Free Radical Hydrosilylation of Polypropylene

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Received 24 October 1996; accepted 30 December 1996

ABSTRACT: Hydrosilylation of terminal double bonds in polypropylene was investigated via a free radical process in the melt-phase. This process involved the following two reactions occurring in parallel: chain scission, which leads to formation of double bonds, and the addition of silyl radicals to such bonds. Fourier Transform Infrared Spectrometry (FT–IR) was used to follow silane incorporation and terminal double bond formation. The experimental trends were verified using elemental analysis obtained from energy dispersive x-ray analysis (EDX). Using a single screw extruder and a model silane compound, a 2^3 full factorial experiment design was implemented with the following investigated factors: residence time, silane concentration, and peroxide concentration. Statistical analysis of the FT–IR results, showed that, for the silane incorporation, residence time, peroxide concentration, and the interaction between the silane and peroxide concentrations had significant effects. The significant effects for the formation of terminal double bonds were residence time, silane concentration, and peroxide concentration. The experimental results have shown that melt-phase hydrosilylation of polypropylene can be accomplished through this noncatalytic free radical method. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 439–447, 1997

Key words: hydrosilylation; reactive extrusion; free radicals; peroxide degradation; polypropylene functionalization

INTRODUCTION

Hydrosilylation is the addition reaction of a hydride terminated silane compound, or a silicon hydride, to a multiple bond.[1] The first published hydrosilylation work was on the addition of trichlorosilane to 1-octene, which was reported on by Sommer et al.[2] in 1947. Research concerning hydrosilylation has mainly been focused on reactions via a catalytic mechanism with a metal complex, such as platinum, rhodium, or iridium. Oro et al.[3] used iridium complexes to perform hydrosilylation and dehydrogenative silylation of hex-1-ene, and they found the formation of both the organosilane and hexane from the reactions. Lewis et al.[4] reported that the morphology of the metal colloid being formed affected the catalytic activity, which showed that the rhodium hydrosilylation catalyst was heterogeneous. As well, the heterogeneous nature of platinum and rhodium catalysts was verified with mercury inhibition tests.[4] The mechanism of catalytic hydrosilylation is not described in this article, but an in-depth review can be found elsewhere.[1,5–8]

Hydrosilylation has been recently investigated as a possible method for polymer functionalization in solution.[1,9,10] Hazziza-Laskar et al.[10] investigated the amine functionalization of polybutadiene with a difunctional silicon hydride. Pan et al.[11] used hydrosilylation as a method for the formation of high molecular weight hindered amine light stabilizers, while Qiu et al.[12] reported on the formation of functionalized organosilane polymers based on poly (methyl silane). Olefin compounds containing the following functional groups can undergo platinum catalyzed hydrosilylation without affecting the desired group: oxirane, ace-

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Contract grant sponsor: Natural Sciences and Engineering Research Council of Canada (NSERC).

tal, ester, nitrile, amine, amide, nitro, ketone, carbamate, ether, isocyanate, phosphate, phosphonic dischloride, dialkoxy borane, sulfide, sulfone, or carborane.[8]

Polypropylene (PP) is a commodity polymer that is used in a wide range of applications. It has good thermal and mechanical properties, chemical inertness, and high crystallinity. However, its hydrophobic nature can limit its use in certain applications. Therefore, methods for modifying the properties of PP have been studied. Peroxide induced degradation of PP has been used to manufacture controlled-rheology PP (CRPP). It has been reported that peroxide induced degradation results in a lower average molecular weight and a narrower molecular weight distribution.[13–16] Research on peroxide induced degradation of PP has given emphasis to the modeling of the degradation through reactive extrusion,[13,14] process control of the reactive extrusion process,[15] and the importance of mixing in the reaction.[16] As well, research has been completed on the melt-phase functionalization of PP.[17–19] Gaylord et al.[17] investigated the melt-phase grafting of maleic anhydride onto PP with peroxide initiators in the presence of dimethylformamide, which inhibits maleic anhydride homopolymerization. By contrast, research was completed on the functionalization of PP with basic functional groups such as oxazoline[18,19] and *t*-butylaminoethyl methacrylate.[19] The functionalized polymers were used in reactive compatibilization of polymer blends of PP and immisicble polymers such as NBR.[19] Terminally functionalized metallocene PP with maleic anhydride, silane, thiol, epoxide, borane and its hydroxyl derivative and carboxylic acid were produced by Mülhaupt et al.[20]

The objective of the current work was to investigate the melt-phase hydrosilylation of PP via a radically induced method with a model silane compound. The following two reactions were performed in parallel: the peroxide induced degradation of PP to produce terminal double bonds and the hydrosilylation of these double bonds. A high peroxide concentration was required to generate both a high level of unsaturation and silyl radicals. The use of high peroxide concentration leads to a significant reduction of PP molecular weight as known from previous studies.[13,14,16] If molecular weight of the final product is critical, a higher molecular weight PP could be used. A general mechanism that describes the possible reactions is discussed, and an experimental design and the investigated factors are presented. Finally, experimental results are presented with particular attention given to the statistical analysis, the presentation of linear regression models and the identification of the most significant factors.

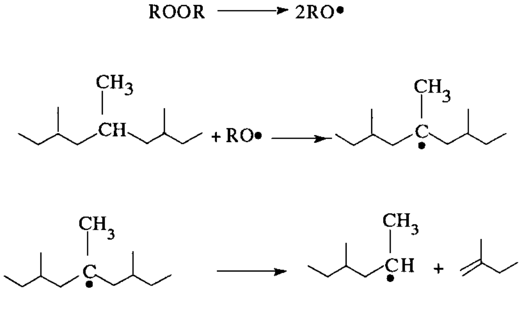

Figure 1 Mechanism for the peroxide induced degradation of polypropylene.

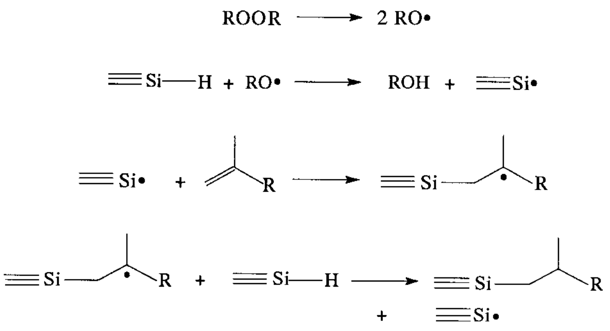

Figure 2 Mechanism for the radical induced hydrosilylation of a terminal double bond.

Reaction Mechanism

Peroxide induced degradation of PP took place according to the well known vis-breaking mechanism (Fig. 1). A primary radical, formed by the thermal decomposition of the organic peroxide, abstracts a hydrogen from the polymer backbone to form a tertiary radical. The tertiary radical undergoes a rapid β-scission to form a terminal double bond and a secondary radical. In the presence of a silane compound, the terminal double bonds may hydrosilylate.

A plausible reaction mechanism for the radically induced hydrosilylation of terminal double bonds is depicted in Figure 2. Silyl radicals are formed by hydrogen abstraction by a radical species. In Figure 2, the hydrogen abstraction is completed by a primary radical, but other radical species can react in a similar manner with the silicon hydride. Radically induced hydrosilylation proceeds by anti-Markovnikov addition (Farmer's rule) of a silyl radical to a terminal double bond.[1] This addition is favored because the produced tertiary carbon radical has greater stability than the primary radical. The tertiary radical then abstracts a hydrogen from another source in the system to form a new radical and the desired terminally functionalized PP chain. If the tertiary carbon radical reacts with another terminal double bond, crosslinking would result. However, crosslinking of the polymer is unlikely, because the concentration of terminal double bonds is very low. As well, the reactions described in this mechanism occurred alongside other possible reactions such as chain transfer and termination reactions.

In the work of Malz,[5] peroxide induced degradation of the PP was completed prior to catalytic hydrosilylation of the terminal double bonds, which guaranteed terminal grafting. Conversely, there was the possibility of side chain grafting the silicon hydride onto the PP when the radically induced method was used. The tertiary polymer radicals and the silyl radicals were produced simultaneously. Side chain grafting would occur if the two radical species had coupled before the β-scission of the polymer chain was completed. Thus, the likelihood of side chain grafting was dependent on the concentration of silyl radicals and the kinetics of the β-scission. However, because the β-scission of a polymer chain occurs very rapidly, the probability of terminal grafting is greater than that of side chain grafting.

EXPERIMENTAL WORK

Materials

The polypropylene used in the experiments was supplied by Montell Canada (KF 6100, $\bar{M}_n$ = 43,600, $\bar{M}_w$ = 348,000) and it had a melt flow index of 3 g/10 min (ASTM D1238 condition L). The peroxide used (Lupersol 101) was supplied by Elf Atochem. Hydride terminated polydimethylsiloxane (PDMS, MW = 400, b.p. = 170–200°C), supplied by United Chemical Technologies, was selected as the model silane compound. Toluene and methanol from BDH were used for sample cleaning. All materials were used as received.

Equipment

Experiments were carried out using a 19.05 mm (3/4 inch) single screw extruder (Haake Rheomex 252) with a length-to-diameter ratio of 25 to 1. The screw was comprised of a feeding, a compression, and a metering section prior to a rod die having a 2 mm diameter nozzle, and the reactants were flood fed into the extruder using a hopper located on the top of the feeding section. Temperature control of the extruder was completed using four heating zones. A Nicolet 520 mid-range (500–4000 cm^{-1}) FT–IR spectrometer was used in the analysis of the reacted polymer samples. As well, elemental analysis was completed at Surface Science Western (University of Western Ontario, London, Ontario, Canada).

Table I Factor Levels

Factor (Units)	Low Level (−1)	Midpoint (0)	High Level (+1)
Screw speed (rpm)	10	30	50
Silane concentration (% wt)	5	9	13
Peroxide concentration (% wt)	2	3.5	5

Experimental Design and Procedures

Using PDMS as a model silane compound, the produced terminally functionalized PP chain is depicted in Figure 3. A 2^3 full factorial experimental design was implemented with the following factors: residence time, silane concentration, and peroxide concentration. The factor levels are presented in Table I. The screw speed was used to manipulate the residence time in the extruder. The silane and peroxide concentrations are presented in terms of weight percent (wt %) of PP. The full factorial experiment design is presented in Table II. Five experiments were completed at the midpoint of the factor levels to study the reproducibility of the experimental results.

In all the experiments, the three reactants were masterbatched, or premixed, prior to charging to the hopper, and each masterbatch contained 100 g of PP. Also, all the experiments were completed with the following barrel temperature profile: 140, 170, 200,and 200°C. At the beginning of all the experiments, pure PP was fed to the extruder to establish steady-state flow. The establishment of steady-state was monitored with online measurements of torque and die pressure. The masterbatch of reactants was fed to the hopper when the steady-state flow was achieved. Online torque plots were used to follow the reactions in the extruder and to estimate the average residence times. An example of a torque plot is shown in Figure 4 for the conditions of Experiment 4.

Table II Factorial Experiment Design with Codified Factor Levels

Experiment #	Residence Time	Silane Concentration	Peroxide Concentration
1	+1	−1	+1
2	+1	+1	+1
3	−1	−1	+1
4	−1	+1	+1
5	+1	−1	−1
6	+1	+1	−1
7	−1	−1	−1
8	−1	+1	−1
Midpoint	0	0	0

The initial constant value of the torque corresponded to pure PP. Once the masterbatch was added to the extruder (at 8.5 min in Fig. 4) the torque was observed to decrease. This decrease indicated that there was a significant reduction in PP molecular weight due to chain scission. When the new steady-state was established, samples were collected and subsequently pure PP was fed (at 18 min in Fig. 4) to purge the system.

The reacted polymer samples were observed to foam at the extruder die. This foaming could be attributed to the presence of unreacted PDMS as well as amounts of *t*-BuOH, which is a by-product of the peroxide decomposition. To ensure accurate analysis of the grafting reaction, the collected polymer samples were cleaned to remove any free PDMS. Eight grams of the collected polymer was dissolved in 60 mL of hot toluene. The cleaned polymer was precipitated using 240 mL of methanol. The precipitated polymer was vacuum filtered and washed with methanol. The procedure was repeated a total of three times, and the final cleaned polymer was dried in an oven at 74°C for 24 h. Precipitation of the polymer with methanol lead to partial conversion of the Si—H groups to Si—CH_3 groups. To preserve the Si—H groups, the precipitation can be completed with dry acetone. Films, with a thickness of 0.3 mm, were compression molded at 170°C at a pressure of 170 MPa. The cleaned polymer powder was preheated in the mold for 3 min before the pressure is applied. Pressure was applied for 2 additional minutes, after which, the mold was water quenched to rapidly cool the film. Rapid cooling was used to control the formation of crystallites in the polymer films, which ensured a high transmission for the FT−IR analysis.

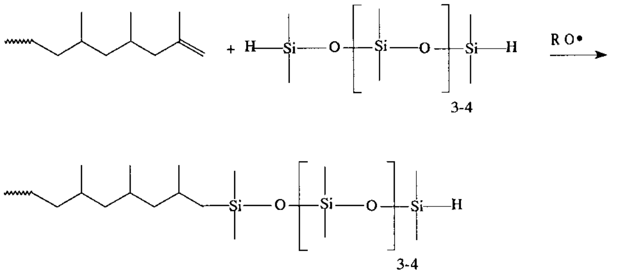

Figure 3 Addition of PDMS to a terminal double bond.

FT−IR spectrometry was used to analyze the polymer films for silane incorporation and terminal double bond formation. The spectra were obtained with a resolution of 2 cm^{-1}. The peak located at 841 cm^{-1} was used as an internal reference to compare the different spectra.[21] The peak height at 1032 cm^{-1} was used to determine the amount of silane incorporated into the polymer. This peak was attributed to the Si—O—Si and C—O—Si stretching vibration of the grafted PDMS.[22] The height of the peak at 888 cm^{-1}, which corresponded to the CH_2 wag of the vinylidine group,[23] was used to determine the amount of

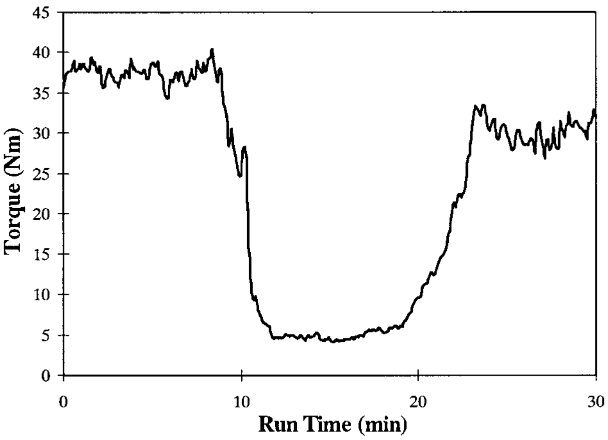

Figure 4 Torque vs. run time for Experiment 4.

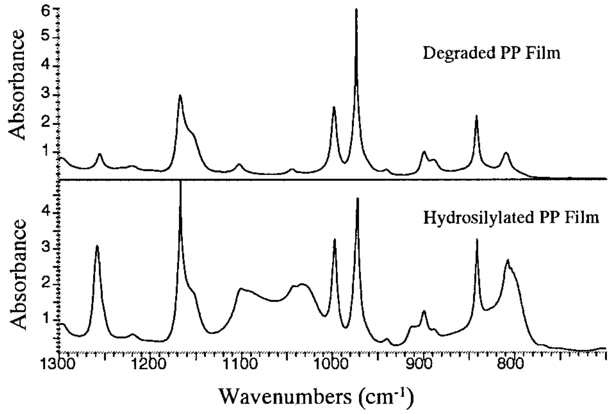

Figure 5 Comparison between the FT–IR spectrum of hydrosilylated polypropylene and degraded polypropylene (5 wt % peroxide).

terminal double bonds formed. In the analysis of the experimental results, the relative peak heights, or the ratios of the specific peak height to the reference peak height, were used.

RESULTS AND DISCUSSION

Experimental Results

A comparison of the FT–IR spectra of a hydrosilylated PP film and a degraded PP film is shown in Figure 5. Both samples were extruded with 5 wt % peroxide and cleaned according to the previously mentioned procedure. The silane was incorporated into the polymer as shown by the broad peak located at 1032 cm^{-1}. Both samples contained terminal double bonds due to the presence of the peak at 888 cm^{-1}. Other peaks that correspond to the grafted PDMS are located at 2136 cm^{-1} (Si—H stretching vibration, outside of the wavenumber range selected in Fig. 5), 1259 cm^{-1} (Si—CH_3 deformation vibration) and 810 cm^{-1} (Si—CH_3 stretching vibration).[22]

The experimental results of the average residence times, steady-state torque values, and the silane and terminal double bond relative peak heights are presented in Table III. The silane concentration in the masterbatch affected both the steady-state torque and the residence time. The small effect of the PDMS concentration on the residence time was attributed to the effect of the liquid reactant on the pumping and backmixing in the extruder. An increase in the amount of liquid in the masterbatch caused a decrease in the viscosity of the polymer melt, which lead to a shorter residence time. As well, the liquid reactants affected the friction at the metal surfaces, which influenced the pumping of the polymer in the extruder. In the analysis of the experimental results, the small effect of the PDMS on the residence time was neglected. Therefore, linear regression analysis of the experimental results was completed using codified factor levels (+1 for the upper level of a factor and −1 for a lower level of a factor). The results from the midpoint analysis showed that the reproducibility of the experimental results was satisfactory. The standard deviations, which were used in the statistical analysis of the experimental results, were calculated to be 0.01579 and 0.00158 for the silane and terminal double bond relative peak heights.

To present the general experimental trends,

Table III Experimental Results

Experiment No.	Average Residence Time (min)	Torque (Nm)	Silane Relative Peak Height	Terminal Double Bond Relative Peak Height
1	10.90	0	0.3834	0.0470
2	10.43	0	0.4301	0.0272
3	3.62	1.55	0.1944	0.0329
4	3.13	3.80	0.3322	0.0240
5	10.97	0.25	0.2461	0.0227
6	10.25	0.38	0.1330	0.0106
7	3.75	7.25	0.0176	0.0139
8	3.12	11.50	0.0079	0.0059
Midpoint 1	5.68	0.85	0.1512	0.0205
Midpoint 2	5.57	0.85	0.1473	0.0201
Midpoint 3	5.63	0.95	0.1868	0.0230
Midpoint 4	5.78	0.75	0.1681	0.0237
Midpoint 5	5.70	0.90	0.1584	0.0212

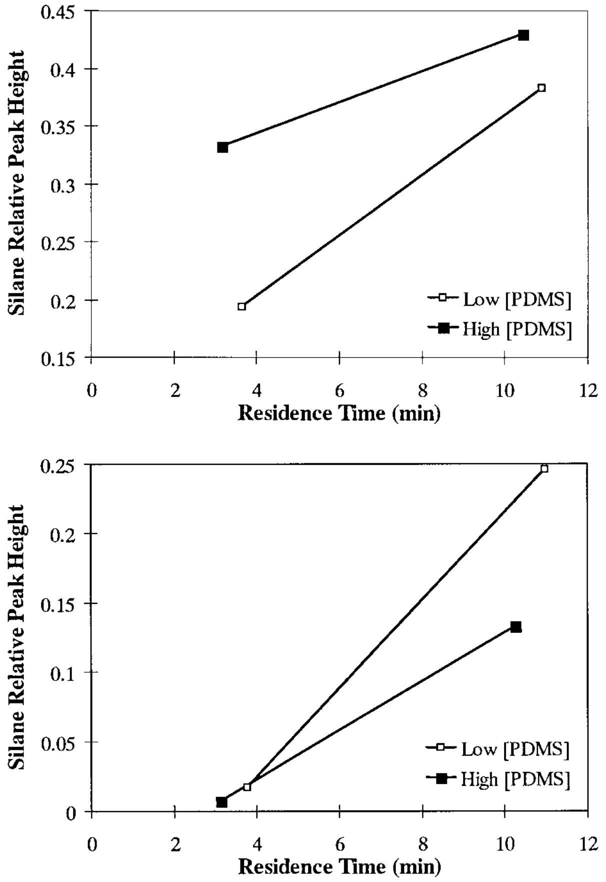

Figure 6 Silane relative peak height vs. residence time. (Top) High peroxide concentration; (Bottom) Low peroxide concentration.

the results are plotted in the form of the relative peak heights versus residence time (Figs. 6 and 7). At the high peroxide concentration, the silane concentration had a positive effect on the silane incorporation [Fig. 6(a)]. The opposite trend was observed at the low peroxide concentration [Fig. 6(b)]. By contrast, the silane concentration effect on the formation of terminal double bonds was not dependent on the peroxide concentration [Fig. 7(a) and (b)].

Statistical Analysis and Discussion

Linear regression, with the codified factor levels, was completed to quantify the effects of the three investigated factors as well as the interaction effects. The analysis was completed separately for the silane incorporation and the terminal double bond formation. The corresponding linear model equations are of the general form depicted in eq. (1).

$$\text{Relative Peak Height} = A_1X_1 + A_2X_2 + A_3X_3 + A_{12}X_1X_2 + A_{13}X_1X_3 + A_{23}X_2X_3 + A_{123}X_1X_2X_3 \quad (1)$$

where:

A_1 = Residence Time Coefficient
A_2 = Silane Concentration Coefficient
A_3 = Peroxide Concentration Coefficient
A_{12} = Residence Time–Silane Concentration Interaction Coefficient
A_{13} = Residence Time–Peroxide Concentration Interaction Coefficient
A_{23} = Silane–Peroxide Concentration Interaction Coefficient
A_{123} = Three-Factor Interaction Coefficient
X_1 = Residence Time Codified Level (-1 or $+1$)
X_2 = Silane Concentration Codified Level (-1 or $+1$)
X_3 = Peroxide Concentration Codified Level (-1 or $+1$)

The factor effects, which are twice the value of the corresponding linear regression coefficients, and 95% confidence intervals are presented in Table IV. Table IV data showed that the significant

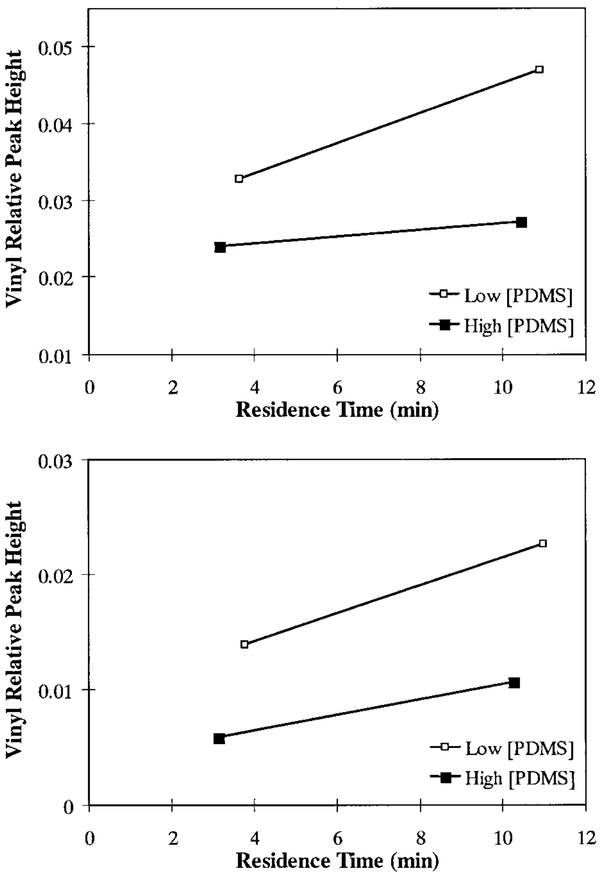

Figure 7 Terminal double bond relative peak height versus residence time. (Top) High peroxide concentration; (Bottom) low peroxide concentration.

Table IV Factor Effects and Confidence Intervals

	Silane		Terminal Double Bond	
Factor	Effect	95% Confidence Interval Limits	Effect	95% Confidence Interval Limits
Residence Time (RT)	0.1602	±0.0196	0.0078	±0.0020
Silane Concentration (S)	0.0154	±0.0196	−0.0122	±0.0020
Peroxide Concentration (P)	0.2338	±0.0196	0.0196	±0.0020
RT*S	−0.0486	±0.0196	−0.0038	±0.0020
RT*P	−0.0166	±0.0196	0.0010	±0.0020
S*P	0.0768	±0.0196	−0.0022	±0.0020
RT*S*P	0.0030	±0.0196	−0.0017	±0.0020

effects for silane incorporation were residence time, peroxide concentration, and the silane–peroxide interaction. For terminal double bond formation the significant effects were residence time, silane concentration, and peroxide concentration. Using only the significant effects, linear regression, with codified factor levels, was completed to form linear models for the silane incorporation and terminal double bond formation, which are of the general form of eq. (2). The factor effects and their test statistics are presented in Table V.

$$\text{Relative Peak Height} = A_1X_1 + A_2X_2 + A_3X_3 \quad (2)$$

where:

A_1 = Residence Time Coefficient
A_2 = Silane Concentration Coefficient (Terminal Double Bond Formation) or Silane-Peroxide Interaction Coefficient (Silane Incorporation)
A_3 = Peroxide Concentration Coefficient
X_1 = Residence Time Codified Level
X_2 = Silane Concentration Codified Level (Terminal Double Bond Formation) or Silane–Peroxide Interaction Codified Level (Silane Incorporation)
X_3 = Peroxide Concentration Codified Level

A test statistic is the ratio of the square of the effect to the square of the standard deviation. The value of the *F*-distribution for 95% confidence, with 1 degree of freedom in the numerator and 4 degrees of freedom in the denominator, is 7.71. Comparison of the test statistics with the corresponding value of the *F*-distribution was used to determine the significance of the effects. The results showed that all the selected factors were significant at the levels studied in the experiments. All the effects were positive except the silane concentration effect on the formation of terminal double bonds. As well, the most significant factor in both models was the peroxide concentration because it affected the concentrations of both the terminal double bonds and the silyl radicals that were available for hydrosilylation.

To test the quality of fit of the two linear regression models, the squares of the multiple correlation coefficients (r^2) and the lack of fit statistics were calculated. The r^2 values for the silane incorporation and terminal double bond formation models were 0.97 and 0.96, respectively. These results indicated that the residual variations were not significant and the linear model equations were adequate representations of the experimental results. The lack of fit statistic is the ratio of the mean square of the lack of fit to the mean

Table V Statistical Analysis of the Selected Factor Effects

	Silane		Terminal Double Bond	
Factor	Effect	Test Statistic	Effect	Test Statistic
Residence time	0.1602	102.8	0.0078	23.8
Silane concentration	Not Included in Model		−0.0122	59.6
Peroxide concentration	0.2338	219.4	0.0196	152.3
Silane–peroxide interaction	0.0768	23.7	Not Included in Model	

square of replication. The former is the square of the standard deviation, which was calculated from the midpoint results. The mean square of the lack of fit is the difference between the sum of squares of the residuals and the sum of squares of the replication, divided by the proper number of degrees of freedom. In general, a proposed model does not accurately fit the experimental data if the lack of fit statistic deviates significantly from unity. The results for the silane incorporation and terminal double bond formation models were 3.93 and 2.81, respectively. The value of the F-distribution for 95% confidence, with 5 degrees of freedom in the numerator and 4 degrees of freedom in the denominator, is 6.26. The observed statistics were not significant at the 5% level, and therefore, the linear model equations were accurate fits of the experimental data.

The significant interaction between the silane and peroxide was attributed to the sample preparation method. In the preparation of the masterbatches, the peroxide and silane mixed together and coated the outsides of the polymer pellets. This intimate mixing was the cause of the interaction because it lead to a higher probability that the peroxide radicals would react with the PDMS to form silyl radicals than with the polymer backbone. The experimental results presented in Table III showed that an increase in the silane concentration, at constant residence time and peroxide concentration, caused an increase in the steady-state torque. This increase indicated that there was less peroxide induced degradation of the PP chains because a larger amount of the primary radicals were consumed by the PDMS. The effect of this consumption on the silane incorporation was dependent on the concentration of the peroxide. At the low peroxide concentration, an increase in the silane concentration lead to an insufficient formation of terminal double bonds for hydrosilylation. Thus, the silane incorporation was very low. The presence of a low concentration of terminal double bonds and a high concentration of silyl radicals increases the probability of side chain grafting of the PDMS on the PP. This possibility requires further investigation. At the high peroxide concentration, there was a sufficient amount of primary radicals available to react with both the silane and the polymer backbone. Therefore, a significantly higher silane incorporation was achieved due to the higher concentration of terminal double bonds.

All the collected polymer samples contained terminal double bonds. The existence of terminal double bonds, after hydrosilylation, indicated that the reaction conversion can be improved. Mixing of low viscosity liquids and polymer melts requires significant distributive mixing to obtain a homogeneous mixture.[24] This homogenization is very important in reactive extrusion to obtain a uniform reacted product. The use of a distributive mixing element in the single screw extruder may improve the conversion. Similarly, a twin screw extruder, with an appropriate screw configuration, would offer much more mixing than the conventional single screw extruder used in this work. In either case, a high concentration of peroxide would be required in the mixing section to produce adequate amounts of both the terminal double bonds and the silyl radicals.

Elemental analysis was completed to investigate the cleaned polymer samples obtained from the experiments completed at the high peroxide concentration (Experiments 1 to 4). The EDX analysis was used to determine the atomic ratio of silicon to carbon in the samples. It is important to note that EDX is a surface analysis, and the measurement accuracy is highly dependent on the sample homogeneity. Therefore, the results were used only to verify the general trends found from the FT–IR analysis. Using the atomic ratios, linear regression analysis was completed to determine the effects of residence time and silane concentration on the silane incorporation. The resulting effects were: 0.0029 for the residence time effect, 0.0032 for the silane concentration effect, and 0.0002 for the interaction effect. Although, the EDX analysis was completed for only half of the samples, the results verified the experimental trends depicted in Figure 6(a). Both EDX and FT–IR analyses showed that, at 5 wt % peroxide, residence time and silane concentration had positive effects on silane incorporation.

CONCLUSIONS

This work has investigated the melt phase hydrosilylation of terminal double bonds in PP by a noncatalytic free radical method. Experimental results showed that the radically induced hydrosilylation of PP is feasible, and the grafting can be affected by the reaction conditions. The radically induced method was completed by simultaneously performing peroxide induced degradation of PP and hydrosilylation of the produced terminal double bonds. The reacted polymer samples contained significant amounts of both the grafted PDMS and terminal double bonds. Statistical analysis of the experimental results showed the significance of the factor and interaction effects, and verified the quality of fit of the linear models. Terminal double bond formation was significantly affected by the residence time, the silane concentration and the peroxide concentration. Incorporation of the silane onto the PP chains was significantly affected by the residence time and the peroxide concentration. As well, the sample preparation method influenced the reactive extrusion process and caused a significant interaction between the silane and the peroxide on the silane incorporation.

Financial assistance from the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged. The authors would also like to thank Mark Biesinger of Surface Science Western for the EDX analysis.

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