested as a hot water distribution pipe, containers and bottles for chemicals, battery cases etc.

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