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Influences of grafting formulations and processing conditions on properties of silane grafted moisture crosslinked polypropylenes

N.C. Liu*, G.P. Yao, H. Huang

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

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Abstract

The melt grafting of unsaturated silanes onto powdered polypropylene (PP) in a Haake Rheocord RC90 batch mixer and curing in hot water were studied. The influences of grafting formulations and processing conditions on the equilibrium torque during processing and the gel percentage of crosslinked PP were investigated. The gel percentages of methacryloylpropyltrimethoxysilane (VMMS) grafted PP were markedly higher than those of vinyltriethoxysilane (VTES) grafted PP, while significantly less degradation of PP during grafting was observed for VMMS grafted PP. When benzoyl peroxide (BPO) was used as initiator, only a minor degradation of PP during grafting was observed; whereas the use of dicumyl peroxide (DCP) as initiator resulted in severe degradation of PP, especially at high DCP concentrations. Introduction of styrene into the grafting system greatly improved the gel percentage of crosslinked PP and reduced the degradation of PP during grafting. Processing temperature and initial particle size of PP also had influences on both gel percentages and degradation of PP. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polypropylene; Crosslinking; Silane

1. Introduction

Polyolefins are the largest volume family of commercially important high-tonnage thermoplastic polymers. Crosslinking of polyolefins may improve their high temperature properties and extend their applications. Peroxide crosslinking, radiation crosslinking, and silane crosslinking are the three main ways of crosslinking employed industrially [1]. Both radiation and peroxide crosslinking techniques suffered some disadvantages such as high investment cost and thickness limitation in radiation crosslinking, and the risk of pre-curing and high production cost in peroxide crosslinking.

In silane crosslinking technique, unsaturated hydrolyzable alkoxysilanes are first grafted onto or copolymerized into polyolefins, grafted (or copolymerized) products are then processed and shaped using conventional thermoplastic processing equipment, followed by catalyzed crosslinking of the shaped products in the presence of trace amounts of water. The silane crosslinking technique offers technological advantages and improvements in many useful properties of silane crosslinked polyolefins in comparison with radiation and peroxide crosslinked polyolefins. Munteanu [2,3] has reviewed the state of the art of moisture crosslinkable silane modified polyolefins. Although silane-modified polyolefins have become an industrial method employed in practice, the literature concerning polyolefin crosslinking by silane grafting consists mainly of patents [2,3]. Little data have been published on the dependence of silane grafting reactions and the properties of crosslinked polyolefins on reaction parameters [4–10].

Crosslinking of polyolefins may be applied to all polyolefin types; however, the vast majority of the publications are concerned with polyethylenes. Few studies concerning the crosslinking of polypropylene (PP) has been reported [11,12]. Crosslinking of PP gained no practical importance. This is most likely a consequence of the nature of the PP chain structure. Chain scission (β-scission) is the dominant reaction in PP when subjected to free radicals at elevated temperatures during processing. Crosslinking of PP by peroxide may only be performed with extremely high peroxide concentrations at low temperatures or in the presence of multifunctional crosslinking co-agents [13–18].

Crosslinking of PP via silane grafting and moisture curing has rarely been reported. Cartasegna [10] reported that a sample of PP, subjected to the same silane grafting and subsequent curing procedure as used for crosslinking other polyolefins, gave a complete absence of insoluble gel. In other studies [19–22], silane crosslinked PP has only been

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* Corresponding author.
E-mail address: ncliu@mail.sjtu.edu.cn (N.C. Liu).

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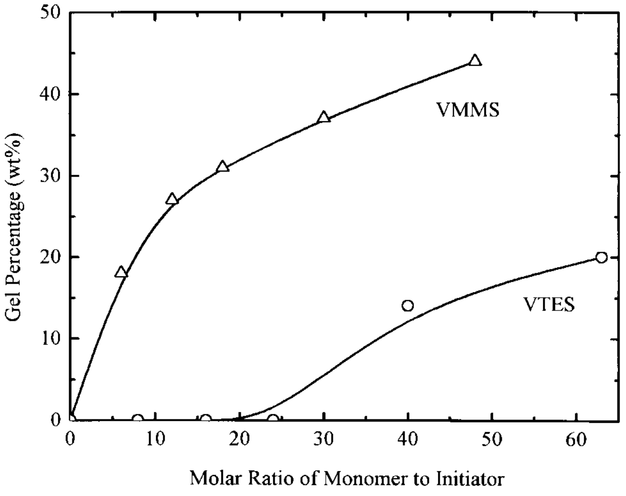

Fig. 1. Influence of the type and amount of monomers on the gel percentage of crosslinked PP (DCP: 0.67 mmol/100 g PP).

obtained under severe processing conditions and strict grafting formulation requirements such as extremely high silane and initiator concentrations.

In this paper, silane crosslinking of PP was studied. The influences of grafting formulations and processing conditions on the equilibrium torques during melt processing and gel percentages of crosslinked PP were investigated.

2. Experimental

2.1. Materials

The starting material was a powdered isotactic PP supplied by Shanghai Petrochemical Complex. It had a melt flow rate of 6.7 dg/min (ASTM D1238, 230°C and 2.16 kg). Silane monomers, methacryloylpropyltrimethoxysilane (VMMS) and vinyltriethoxysilane (VTES), were provided by Osi Specialties Asia Ltd. Initiators dicumyl peroxide (DCP) and benzoyl peroxide (BPO), catalyst dibutyltindilaurate, additives styrene and ethylene glycol dimethacrylate were analytical grade and used as received.

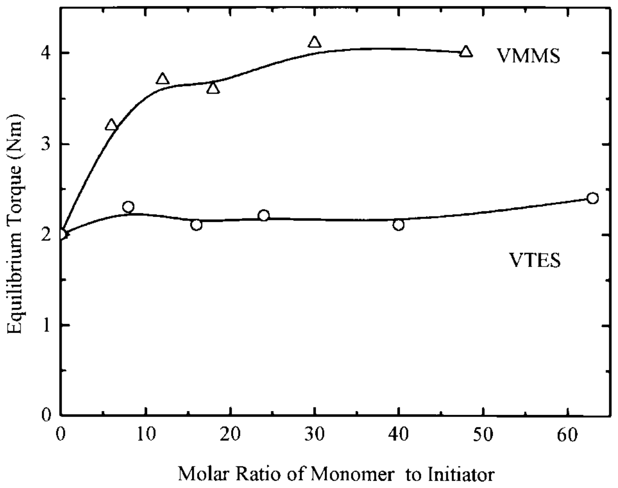

Fig. 2. Influence of the type and amount of monomers on the equilibrium torque during processing (DCP: 0.67 mmol/100 g PP).

2.2. Grafting procedure

The grafting reaction was carried out in a Haake Rheocord 90 batch mixer equipped with roller blades. A 45 g charge of powered PP was dry blended with desired amounts of monomers, initiators, and additives, and then fed into the mixer, which already had been adjusted to required conditions. The reaction temperature was 180°C unless otherwise specified. The reaction time and mixing speed were maintained at 9 min and 100 rpm, respectively, for all runs. 2.2 g of catalyst concentrate was added into the mixer after 6 min of reaction. Catalyst concentrate was prepared by extruding four parts of dibutyltindilaurate with 100 parts of PP in a twin screw extruder at 190°C and 30 rpm. The catalyst concentrate was extruded twice in order to obtain uniform distribution of the catalyst.

The equilibrium torque required to process a polymer is proportional to the intrinsic viscosity of the polymer, which is in turn a direct measure of the molecular weight of the polymer. Therefore, the equilibrium torque may be used to indicate the degradation or crosslinking of a polymer during melt processing. In this paper, equilibrium torques were calculated from the average torques during the last 2 min of processing.

2.3. Determination of gel percentages

The reaction products from Haake mixer were ground into small pellets and compression molded into thin sheets of 1 mm thick. The sample sheets were then immersed in boiling water for 6 h, allowing for the hydrolyzation of alkoxy groups and formation of three-dimensional networks. The hydrolyzed samples were dried and cut into small pieces with sizes of about 1 mm.

The crosslinking ability was compared by measuring the percentages of insoluble gel after extraction in refluxing xylene. 0.2–0.3 g of a sample was packaged in a copper cloth of 120 mesh and extracted with refluxing xylene for 12 h using a Soxhlet extractor. Samples were dried in a vacuum oven at 120°C for 24 h. The gel percentage of crosslinked PP was calculated as the percentage of the weight remaining with respect to the initial weight. At least three extractions were performed for each sample and the average gel percentages were calculated and used for discussion.

3. Results and discussion

3.1. Influences of monomer type and concentration

Fig. 1 shows the influences of monomer type and concentration on the gel percentages of crosslinked PP. With increasing molar ratio of monomer to initiator, the gel

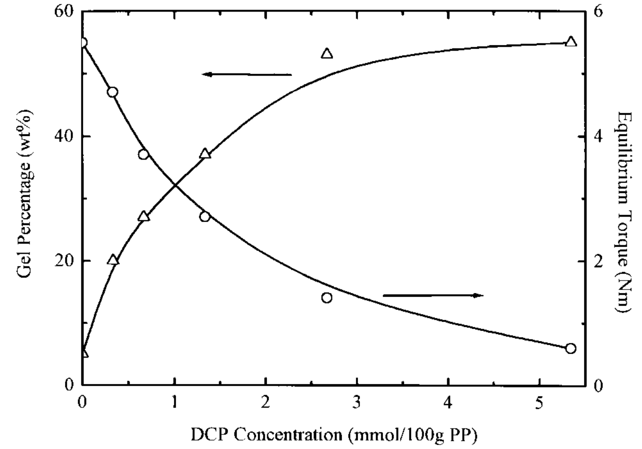

Fig. 3. Influence of initiator concentration on the gel percentage of VMMS crosslinked PP and equilibrium torque during processing (VMMS: 8.0 mmol/100 g PP).

percentages of VMMS crosslinked PP increased rapidly from zero to about 30 wt% at low molar ratios, and the gel percentage increased slowly at high molar ratios. In the case of VTES as monomer, no insoluble gel was obtained even when the molar ratio of monomer to initiator was increased to 24, after which slow increases in gel percentages were observed. These indicate much greater grafting and crosslinking efficiency of VMMS than VTES, which is probably a result of large steric hindrance in the case of VTES since the reactive sites are close to the bulky triethoxysilane groups. Further, the conjugated structure in VMMS could improve grafting efficiency by stabilizing macroradicals of VMMS grafted PP.

The influences of monomer type and concentration on the degradation of PP during grafting are shown in Fig. 2. Without any monomer in the system, the equilibrium torque dropped remarkably to about 2 N m in the presence of peroxide compared to 5.6 N m for processing PP alone, indicating severe degradation of PP during processing with initiator but no monomer. With the introduction of VMMS in the grafting system, the equilibrium torque quickly reached a level of about 4 N m, indicating reduced degradation of PP during grafting. In the case of VTES, however, the equilibrium torque kept almost constant even when relatively high gel percentages were obtained. These again could be a result of large steric hindrance in VTES grafted PP macroradicals, which inhibits the termination of macroradicals by combination. In addition, stabilization of VMMS grafted PP macroradicals by conjugation could increase the possibility of termination by combination.

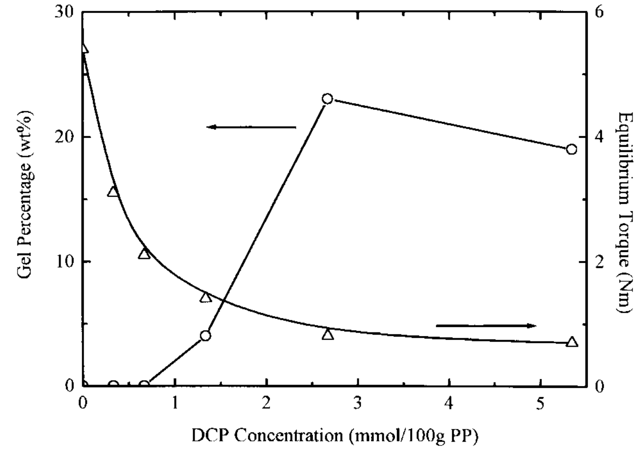

Fig. 4. Influence of initiator concentration on the gel percentage of VTES crosslinked PP and equilibrium torque during processing (VTES: 10.0 mmol/100 g PP).

3.2. *Influences of initiator type and concentration*

Fig. 3 shows the influence of DCP concentration on the gel percentages of VMMS crosslinked PP and equilibrium torques during processing. With increasing DCP concentration, the gel percentage increased gradually to a high level of about 55 wt% after which no significant increases were observed. The equilibrium torque during processing decreased rapidly with increasing DCP concentration and reached a very low value of 0.6 N m at a DCP concentration of about 5.3 mmol/100 g PP, indicating that severe degradation of PP occurred at high DCP concentrations. When VTES was used (Fig. 4), the degradation of PP was severe even at relatively low DCP concentrations; no insoluble gel was obtained at DCP concentrations below 1 mmol/100 g PP. These further confirm the low grafting and crosslinking efficiency of VTES as monomer.

Fig. 5 shows the influences of initiator type on the gel percentages of crosslinked PP. In order to compare the performance of BPO and DCP at the same half-life time of about 1 min, the processing temperature was set to 130°C when BPO was used as initiator, the processing temperature finally increased to about 170°C as a result of shearing and viscous dissipation. In the ranges studied, BPO resulted in higher gel percentages than DCP at a fixed initiator concentration. More importantly, BPO showed very different behavior when degradation of PP during processing is considered (Fig. 6). The equilibrium torque of PP processed with BPO but no monomer was about 5.3 N m, which is rather high, indicating that degradation of PP during processing was minor. Firstly, this is due to the low processing temperature used in the case of BPO, PP macroradicals are more stable at low temperatures and thus termination of PP macroradicals by combination is preferred instead of disproportionation. Secondly, the different nature of BPO and DCP may also be a reason for such behavior; BPO radicals have a larger tendency of termination by combination with PP macroradicals than DCP radicals as a result of smaller steric hindrance, reducing the possibility of PP macroradicals terminated by disproportionation.

In contrast to the case of DCP, the extent of PP degradation with BPO as initiator increased slightly with increasing

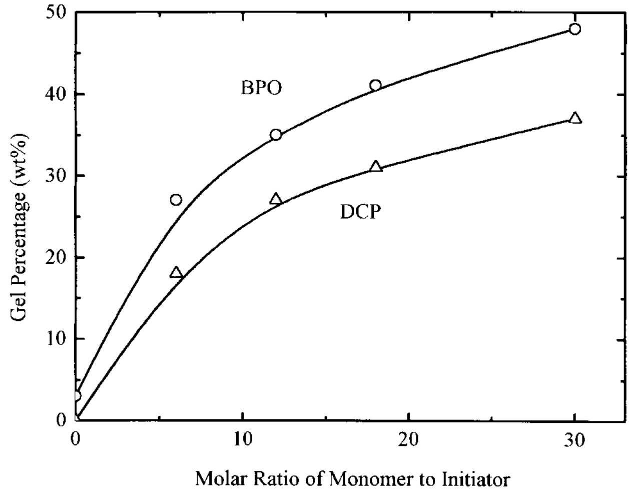

Fig. 5. Influence of the type of initiators on the gel percentage of crosslinked PP (Initiator: 0.67 mmol/100 g PP; set processing temperature was 130°C when BPO was used as initiator).

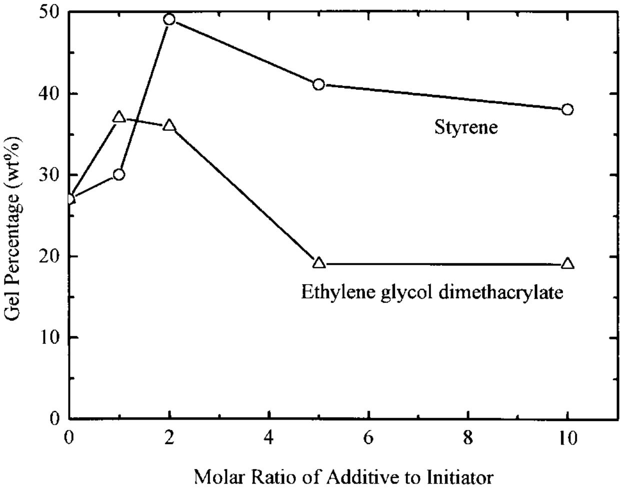

Fig. 7. Influence of the type and amount of additives on the gel percentage of crosslinked PP (DCP: 0.67 mmol/100 g PP; VMMS: 8.0 mmol/100 g PP).

molar ratio of monomer to BPO as indicated by the reduction in equilibrium torques. In the case of DCP without monomer, severe degradation of PP occurred; with increasing monomer concentration, more PP macroradicals may be terminated by grafting of monomer onto the macroradicals, reducing the amount of PP macroradicals terminated by disproportionation. In the case of BPO without monomer, no significant degradation of PP occurred; with increasing monomer concentration, more BPO radicals are consumed by reaction with monomer, reducing the possibility of PP macroradicals terminated by combination.

3.3. *Effects of additives*

Two additives, styrene and ethylene glycol dimethacrylate, were chosen to improve the crosslinking efficiency of unsaturated silanes. The effects of additive type and amount on the gel percentages of crosslinked PP are shown in Fig. 7. The gel percentages increased markedly with the introduction of styrene in the ranges studied, and went through a maximum of about 50 wt% at a molar ratio of styrene to initiator of 2. The introduction of ethylene glycol dimethacrylate improved the gel percentage only at low molar ratios of additive to initiator. Fig. 8 shows the effects of additive type and amount on the equilibrium torques during processing. Both styrene and ethylene glycol dimethacrylate were effective in reducing the degradation of PP during grafting; nevertheless, ethylene glycol dimethacrylate was more effective than styrene, especially when large amounts of additives were used. This is probably because ethylene glycol dimethacrylate is a multifunctional additive and can

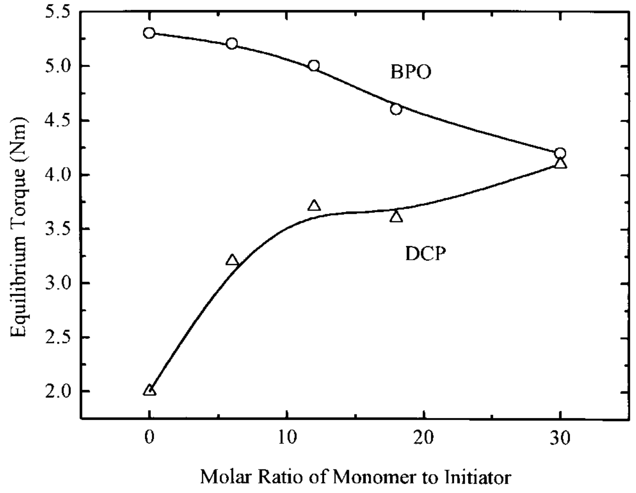

Fig. 6. Influence of the type of initiators on the equilibrium torque during processing (Initiator: 0.67 mmol/100 g PP; set processing temperature was 130°C when BPO was used as initiator).

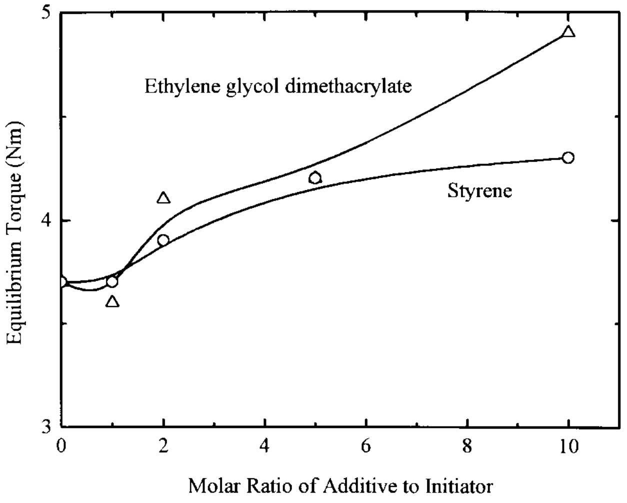

Fig. 8. Influence of the type and amount of additives on the equilibrium torque during processing (DCP: 0.67 mmol/100 g PP; VMMS: 8.0 mmol/100 g PP).

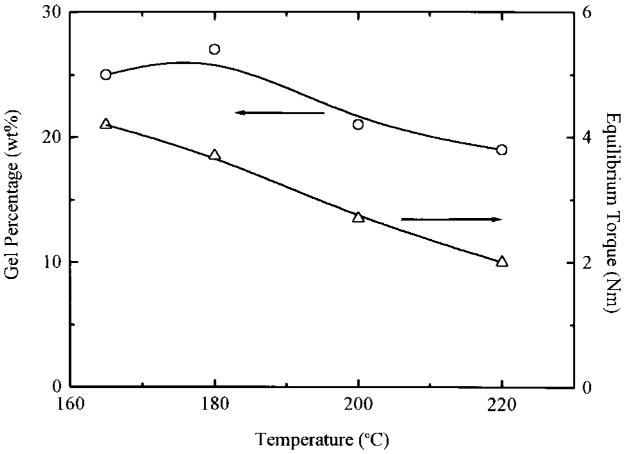

Fig. 9. Influence of processing temperature on the gel percentage of crosslinked PP and equilibrium torque during processing (DCP: 0.67 mmol/100 g PP; VMMS: 8.0 mmol/100 g PP).

minimize unwanted side reactions such as chain scission and disproportionation [11,12].

3.4. Effects of processing temperature and initial particle size of PP

The influences of processing temperature on the gel percentages of crosslinked PP and equilibrium torques during processing are shown in Fig. 9. The gel percentages of crosslinked PP went through a maximum at a processing temperature close to 180°C. Equilibrium torques during processing decreased almost linearly with increasing temperature. This should be the combined effects of increased temperature itself and increased degradation of PP at high processing temperatures, which is in agreement with literature reports [18]. Therefore, processing temperatures between 170 and 180°C may be the optimum choices considering both gel percentage and degradation of PP.

It was reported in a patent [22] that the initial particle size of PP must be smaller than 500 μm in order to obtain high gel percentages of crosslinked PP. The powdered PP was separated into several fractions with various particle size ranges by sieving. The influences of initial particle size of PP on the gel percentages of crosslinked PP and equilibrium torques during processing are shown in Table 1. There seemed to exist an optimum initial particle size range of about 190–300 μm at which the highest gel percentage of crosslinked PP and least degradation of PP during grafting were observed. Large particle sizes may cause insufficient mixing of PP with monomers and initiators before processing, which is not favorable for grafting. On the contrary, monomers and initiators can be mixed uniformly with very small particles; however, this would cause relatively low localized radical concentration at fixed monomer and initiator concentrations, reducing the possibility of grafting reaction of PP macroradicals with monomer or termination reaction of PP macroradicals with monomer radicals.

Table 1
Influence of initial PP particle size on the gel percentage of crosslinked PP and equilibrium torque during processing

Particle size (μm)	Gel percentage (wt%)	Equilibrium torque (N m)
53–107	29	3.0
107–190	34	3.5
190–300	39	4
300–740	33	3.7
53–740 (original sample without separation by sieving)	29	3.7

Among the samples studied, the original sample before sieving had the lowest gel percentage after crosslinking, indicating that narrow distribution of the initial particle size of PP is favorable for improving the gel percentage of crosslinked PP.

4. Conclusions

Effects of the type and amount of monomer on the gel percentage of crosslinked PP and degradation of PP during grafting were remarkable. The gel percentages of VMMS grafted PP were much higher than those of VTES grafted PP, while less degradation of PP during grafting was observed for VMMS grafted PP.

DCP and BPO showed different behaviors. When BPO was used as initiator, only minor degradation of PP during grafting was observed, and the extent of PP degradation increased slightly with increasing monomer concentration at a fixed initiator concentration; whereas the use of DCP as initiator resulted in severe degradation of PP. BPO resulted in higher gel percentages than DCP.

Introduction of styrene into the grafting system markedly improved the gel percentage of crosslinked PP and reduced the degradation of PP during grafting. Ethylene glycol dimethacrylate showed a better performance in reducing the degradation of PP during grafting, but it was not as effective in improving the gel percentage of crosslinked PP.

Equilibrium torques during processing decreased almost linearly with increasing temperature as a result of increased temperature itself and increased degradation of PP. Processing temperatures between 170 and 180°C would be optimum choices considering both gel percentage and degradation of PP.

There seemed to exist an optimum initial particle size range of about 190–300 μm for improving the gel percentage of crosslinked PP and reducing the degradation of PP during grafting. Narrow distribution of the initial particle size of PP was favorable for improving the gel percentage of crosslinked PP.

Acknowledgements

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