Polypropylene Functionalization with Vinyltriethoxysilane

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ABSTRACT: Polypropylene (PP) functionalization with vinyltriethoxysilane (VTES) was accomplished via a free radical process in a melt-mixer chamber, using dicumyl peroxide as the initiator. Fourier-Transform Infrared Spectroscopy (FTIR), Rutherford Backscattering Spectrometry (RBS), and gel permeation chromatography (GPC) were used to follow silane incorporation and product molecular weights. The influence of silane (0-10.0 wt %) and peroxide (0-1.0 wt %) concentrations on the functionalization degree and molecular weight of products was investigated. Chain-breaking reactions were present in all experiments, evidenced by smaller product molecular weights. This decrease was more pronounced for higher peroxide concentrations. Silane incorporation occurred even in peroxide absence, and it was seen to increase with increasing silane concentration. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1313–1319, 1999

Key words: polypropylene functionalization; vinylsilane; melt mixing; Rutherford Backscattering Spectrometry; molecular weight

INTRODUCTION

Polypropylene (PP) has considerable application in the polymer market as a plastic due to its good mechanical properties and low cost. However, the lack of functional groups limits its use in various and important technological fields. Chemical modification of the apolar backbone by means of radical reactions strongly increases its range of applications, improving the adhesion with conventional materials (metals, wood, leather, glass) and the compatibility with other synthetic polymers.¹

The most commonly used procedure for PP chemical modification involves the grafting of maleic anhydride. This reaction has been successfully achieved in solution,²⁻⁴ molten-,⁵⁻⁷ and even solid-state⁸ routes using peroxides as initiators. Other monomers were used in PP functionaliza-

tion such as α -methylstyrene,⁴ vinyl acetate,⁹ acrylic acid,¹⁰ diethyl maleate,^{11,12} diethylfumarate,⁴ and itaconic anhydride,⁷ besides others.^{9,13–17}

In an earlier study Minoura et al.³ proposed that grafting occurs mainly at the tertiary carbon atoms along the PP backbone. More recently, de Roover and collaborators¹⁸ reported that grafting occurs exclusively at the PP chain ends, after scission reactions. Heinen et al.¹⁹ suggested that the monomer attaches to tertiary carbon atoms promoting chain scission and so leading to terminal grafts. It is already well established that PP radical functionalization leads mainly to chain scission as a side reaction.⁵

The primary step for bonding vinyl monomers to PP is the formation of radical species by thermal decomposition of the initiator (Scheme 1).²⁰ It is generally assumed that these primary radicals preferentially abstract hydrogen from PP chains producing macroradicals. Then, the macroradicals can add to the vinylmolecule or they can undergo a β -scission reaction, originating lowweight molecular chains.

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Scheme 1

In the last years, the use of coupling agents in the development of particulate-filled polymer composites has attracted the attention of polymer researchers. Silane coupling agents are extensively used to improve adhesion between polymer matrices and inorganic fillers like mica,¹⁰ glass fibers,²¹ and talc.²² A silane coupling agent applied to the surface of the inorganic filler can enhance the mechanical, thermal, and electrical properties, as well as decrease mold shrinkage and color differences of the composites.¹⁰ When thermosetting resins are used, it is believed that the matrix reacts chemically with the coupling agent.²² For thermoplastic resins, as it is the case of PP, the mechanism is thought to be more complex.²³

Because PP is a nonpolar hydrophobic polymer, only a limited amount of hydrophilic filler can be added to it. So, its chemical modification with a typical coupling agent seems to be an effective way to achieve good results in improving properties for inorganic particulate-filled PP composites.

Few works were found in the literature describing the study of reactions between polyolefin and coupling agents, although there is extensive patent literature dealing with their use.^{24–29} Ak-

ovali et al.³⁰ reported the plasma surface modification of PE with organosilicon and organotin monomers. They showed that mainly polysiloxane type fragments emerged, resulting in materials with higher surface energies as compared with virgin PE.

Recently, a work by Feller and colaborators³¹ described the synthesis of silane-grafted i-PP to be used as a coupling agent on composites of PP and Fiberglass. The method consisted of preparing a propene-diene copolymer, which was submitted to a Speyer-hydrosilylation in order to obtain silane-functionalized oligopropenes.

Most of the works dealing with polyolefin functionalization with vinylsilanes attempts to obtain crosslinkable materials.^{32,33} Silane-grafted polymers can be easily moisture crosslinked in the presence of a suitable catalyst. Polyolefin crosslinking through silane grafting has many advantages such as easy processing, low cost, and capital investment, and favorable properties in the processed materials like heat resistance and improved adhesion.³² These products have been successfully exploited on a commercial scale in cable insulation and water heating pipes.^{20,33}

Surprisingly, despite the high reactivity of vinylsilanes towards polymer functionalization, we found no reports on the literature describing the formation of vinylsilane homopolymers. According to Kim and Jang³⁴ vinyltrimethoxysilane does not homopolimerize due to its bulky side groups, and the same behavior is expected for other similar silanes.

This article reports on the PP functionalization with vinyltriethoxysilane (VTES) in a melt-mixing process, aiming to study the effects of the amount of monomer and peroxide in the reaction medium on the incorporation degree and on the molecular weight of the resulting products.

EXPERIMENTAL

Materials

Commercial polypropylene (PPH 301), without additives, melt flow index 12 g/10 min at 230°C and a 2.16-kg load, M_w : 233,000, M_w/M_n : 6.5, and vinyltriethoxysilane (silan GF56–Wacker-Chemie) were generously supplied by OPP Petroquímica (Triunfo-RS, Brazil), and were used as received.

Dicumyl peroxide (DCP) 98% from Aldrich Chemical Company, was used as received. Commercial xylene and acetone were distilled prior to use.

Melt-Mixing Reactions

These reactions were performed in a Haake Rheomix 600p mixer. The mixer chamber was initially heated to 170°C and saturated with argon. PP was introduced into the chamber and, after 2 min, a solution of VTES and DCP was added. The rotors speed was fixed at 50 rpm. After mixing, the product was removed, cut in small pieces, and kept under reduced pressure for 40 h to remove the unreacted VTES and other volatiles. Total time of mixing was 10 min.

Fourier-Transform Infrared Spectroscopy (FTIR)

A FTIR spectrometer Mattson 3020, Galaxy 3000 series, was used for infrared analysis to measure relative functionalization. Measurements were performed using films prepared at 170°C, 2.5 ton/ cm², in a Carver press, Monarch Series, model 3710-ASTM. The scanned wavenumber range was 4000–400 cm⁻¹. The absorbance band areas of the Si—O—C stretching of the grafted silane at 1108 cm⁻¹ and 1080 cm⁻¹ (A1)³⁵ were compared with the absorbance band area of the methyl groups at 899 cm⁻¹ (A2-internal reference) to evaluate the functionalization degree. Ratios A1/A2 correspond to the amount of VTES incorporated in the PP chains.

Gel Permeation Chromatography (GPC)

Molecular weights were determined by means of gel permeation chromatography (GPC) with a Waters 150 CV system equipped with three columns Styragel HT3, HT4, and HT6 (10^3 , 10^4 , and 10^6 Å) and a refractive index detector. Analysis were undertaken using 1,2,4-trichlorobenzene as solvent, at 140°C, and molecular weights were calculated using an universal calibration curve constructed with polypropylene and polystyrene standards.

Rutherford Backscattering Spectrometry (RBS)

The functionalization degree of the polymer was determined by RBS using ${}^{4}\text{He}^{+}$ beams of 2.0 MeV incident on homogeneous polymer films (see FTIR section for film preparation details). The method is based on the determination of the number and the energy of the detected particles of a monoenergetic ion beam that are elastically scattered in

the coulombic field of the atomic nuclei in the target.³⁶ Backscattered-particle detection is accomplished with two surface barrier detectors placed at ± 165 (with respect to the incidence direction of the ion beam. Among other factors,^{36,37} the energy of the scattered particles depends on their energy of incidence, on the atomic masses of the atoms involved (probe and target), and on the depth in the sample where the scattering event occurs. The height of the signal (number of counts) corresponding to a certain element is proportional to the areal density of that element in the depth in which scattering occurs. In this study, Si/C atomic ratios were determined from the ratio of the signals corresponding to each of the elements (Fig. 1). Homogeneity of element distribution in the samples in the probing depth can be assured from the plateaus obtained for the C, O, and Si signals, while lateral homogeneity was confirmed from similar RBS spectra obtained from different spots, 1 cm apart, on the same film.

RESULTS AND DISCUSSION

The FTIR spectra of the initial PP and of a typical silane-grafted PP are represented in Figure 2. Strong absorption bands are observed for the grafted polymer at 1080 and 1108 cm⁻¹ (A1), which can be compared to the absorption band at 899 cm⁻¹ (A2), characteristic of the PP methyl group rocking.

Some products were submitted to Rutherford backscattering analysis. This technique allows the determination of the amount of each atom present, even for small concentrations (Si/C $\sim 10^{-3}$). Figure 1 shows a RBS spectrum for a silane-grafted polymer. The presence of carbon atoms is characterized by the signal which edge is at 512 keV, while the ones of oxygen and silicon appear at 732 and 1138 keV, respectively. Molar ratios between these atoms were calculated from the relative heights of the signals. The Si/C ratio informs about the actual functionalization degree of VTES on PP.

Ratios A1/A2 obtained from FTIR analysis were plotted as a function of the degree of functionalization determined from RBS analyses (Fig. 3). Good correlation (r = 0.978) among the data was obtained and the linear relation was used as a calibration curve. In this way absolute functionalization degree could be easily inferred by simple and inexpensive FTIR analysis in later experiments.



Figure 1 RBS spectrum of a silane grafted PP (Si/C: 0.0053), obtained with normal incidence on the sample of the 2.0 MeV 4 He $^{+}$ beam. The arrows indicate the outermost position of the corresponding elements in the sample. The Si edge is enlarged in the inset.

Reactions in the mixer chamber were torque monitored. Figure 4 shows representative torque curves for pure PP and for three functionalized polymers. All these torque curves are characterized by an early sharp peak due to material loading, followed by a decrease and finally a plateau region of nearly constant mixing torque. The torque decrease is initially attributed to the plasticization of the materials and subsequently to chain scission reactions. The presence of such reactions even in peroxide absence can be corroborated by molecular weight analysis. Mixing pure PP in the chamber for 10 min at 170°C decreased the M_w from 233,000 to 187,000. Chain scission reactions in this case were determined by free radicals produced by high temperature and/or mechanical shear. When DCP was present, torque and molecular weight decreases were more pronounced, probably due to the free radicals generated by the initiator decomposition.

Figure 4 also shows that mixing torque decreases with the organic peroxide content, but it



Figure 2 Infrared spectra of pure (dotted line) and grafted PP (solid line, 3.5 wt %).



Figure 3 Calibration curve relating FTIR and RBS results. Characteristic error bars ($\sim 10\%$) are shown for each experimental point.



Figure 4 Mixing torque in function of mixing time for pure PP (a) and grafted PP: (b) 5% VTES, 0.1% DCP; (c) 10% VTES, 0.1% DCP; (d), 5% VTES, 0.2% DCP, at 170°C and 50 rpm.

is almost not influenced by VTES concentration [VTES] for the selected experimental conditions. However, polymer processed in the presence of only VTES, without initiator (line 12 of Table I) showed smaller final torque than pure processed PP. This may be due to a plasticization effect inferred by the VTES and it is an additional effect to decrease final torque.

Chain scission reactions lead to molecular weight decrease, and they are attributed to the well-known β -scission²⁰ (see Scheme 1). Chain scission was seen to be always present in the experimental sets as demonstrated by low product molecular weights (Table I). When the [VTES] was kept constant and the peroxide concentration [DCP] in the charge increased M_n and M_w showed a decreasing tendency, as it can be seen from data in Table I and, more clearly, in Figure 5. This means that a higher free radical concentration resulted in more extensive degradation. For low [DCP], this tendency was not as evident, because probably ${\cal M}_n$ and ${\cal M}_w$ variations were smaller than the experimental error of the GPC analyses.

It is well known that PP is very susceptible to degradation in the presence of oxygen. When the oxidative degradation occurs, the molecular weight distribution (M_w/M_n) is expected to become broader due to fragmentary breakdown.¹⁸ Table I shows that the products obtained have narrower M_w/M_n than the virgin PP. Moreover, FTIR spectra of the products do not show car-

bonyl absorption bands, characteristic of oxidation products. These seem to suggest that PP mainly underwent degradation due to radicals produced by peroxide decomposition or by mechanical shear and/or temperature and not by oxidative reactions in our systems.

Increasing VTES concentration resulted in increasing grafting degree for constant DCP levels in almost all cases, indicating a good monomer reactivity (Table I and Fig. 6).

Figure 7 gives curves of interdependence of the degree of functionalization and initiator concentration for 5 and 10 wt % silane concentrations. Both curves pass through maxima and same behavior seems to occur for lower [VTES] as it can be seen from data in Table I. Maximum functionalization occurred about 0.5-0.75 wt % [DCP], for 5 and 10 wt % silane, while for lower silane concentrations the highest grafting degree seems to occur at lower [DCP]. The initial increase of the functionality as a function of [DCP] is probably due to the increasing number of free radicals produced by peroxide decomposition, which promote the formation of reactive sites in the polymeric chains. After the maximum, it seems that the higher concentration of free radicals is prone in promoting side reactions leading to less functionalized products. Interestingly, even in the absence of the initiator, it can be observed a significant VTES incorporation degree, as in the case of 5 wt % silane, indicating a very high VTES reactivity. At this condition, macroradicals probably are produced by mechanical shear and/or high temperature. According to the reaction mechanism depicted in Scheme 1, after VTES incorporation of an hydrogen atom is abstracted from another chain, generating a new macroradical. So, low free radical concentration in the medium can produce high levels of VTES-grafted polymers, depending only on the monomer concentration employed.

CONCLUSION

Functionalization of polypropylene with vinyltriethoxysilane was accomplished using dicumyl peroxide as the initiator in the melt-mixing process. Reactions were monitored by torque measuring, while the products were characterized by FTIR, GPC, and RBS.

FTIR and RBS results on the functionalization degree showed a good agreement, allowing the construction of a calibration curve, which enabled

VTES (wt %)	DCP (wt %)	F (mol %)	F (wt %)	Final Torque (N · m)	$M_n imes 10^{-3} \ (ext{g/mol})$	$M_w imes 10^{-3} \ m (g/mol)$	M_w/M_n
0*	0.00	0.00	0.00	_	36	233	6.5
0	0.00	0.00	0.00	2.60	48	187	3.9
0	0.20	0.00	0.00	0.55	41	85	2.1
1	0.10	0.17	0.77	1.00	28	98	3.5
1	0.20	0.22	0.99	0.45	30	83	2.8
1	0.25	0.12	0.55	0.60	24	87	3.5
1	0.30	0.14	0.62	0.20	24	75	3.1
2	0.10	0.14	0.62	1.02	28	128	4.6
2	0.20	0.26	1.18	0.55	27	89	3.3
2	0.25	0.29	1.31	0.35	28	68	2.4
2	0.30	0.13	0.59	0.05	28	84	3.0
5	0.00	0.62	2.81	0.55	41	136	3.3
5	0.10	0.58	2.63	0.70	28	118	4.1
5	0.20	0.62	2.81	0.40	24	79	3.3
5	0.25	0.67	3.04	0.20	27	96	3.5
5	0.30	0.77	3.49	0.30	27	84	3.1
5	0.50	1.04	4.71	0.20	22	53	2.4
5	0.75	0.83	3.76	0.10	25	51	2.0
5	1.00	0.70	3.17	0.00	17	47	2.8
10	0.10	1.18	5.35	0.80	44	121	2.8
10	0.20	1.16	5.26	0.30	34	82	2.4
10	0.30	1.34	6.07	0.15	24	69	2.9
10	0.50	1.54	6.98	0.15	25	55	2.2
10	0.75	1.60	7.25	0.10	22	69	3.1
10	1.00	1.33	6.03	0.00	15	53	3.6

Table IPP Functionalization with Vinyltriethoxysilane (VTES) under Different Initiator (DCP) andSilane Concentrations, at 170°C, 50 rpm, and 10 min

^a Pure non-processed PP.

the determination of the amount of silane incorporated in later experiments by simple infrared analysis. From torque and molecular weight measurements it was possible to conclude that chain scission was always present, and that it was more



Figure 5 M_w as a function of [DCP] for different [VTES], at 170°C and 50 rpm.



Figure 6 Grafted VTES degree as a function of [VTES] for different [DCP], at 170°C, 50 rpm and 10 min.



Figure 7 Grafted VTES degree as a function of [DCP] for different [VTES], at 170°C, 50 rpm, and 10 min.

important for higher peroxide concentration. Variation in VTES concentration did not show a clear effect in molecular weight.

The degree of functionalization showed maximum with [DCP], for each [VTES]. Vinyltriethoxysilane proved to be a very reactive compound because even in the absence of peroxide or with a small concentration, the initiator grafting was accomplished. In these cases macroradicals could be produced by mechanical shear and/or high temperature, leading to the chain sites for silane incorporation.

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