Strategies for Maximizing Free-Radical Grafting Reaction Yields

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ABSTRACT: It is very challenging to obtain very large amounts of vinyl monomers grafted onto polymer backbones in the melt through a free-radical mechanism. The objective of this study was to develop strategies that would allow one to maximize the amount of 3-isopropenyl-α,α-dimethylbenzene isocyanate (TMI) grafted onto polypropylene (PP) by reactive extrusion processes. For that purpose, an internal batch mixer was used to simulate potential reactive extrusion processes. Two strategies were studied: The first one was to apply the comonomer concept developed in previous studies. More specifically, styrene (St) was used as a comonomer to control the grafting yield and the molar mass of TMI-grafted PP. The second strategy delt with the feeding mode of the reactants. Two feeding modes were investigated: (a) one-pot feeding, that is, the total amount of TMI, St, and a peroxide were premixed with PP and the whole mixture was then charged to the reactor at once; (b) stepwise feeding, that is, the total amount of TMI, St, and the peroxide was divided in several equal fractions. The first fraction of the mixture was premixed with PP and then charged to the reactor. After a certain reaction time, the other fractions were charged to the reactor one after another in certain time intervals. Both strategies were shown to be very good at maximizing free-radical grafting reaction yields. They can be easily adopted if free-radical grafting is to be carried out by reactive extrusion in a screw extruder.
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Key words: reactive extrusion; reactive processing; poly(propylene) (PP)

INTRODUCTION

Reactive extrusion via free-radical chemistry is an important postreactor technology to functionalize otherwise chemically inert polymers such as polypropylene (PP) and polyethylene (PE).[1] Such functionalized polymers can have many applications: For example, they can react with other functional polymers to form copolymers. The latter are useful for numerous applications including improvement in compatibility and interfacial adhesion between immiscible polymers.[2]

Vinyl monomers chosen for free-radical grafting should satisfy at least the following criteria: (a) Monomers themselves and the corresponding grafted species have to be stable enough under processing conditions; (b) polymerization should be as little as possible and should be controllable; and (c) monomers should meet all health and safety regulations. The last criterion is very important for industrial perspectives. 3-Isopropenyl-α,α-dimethylbenzene isocyanate (TMI) was chosen for this study because of its interesting bifunctional character: a free radically reactive double bond and an isocyanate group. Unlike classical isocyanates, the isocyanate group of TMI is relatively insensitive to moisture under typical polymer processing conditions. Moreover, TMI does not homopolymerize by a free-radical mechanism.[3,4] However, monomers that do not undergo homopolymerization most probably have low free-radical grafting reactivity. Therefore, their grafting yields are generally low, unless very large amounts of peroxide are charged. The latter are highly undesirable because they cause important side reactions such as chain degradation for PP and chain crosslinking for PE. As far as TMI's toxicity is concerned, it remains controversial. The objective of this study was to develop strategies that would allow one to maximize the amount of TMI grafted onto PP by reactive extrusion processes while minimizing side reactions, especially PP chain degradation.

Two strategies were studied: The first one was to apply the comonomer concept developed in the literature[1,5–14] to the PP/TMI/peroxide grafting system. More specifically, styrene (St) was used as a comonomer to control the grafting yield and the molar mass of TMI-grafted PP, PP-*g*-TMI. The comonomer concept works well only when the two following conditions are met: The comonomer has a high reactivity toward the macroradical of the polymer and the resulting comonomer macroradical copolymerizes readily with the grafting monomer. A previous study showed that St reacts rapidly with PP macroradicals.[11] Another

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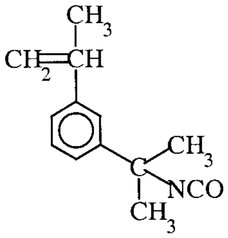

Figure 1 Molecular formula of 3-isopropenyl-α,α-dimethylbenzene isocyanate (TMI).

previous study showed that copolymerization in solution between St and TMI proceeds reasonably well if the composition of TMI is not very high compared to that of St.[15] This is in agreement with other studies reported in the literature.[3,4] It was expected that using St as a comonomer would improve the free-radical grafting yield of TMI onto PP. Moreover, PP chain degradation would be limited.

The second strategy delt with the feeding mode of reactants. Two feeding modes were examined: (i) one-pot feeding, that is, the total amount of TMI, St, and the peroxide were premixed with PP and the whole mixture was then charged to the reactor at once; (ii) stepwise feeding, that is, the total amount of TMI, St, and the peroxide was divided in several equal fractions. The first fraction of the mixture was premixed with PP and then charged to the reactor. After a certain reaction time, the other fractions were charged to the reactor one after another at certain time intervals.

EXPERIMENTAL

Materials

The PP used in this study was a commercial grade of Borealis (BCB 95) (Norway), as porous pellets. Its number and weight-average molar masses were 280,000 and 620,000 g/mol, respectively. Its melt-flow index was 3.5 g/10 min at 230°C under 2.16 kg (ASTM 1238L). Its melting temperature was 163°C. The monomer, TMI and the comonomer, St, were purchased from Aldrich (Saint Quentin, France) and used without further purification. TMI was liquid at room temperature and had a boiling point of approximately 270°C/760 mmHg. The free-radical initiator used was bis(*tert*-butylperoxyisopropyl)benzene (Perkadox-14). Its half-life was approximately 37 s at 180°C and 7 s at 200°C. Characteristics of different types of free-radical initiators and basic principles for the choice of initiator can be found in ref. 1. The molecular formula of TMI is shown in Figure 1.

Free-radical grafting of TMI onto PP

Free-radical grafting reactions were carried out in a Haake Rheocord mixer in which two sigma rotors rotated in opposite directions. The rotation speed was 64 rpm and the temperature of the mixing chamber was set at 175°C, unless specified otherwise. The peroxide was first dissolved in liquid TMI and St, forming a solution. The latter was then fed to the mixer in two different ways: (a) one-pot feeding, that is, the low-molecule solution was first mixed with PP porous pellets (40 g) and then charged to the mixer for 10 min of reaction; (b) a given amount of the solution was divided into several equal fractions. The first fraction of the mixture was premixed with PP and then charged to the reactor. After a certain reaction time, the other fractions were charged to the reactor one after another at certain time intervals.

Characterization of PP-*g*-TMI

Three types of TMI could be present in the reaction product: unreacted TMI monomer, grafted TMI onto PP, PP-*g*-TMI, and (co)polymerized TMI. The performance of the free-radical grafting was characterized by TMI's grafting yield, which was the amount of grafted TMI in PP-*g*-TMI, $[\mathrm{TMI}]_g$ in phr (parts per hundred parts of resin, PP), TMI's grafting efficiency, which was defined as the ratio between the amount of grafted TMI and its initial amount, $[\mathrm{TMI}]_g/[\mathrm{TMI}]_i$, and the torque of the grafting system, which was a rough measure of the molar mass of TMI-modified PP. For the sake of TMI's grafting yield determination, reaction products were first dissolved in hot xylene. The solution was then charged dropwise to acetone at room temperature. PP-*g*-TMI precipitated out while the unreacted TMI monomer and (co)polymerized TMI remained soluble. PP-*g*-TMI was separated by filtration. To remove completely unreacted TMI and (co)polymerized TMI from the purified PP-*g*-TMI, the latter was redissolved in hot xylene and the remaining procedure was repeated. The PP-*g*-TMI thus obtained was then dried and pressed into films about 100 μm thick for subsequent determination of TMI's grafting yield by FTIR (Nicolet 60 SX).

Figure 2 shows the IR spectra of the pure PP, PP-*g*-TMI without St in the grafting system, and PP-*g*-TMI in the presence of St as a comonomer. Compared with the pure PP, the PP-*g*-TMI without St was characterized by an additional peak at 2255 cm^{-1}, corresponding to the isocyanate group of grafted TMI. The PP-*g*-TMI with St was characterized by two additional peaks at 2255 and 700 cm^{-1}, corresponding to the isocyanate group of grafted TMI and the C—H of the benzene ring of St, respectively.

The peak at 2722 cm^{-1} corresponding to the PP backbone was chosen as the internal reference and the peak at 2255 cm^{-1} corresponding to the isocyanate group of TMI was used to determine TMI's graft yield. For that purpose, a calibration curve was needed. That was done using two different methods: The first one was to prepare a series of mixtures of TMI and PP in

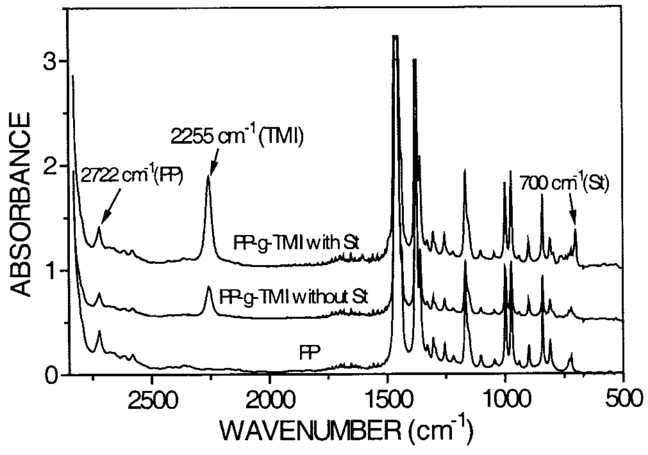

Figure 2 FTIR spectra of the pure PP, PP modified by TMI without St, and PP modified by TMI with St as a comonomer.

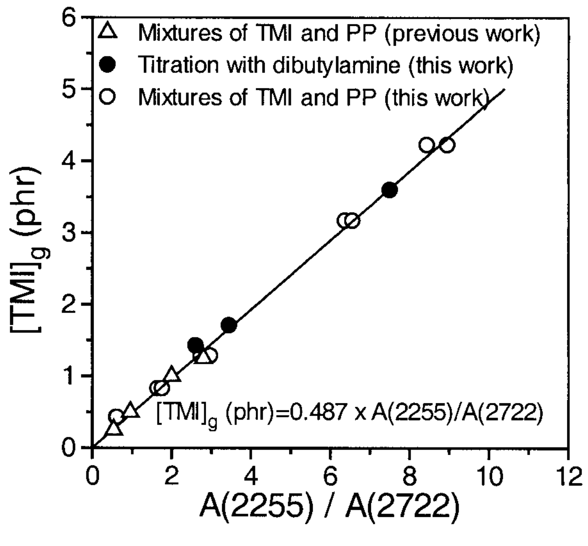

Figure 3 Relationship between the IR absorption ratio defined as the ration 2255 and 2722 cm^{-1}, $A(2255)/A(2722)$, and TMI's grafting yield in parts per hundred parts of PP (phr): (△) Mixtures of known amounts of TMI and PP[16]; (○) mixtures of known amounts of TMI and PP (this work); (●) titration with dibutylamine (this work).

the batch mixer at 180°C for 4 min. The corresponding values of the IR absorption ratio between 2255 and 2722 cm^{-1}, $A(2255)/A(2722)$, were then calculated. The second one was to titrate grafted TMI onto PP by dibutylamine. Known amounts of PP-*g*-TMI and dibutylamine (approximately half the molar number of grafted TMI) were reacted in xylene at about 130°C for 40 min. The polymer products were then obtained by precipitation in acetone. The values of $A(2255)/A(2722)$ of the reacted PP-*g*-TMI were then determined. Knowing the initial amounts of PP-*g*-TMI and dibutylamine and the values of $A(2255)/A(2722)$ of the PP-*g*-TMI before and after titration, the relationship between the amount of grafted TMI in PP-*g*-TMI and the corresponding value of $A(2255)/A(2722)$ was then established. As shown in Figure 3, both methods led to a single and linear relationship between TMI's grafting yield and the value of $A(2255)/A(2722)$. The results were also in good agreement with those reported in the literature.[16]

RESULTS AND DISCUSSION

Free-radical grafting kinetics

Free-radical grafting in the melt usually goes to completion within less than a few minutes depending mainly on the melting rate and the half-lifetime of the free-radical generator used. This is also the case for the free-radical grafting of TMI onto PP with or without St. Figure 4 shows the evolution of TMI's grafting yield, $[TMI]_g$ in phr, and grafting efficiency, $[TMI]_g/[TMI]_i$, as a function of the mixing time for the PP/TMI/St/peroxide (100/10/5/2.5) grafting system at two different set temperatures: 175 and 190°C. As expected, the grafting rate was faster when the wall temperature of the mixer was higher. For example, the grafting reaction went to completion in about 6 and 4 min when the wall temperature of the mixer was set at 175 and 190°C, respectively. The grafting yields were virtually the same. However, at 190°C, TMI's grafting yield started to decrease after 4 min of mixing, implying that grafted TMI seemed to start to suffer thereafter under the processing conditions. Such a phenomenon can also be observed for bulk free-radical grafting of maleic anhydride and glycidyl methacrylate onto PP under certain circumstances.

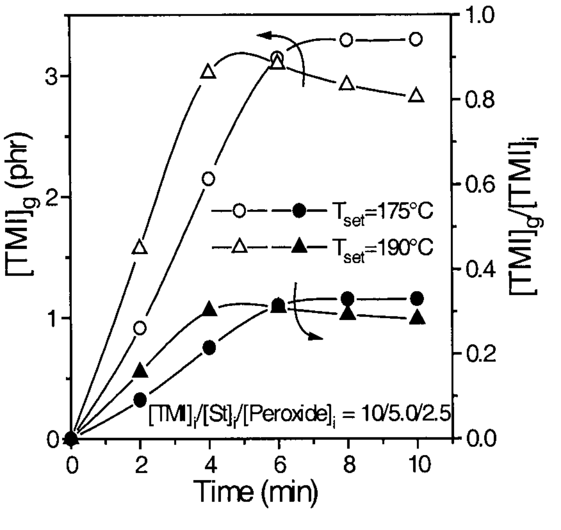

Figure 4 TMI's grafting yield as a function of time for the PP/TMI/St/peroxide (100/10/5/2.5) grafting system at two different set temperatures: 175 and 190°C: (○) TMI's grafting yield, $[TMI]_g$ in phr, for T_{set} = 175°C; (●) TMI's grafting efficiency, $[TMI]_g/[TMI]_i$, for T_{set} = 175°C; (▲) TMI's grafting yield for T_{set} = 190°C; (△) TMI's grafting efficiency for T_{set} = 190°C.

As shown in Figure 5, the material temperature was higher at the higher wall temperature. The corresponding times necessary for melting PP and homogenizing the grafting system were shorter. The time for melting PP was about 1.8 min for a set temperature of 175°C and 1.2 min for a set temperature of 190°C. The peroxide also decomposed more rapidly at the higher set temperature. All those led to an increase in the grafting rate. In fact, during the first 2 min, both PP melting and TMI grafting occurred almost simultaneously and the material temperatures were below their respective set temperatures. The final material temperatures (183 and 197°C) always exceeded their respective set temperatures (175 and 190°C) because of viscous dissipation.

Efficiency of the comonomer concept

Free-radical grafting of monomers onto polymers is often carried out at low peroxide concentrations (<0.5 phr) to reduce side reactions. Previous studies showed that, in the case of PP, adding St as a comonomer greatly improved the monomer grafting yield and reduced PP chain degradation. Since the objective of this study was to obtain as high grafting yields as possible, the monomer and peroxide concentrations had to be much higher than those in the literature. A question then arose of whether the comonomer concept would still work well under those conditions. To answer that question, grafting reactions were carried out under the following conditions: $[TMI]_i$ = 5 or 10 phr, $[peroxide]_i$ = 0 to 5.0 phr, and $[St]_i$ = 0 to 10 phr. Figure 6 shows the effect of adding St on TMI's graft yield as a function of the peroxide concentration. As expected, TMI's graft yield increased with increasing peroxide concentration. As for the effect of St's concentration on TMI's grafting yield, it was very significant at low and moderate peroxide concentrations and vanishes at very high peroxide concentrations. For example, when the peroxide concentration was 1 phr, TMI's graft yield was 1.16 phr without St and 2.16 phr with St (5 phr), almost doubled. The fact that adding St increased TMI's grafting yield confirmed that the comonomer concept worked for the PP/TMI/St/peroxide grafting system. The underlying principle is that when St was added to the PP/TMI/peroxide grafting system it reacted with PP macroradicals much more rapidly than did TMI and the resulting styryl radicals copolymerized readily with TMI. The free-radical reactivity ratios are r_{TMI} = 0.16 and r_{St} = 0.84 for TMI and St, respectively.[4] It should be noted that the positive effect of adding St on TMI's grafting yield was partially counterbalanced by the fact that a fraction of TMI might have been consumed by copolymerization with TMI, leading to a copolymer of TMI and St. This copolymerization decreased the amount of TMI available for the grafting reaction. This is why St's effect on improving TMI's grafting yield was high at a low peroxide concentration and insignificant at a high peroxide concentration. A thorough analysis of St's effects will be made in a forthcoming article.[17]

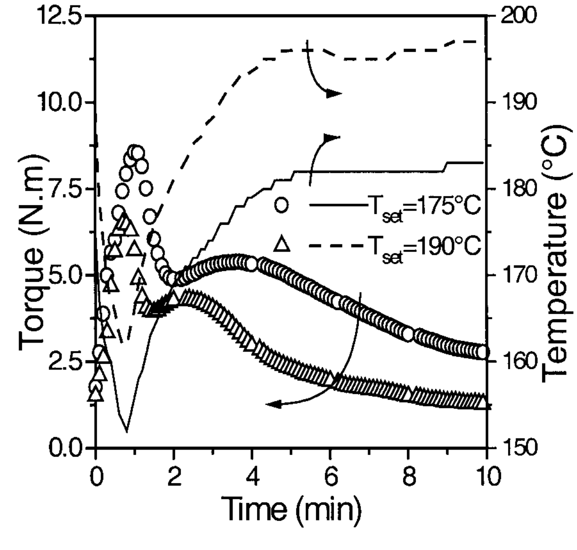

Figure 5 Evolution of torque and material temperature of the PP/TMI/St/peroxide (100/10/5/2.5) grafting system as a function of time for two different set temperatures: 175 and 190°C: (○) torque for T_{set} = 175°C; (△) torque for T_{set} = 190°C; (solid line) material temperature for T_{set} = 175°C; (dashed line) material temperature for T_{set} = 190°C.

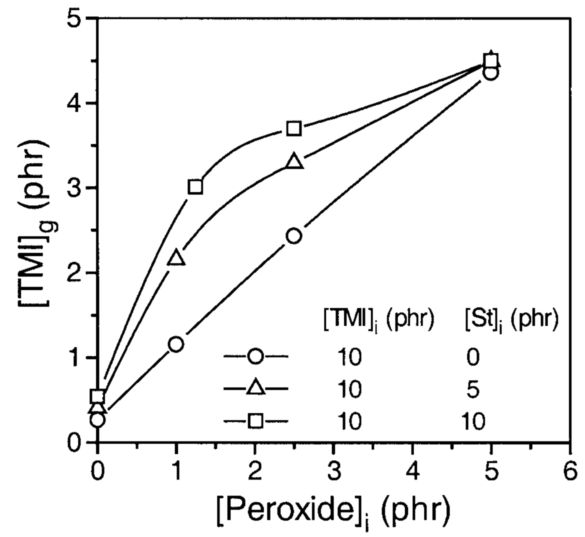

Figure 6 Effect of adding St on TMI's graft yield as a function of the peroxide concentration. $[TMI]_i$ = 10 phr; $[St]_i$ = (○) 0 phr, (△) 5 phr, and (□) 10 phr. Set temperature, 175°C; mixing speed, 64 rpm; mixing time, 10 min.

To better appreciate the combined effects of St and peroxide on TMI's grafting yield, a grafting reaction was carried out upon varying their concentrations to a large extent. As shown in Figure 7, the results are in line with those shown in Figure 6. When the peroxide concentration was low, 0.5 phr, TMI's graft yield was almost doubled by adding 5 phr of St compared with that obtained without St. When it was increased to 2.5

phr, the efficiency of adding St was largely reduced. Moreover, adding St was efficient only when its concentration was below a certain limit, beyond which its effect was insignificant.

Control of the molar mass of PP-*g*-TMI

During free-radical grafting of monomers onto PP, chain degradation is concomitant with grafting per se. The higher the peroxide concentration, the more severe the PP chain degradation is expected to be. It is generally believed that PP chain degradation proceeds through the β-scission mechanism (Fig. 8; path A), by which a tertiary macroradical is transformed into a terminal double bond and a more stable terminal secondary macroradical. The macroradical concentration remains unchanged, while the molar mass of the polymer is reduced. The key to controlling PP chain degradation is to transform highly unstable tertiary macroradicals to more stable species. This can be achieved by promoting grafting, termination, and/or transfer reactions. For example, it was reported that adding a transfer reagent such as stearamide suppressed the β-scission occurring during the free-radical grafting of maleic anhydride onto a copolymer of ethylene and propylene.[18]

Adding St is expected to reduce PP chain degradation. This is because St is able to react rapidly with tertiary macroradicals, transforming the latter to more stable styryl radicals (Fig. 8; path B). PP chain degradation via β-scission is thus prevented. Styryl radicals then copolymerize easily with TMI, allowing the latter to be attached onto the PP backbone. Therefore, the use of St as a comonomer plays two important roles: reduction in PP chain degradation and increase in TMI's grafting yield.

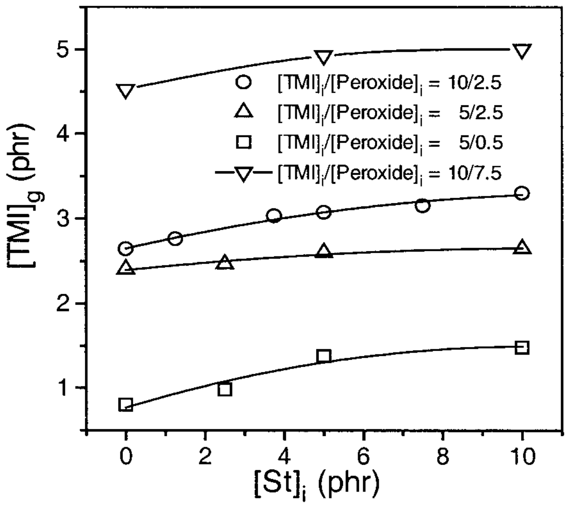

Figure 7 Effect of St's concentration on TMI's grafting yield: (○) $[TMI]_i/[peroxide]_i$ = 10 phr/2.5 phr; (△) $[TMI]_i/[peroxide]_i$ = 5 phr/2.5 phr; (□) $[TMI]_i/[peroxide]_i$ = 5 phr/0.5 phr; (▽) $[TMI]_i/[peroxide]_i$ = 10 phr/2.5 phr. Set temperature, 175°C; mixing speed, 64 rpm; mixing time, 10 min.

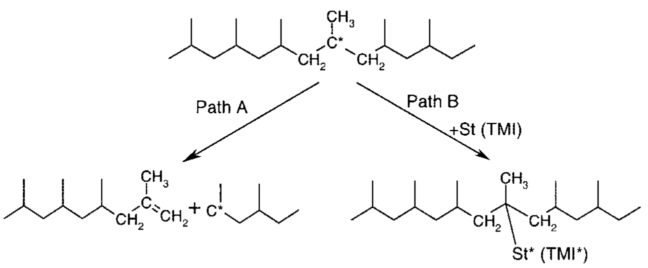

Figure 8 Path A: PP chain degradation through the β-scission mechanism, by which a tertiary macroradical is transformed into a terminal double bond and a more stable terminal secondary macroradical; path B: St or TMI is grafted onto the PP backbone and the free-radical active center is transferred to St or TMI.

The extent of the PP chain degradation during free-radical grafting in the mixer was estimated by the torque value of the grafting system. The latter is a rough measure of the viscosity of the grafting system and the molar mass of the PP. The higher the molar mass of PP, the higher the viscosity of the grafting system and, consequently, the higher the torque value. The torque value, Γ, is related to the mass-average molar mass, M, of the polymer by the following expression (see the Appendix for details):

$$\Gamma = 30 \frac{\Phi(\tilde{T}, \tilde{\dot{\gamma}}, n, \lambda, \ldots)}{\pi\omega} M^{\alpha} \tag{1}$$

where $\tilde{T}$ and $\tilde{\dot{\gamma}}$ are the temperature and shear rate distribution functions, respectively; α, a constant which is about 3.4 at low shear rates; ω, the rotation speed of the rotors in the mixer; and $\Phi(\tilde{T}, \tilde{\dot{\gamma}}, n, \lambda, \ldots)$, a function of temperature and shear rate distribution functions and material constants such as n and λ.

Figure 9 shows the evolution of the torque of the PP/TMI/St/peroxide grafting system as a function of mixing time for various St concentrations. That of the pure PP is also shown as a reference. The effect of adding St on reducing the PP chain degradation is evident. The higher the St concentration, the higher the final torque value and the higher the PP molar mass was expected to be. When its concentration was 7.5 phr, the final torque value of the grafting system was very close to that of the pure PP. This indicates that it is possible to increase the molar mass of PP by free radically grafting St onto it.

The torque value depends on temperature because the latter affects the viscosity of the grafting system. For the experiments shown in Figure 9, the material temperature values after 10 min of mixing were virtually the same (183°C). Therefore, it can be assumed that the material parameters described in eq. (1) be the same. This equation then reduces to

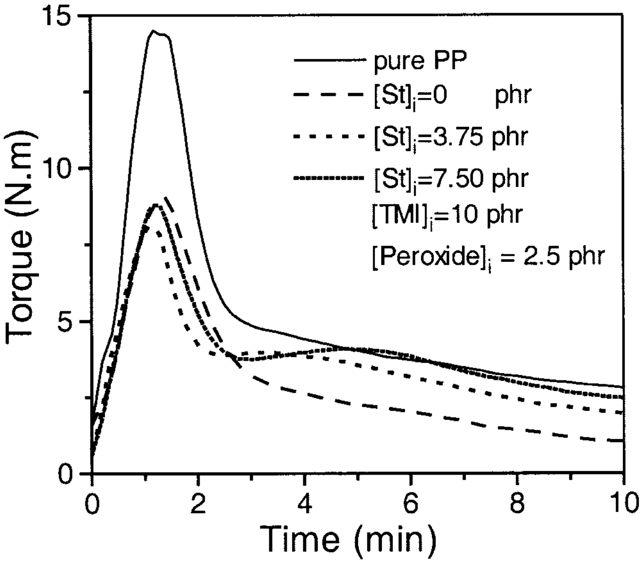

Figure 9 Effect of adding St on the evolution of the torque of the pure PP and those of the PP/TMI/St/peroxide grafting systems as a function of mixing time. $[\mathrm{TMI}]_i = 10$ phr; $[\mathrm{peroxide}]_i = 2.5$ phr.

$$\Gamma = AM^{\alpha}, \tag{2}$$

where A is a constant. Upon applying eq. (2) to the grafting system, one obtains the following expression:

$$\frac{M_{\text{PP-}g\text{-TMI}}}{M_{\text{purePP}}} = \left(\frac{\Gamma_{\text{grafting system}}}{\Gamma_{\text{purePP}}}\right)^{1/\alpha} \tag{3}$$

where M_{purePP} and $M_{\text{PP-}g\text{-TMI}}$ are the mass-average molar masses of the pure PP and TMI-modified PP, respectively, and Γ_{purePP} and $\Gamma_{\text{grafting system}}$ are their respective torque values.

If the shear rate is low enough, the value of α can be taken approximately as 3.4. Equation (3) then becomes

$$\frac{M_{\text{PP-}g\text{-TMI}}}{M_{\text{purePP}}} \approx \left(\frac{\Gamma_{\text{grafting system}}}{\Gamma_{\text{purePP}}}\right)^{0.29} \tag{4}$$

As shown in Table I, the values of the mass-average molar mass of PP-*g*-TMI calculated by eq. (4) were relatively close to those measured by high-temperature size-exclusion chromatography. This implies that torque can be used as a control parameter for the molar mass of the modified polymer. Indeed, it was successfully used to control the molar mass of glycidyl methacrylate-modified PP in a twin-screw extruder.[19] Nevertheless, the calculated values are always slightly higher than are the measured ones. It is not surprising that, considering the assumptions made, some differences exist between the calculated and measured values. It is worthy of noting that the calculated ones are always slightly higher than are the measured ones. If a slightly smaller value of α rather than 3.4 is used, they will become much closer. This may because, under the grafting conditions, the shear rate is such that the viscosity of the grafting system does not correspond to its zero shear rate viscosity. The value of α should then be smaller than 3.4.

TABLE I

Comparison Between the Values of the Mass Molar Mass of PP-*g*-TMI Calculated by Eq. (4) and Those Measured by High-temperature Size-exclusion Chromatography (SEC) For Experiments Shown in Figure 9

St (phr)	Final torque (N m)	$M_{\text{PP-}g\text{-TMI, eq.(4)}}$ (g/mol)	$M_{\text{PP-}g\text{-TMI, SEC}}$ (g/mol)
0	1.0	416,000	401,000
3.75	2.0	509,000	493,000
7.50	2.5	543,000	524,000
Pure PP	2.8	—	561,000

After 10 min of mixing, the mass-average molar mass of the pure PP, M_{purePP}, measured by SEC was 561,000 g/mol.

Effects of TMI's concentration on its grafting yield and grafting efficiency

Figure 10 shows that the initial concentration of TMI on its grafting yield and grafting efficiency for given St and peroxide concentrations (triangles) or given $[\mathrm{St}]_i/[\mathrm{TMI}]_i$ ratio and peroxide concentration (circles). As expected, TMI's graft yield increased and its grafting efficiency decreased with an increasing TMI concentration.

Increasing TMI's grafting yield by stepwise feeding

It was shown above that, in addition to increasing the peroxide concentration, the use of St as a comonomer

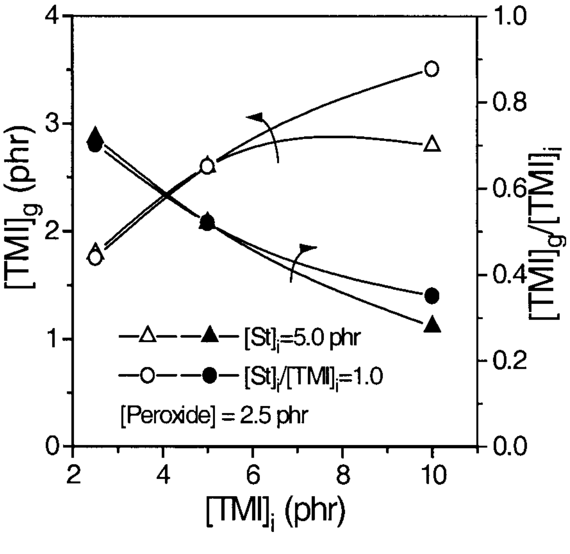

Figure 10 Effects of TMI's concentration on its (open symbols) grafting yield, $[\mathrm{TMI}]_g$ and (closed symbols) grafting efficiency, $[\mathrm{TMI}]_g/[\mathrm{TMI}]_i$ for (triangles) given St and peroxide concentrations or (circles) given $[\mathrm{St}]_i/[\mathrm{TMI}]_i$ ratio and peroxide concentration. $[\mathrm{Peroxide}]_i = 2.5$ phr; (△,▲) $[\mathrm{St}]_i = 5$ phr; (●,○) $[\mathrm{St}]_i/[\mathrm{TMI}]_i = 1$ phr/phr.

is another very efficient strategy for increasing TMI's grafting yield. Moreover, at very high concentrations of peroxide and/or St, further increasing their concentrations does not further increase TMI's grafting yield much (see Figs. 6 and 7). This implies that the strategy which consists of adding very large amounts of TMI, St, and peroxide may not necessarily be efficient for obtaining very high TMI's grafting yields. It would be more efficient if the very large amounts of TMI, St, and peroxide are divided into several fractions. The latter are charged to the mixer one after another after certain time intervals. This way, the amounts of the reactants such as TMI, St, and peroxide are always kept low during the free-radical grating process. This feeding mode is called stepwise feeding. One-pot feeding then refers to situations where the total amounts of the reactants are charged to the mixer at once.

One-pot feeding and stepwise feeding were compared in terms of TMI's grafting yield for the PP/TMI/St/peroxide (100/9/9/3 by weight) grafting system. In both cases, the required amounts of TMI, St, and peroxide were first mixed up, forming a solution. In the case of one-pot feeding, the total amount of the solution was premixed with the required amount of PP. The whole mixture was then charged to the mixer for 10 min of reaction. As for the stepwise feeding, the total amount of the solution was divided into three equal fractions. A fraction of the solution was premixed with the total amount of PP. The whole mixture was then charged to the mixer for reaction. Five minutes later, one of the two remaining fractions of the solution was charged to the mixer. When 3 min elapsed, the last fraction of the solution was charged to the mixer. At this point, the total weight fractions of TMI, St, and the peroxide with respect to that of PP were the same as those of the one-pot feeding. The reaction proceeded for an additional 3 min. As shown in Figure 11, TMI's grafting yield (●) and grafting efficiency (▲) corresponding to the one-pot feeding grafting experiment were 3.1 phr and 34.4%, respectively. As for the stepwise feeding, the final TMI's grafting yield and grafting efficiency were significantly higher, 4.5 phr and 50.0%, respectively. In the latter case, every addition of a fraction of the solution brought about a proportional increase in TMI's grafting yield and its grafting efficiency remained almost the same (50.0%). In other words, stepwise feeding of the solution allowed one to maintain TMI's grafting efficiency at a level that was significantly higher than that of the one-pot feeding (50.0% against 34.4%).

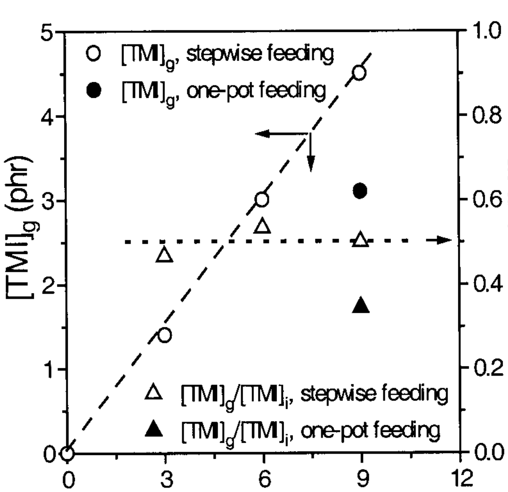

Figure 11 Comparison between one-pot and stepwise feeding grafting experiments in terms of TMI's grafting yield and grafting efficiency for the PP/TMI/St/peroxide (100/9/9/3) grafting system.

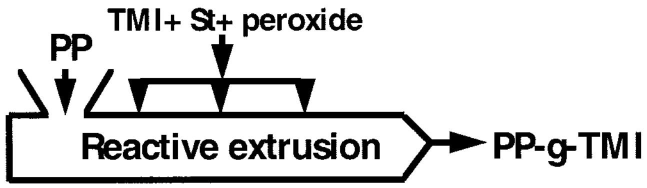

Figure 12 Scheme of parallel feeding for free-radical grafting by reactive extrusion: A grafting solution composed of a grafting monomer (TMI), a comonomer (St), and a peroxide is fed to the extruder at various locations along the extruder length. This way, the weight fraction of the grafting solution is always kept low with respect to that of the grafting polymer (PP).

If the free-radical grafting is to be carried out by reactive extrusion, the above stepwise feeding mode can easily be adopted upon feeding the first fraction of the solution in the main hopper and the second and third ones further down stream at two different locations along the extruder length. For the sake of safety and health reasons, it would be better not to feed the first fraction of the solution in the main hopper but further downstream of the extruder length. This is described schematically in Figure 12. This feeding mode can be called "parallel feeding." The literature reported that, for this type of feeding, screw designs and flow patterns at these injection locations are very important for ensuring adequate mixing between the low viscosity solution and the high viscosity polymer melt.[12]

To simulate the possibility of obtaining very high TMI grafting yields by a reactive extrusion process, three stepwise feeding grafting experiments were done in the batch mixer with three solutions of TMI, St, and the peroxide. The weight fractions of TMI, St, and the peroxide, TMI/St/peroxide, were 10/5.0/1.25, 10/5.0/2.50, and 10/2.5/2.50, for the first, second, and third solutions, respectively. The first stepwise feeding grafting experiment was done by premixing a given amount of the first solution with a given amount of PP such that the weight fractions of PP, TMI, St, and the peroxide, PP/TMI/St/peroxide, were 100/10/5.0/1.25. That mixture was then charged to the mixer for reaction. A certain amount of the

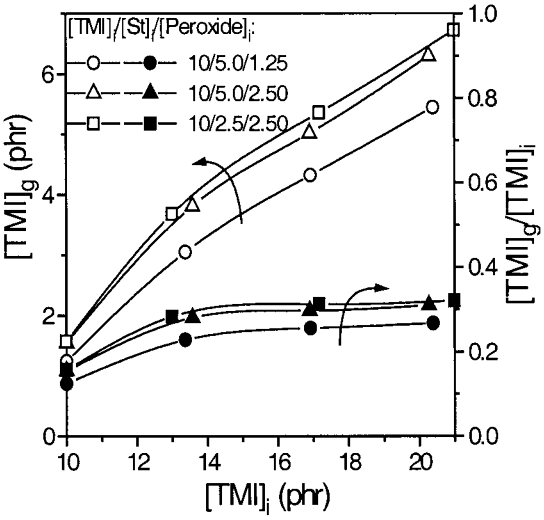

Figure 13 Stepwise feeding grafting experiments in the batch mixer for the PP/TMI/St/peroxide grafting system. Three solutions of TMI, St, and the peroxide were tested. Their weight fractions in those solutions were [TMI]/[St]/[peroxide] = (△,▲) 10/5/1.25 for the first solution, and (○,●) 10/5/2.5 for the second solution, and (□,■) 10/2.5/2.5 for the third solution.

solution was added to the mixer after every 3 min of the reaction. The second and third stepwise feeding grafting experiments were carried out in the same manner using the second and third solutions, respectively. For all three stepwise feeding experiments, TMI's grafting yield increased almost linearly with the amounts of the grafting solutions, except for the first experimental points (Fig. 13). Those results confirmed the great interest of stepwise feeding for free-radical grafting in a batch mixer and that of parallel feeding for reactive extrusion in a screw extruder. The fact that the first experimental points were lower could be explained as follows: First, the reaction times corresponding to the first experimental points were less than 3 min because certain times were necessary for melting PP and homogenizing the grafting systems. Second, losses in reactants could have been inevitable because of feeding the very large amounts of TMI, St, and the peroxide. Moreover, the corresponding TMI grafting efficiency was expected to be lower.

Why did TMI's grafting yield increase linearly with its concentration in the stepwise feeding grafting experiments while it increased with a much smaller pace in the one-pot feeding grafting experiment? A free-radical grafting process starts with the formation of macroradicals along polymer chains by the so-called hydrogen abstraction mechanism.[1] In PP, each propylene moiety contains one tertiary hydrogen atom, two secondary hydrogen atoms, and three primary hydrogen atoms. Their concentrations are 0.238, 0.475, and 0.713 mpr (moles per hundred grams of resin, PP), respectively. This means that even if TMI's grafting yield is as high as 10 phr (0.0497 mpr) it represents only one-fifth of the molar number of the tertiary hydrogen atoms. In other words, the molar fraction of the tertiary hydrogen atoms of PP consumed by the grafting reaction per se is very small. Therefore, every additional amount of the grafting solution charged to the mixer leads to a proportional increase in TMI's grafting yield, as if one started a new grafting reaction with a previously TMI-modified PP.

CONCLUSIONS

In this article, two strategies were reported to obtain very large amounts of grafted TMI onto PP in the melt by a free-radical mechanism using an internal batch mixer as the reactor. The first one is to apply the comonomer concept developed in the literature using styrene as the comonomer. The second one is to feed very large amounts of TMI, St, and the free-radical generator in various fractions (stepwise feeding), instead of feeding them at once (one-pot feeding). While both strategies are useful for improving TMI's grafting yield and grafting efficiency, when combined, the magnitude of improvement is much greater, especially for very high concentrations of TMI, St, and the free-radical generator. All these results imply that if the free-radical grafting is to be carried out by reactive extrusion in a screw extruder, much higher grafting yields will be obtained if TMI, St, and the free-radical generator are charged to the extruder at different locations along the extruder length (parallel feeding). This is especially so if the their weight fractions are very high with respect to that of the polymer (PP).

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APPENDIX

Relationship between torque and molar mass

Torque is a process parameter that can be easily measured in an internal batch mixer. Since it is a rough measure of the viscosity of the material, it is often used as a qualitative indicator of degradation, crosslinking, or polymerization.

For an incompressible fluid in an internal batch mixer, the mechanical energy is consumed by viscous dissipation. It is easy to show that the mechanical energy input rate, $\dot{E}_m$ (J/s), has the following formula:

$$\dot{E}_m = \frac{\partial E_m}{\partial t} = \frac{1}{30} \pi \Gamma \omega \qquad (A.1)$$

where Γ is the torque (N m), and ω, the rotation speed (rpm). The energy consumption rate, $\dot{E}_s$ (J/s), by viscous dissipation is

$$\dot{E}_s = \iiint_V (\tau : \nabla u)d\Omega \tag{A.2}$$

where τ is the stress tensor; ∇u, the velocity gradient; and V, the space occupied by the fluid. For a generalized Newtonian fluid, the constitutive equation is

$$\tau = \eta \vec{\dot{\gamma}} \tag{A.3}$$

where η is the viscosity, which is a function of temperature, pressure, and the second invariant of the shear rate tensor, and $\dot{\gamma}$, the shear rate tensor. Substituting eq. (A.3) into (A.2) leads to

$$\dot{E}_s = \iiint_V \left(\frac{1}{2}\,\eta \vec{\dot{\gamma}} : \vec{\dot{\gamma}}\right) d\Omega = \iiint_V (\eta \dot{\gamma}^2) d\Omega \tag{A.4}$$

where $\dot{\gamma}$ is a scalar and is defined as

$$\dot{\gamma} = \tfrac{1}{2}\,(\vec{\dot{\gamma}} : \vec{\dot{\gamma}}) \tag{A.5}$$

Several models can describe the viscosity in eq. (A.4). If the Carreau model is used, then eq. (A.4) becomes

$$\dot{E}_s = \iiint_V \{\eta_0 \dot{\gamma}^2 [1 + (\lambda \dot{\gamma})^2]^{(n-1)/2}\} d\Omega \tag{A.6}$$

where η_0 is the zero shear rate viscosity, and λ and n, constants which are related to material properties. If the fluid is a single polymer whose molar mass is M, then its zero shear rate viscosity is related to M by the following equation:

$$\eta_0 = K(T) M^{\alpha} \tag{A.7}$$

where $K(T)$ is a function of temperature and the characteristics of the polymer and α is a constant of about 3.4. Combining eqs. (A.6) and (A.7) leads to

$$\dot{E}_s = M^{\alpha} \iiint_V \{K(T) \dot{\gamma}^2 [1 + (\lambda \dot{\gamma})^2]^{(n-1)/2}\} d\Omega \tag{A.8}$$

Equation (A.8) can be rewritten as

$$\dot{E}_s = M^{\alpha} \Phi(\tilde{T}, \tilde{\dot{\gamma}}, n, \lambda, \ldots) \tag{A.9}$$

where $\tilde{T}$ and $\tilde{\dot{\gamma}}$ are the temperature and shear rate distribution functions, respectively, and $\Phi(\tilde{T}, \tilde{\dot{\gamma}}, n, \lambda, \ldots)$ is a function of temperature and shear rate distribution functions and material properties such as n and λ.

Since the viscous dissipation rate is equal to the mechanical energy input, eq. (A.9) is equal to eq. (A.1). This leads to the relationship between torque and molar mass of the polymer:

$$\Gamma = 30\, \frac{\Phi(\tilde{T}, \tilde{\dot{\gamma}}, n, \lambda, \ldots)}{\pi \omega} M^{\alpha} \tag{A.10}$$

It is important to note that, for a given rotation speed, a variation in torque can be directly related to a variation in molar mass only when the temperature and shear rate distribution functions are the same and the polymer properties are not changed except for its molar mass.

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