

Research Article

Organically Modified Montmorillonite as Nanoreactor to Improve the Grafting Degree of Maleic Anhydride onto Polypropylene

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The application of an organically modified montmorillonite nanoreactor in the reactive extrusion process of the free radical grafting of maleic anhydride onto polypropylene (PP) can increase the MAH grafting degree on the PP. The mechanism of grafting was studied by using transmission electron microscopy and high temperature gel permeation chromatography. It was found that both the strong interactions between MAH and MMT surface and the encapsulation effect of active species confined in o-MMT improved the grafting degree.

1. Introduction

The functionlization of polypropylene (PP) through grafting unsaturated monomers such as maleic anhydride (MAH) and its derivatives, in the presence of organic peroxide as an initiator, has received much attention over the past decades. The modified PP has been used extensively for compatibilization of immiscible polypropylene-polyamide and polypropylene-polyester blends, as well as to improve the interfacial adhesion of PP with glass and carbon fibers, and even as a processing aid for degradable plastic. Functionalized PP has been prepared successfully by using solution [1], melt [2], and solid state routes [3, 4] Among them, the melt process has widely been used in the industry owing to its economic and operational advantages.

However, the grafting degree of MAH onto PP is low. During the past few decades, to find a way of improving the grafting degree of MAH, many studies have focused on the grafting mechanism [1, 2, 5–7], but few on the grafting method. In the past decade, a variety of mesoporous materials such as MCM-41, FSM-16, SBA-15, MCM-48, and layered silicate, mesoporous silica have been used as a nanoreactor in olefin polymerization [8–10]. Among nanoreactors with small particle size, montmorillonite (MMT) is one of the most widely used ones that have very small micron-sized particles. The layers of MMT have thickness of about 1 nm and length of 100 nm or a little more [11–13]. A large surface area, nonhazardous nature, noncorrosiveness, low cost, nanosized, ease of handling, high stability, and simple processing are the featured properties of MMT. It has nanolayered aluminosilicate clay where one octahedral alumina sheet is sandwiched between two tetrahedral silica sheets, and can act as a nanoreactor for the chemical reactions and a drug nanocarrier [14–16].

On the basis of a detailed study on the molecular structure of MAH-grafted PP and the results of the literature [5, 6], Shi et al. presented the concept of nanoreactors of organically modified montmorillonite [17–19]. Preconfinement of dicumyl peroxide (DCP) in the nanometer-scale galleries of an o-MMT allowed concentrating MAH molecules on its outer surface and slowing down the release of primary radicals to the grafting reaction volume. Consequently, the selectivity of the grafting of MAH onto PP was significantly increased, and the encapsulation effect of active species preconfined in organically modified montmorillonite was considered the primary reason. In this work, organically modified montmorillonite (o-MMT) was used as a nanoreactor. Not only were the preconfinement effect of the MMT and the relationship between MMT and MAH considered, but also the mechanisms of the grafting were studied.

2. Experimental

2.1. Materials. The PP powder used in this work was kindly supplied by Sinopec Yangzi petrochemical Company Ltd. The peroxide, DCP (98%), and the monomer, MAH, were purchased from Sinopharm Chemical Reagent Co. Ltd. They were used without further purification. Organically modified MMT denoted as o-MMT (Nanomer I.44PA) was purchased from Amcol Inc, USA.

2.2. Confinement of Peroxide in o-MMT. A given amount of the o-MMT was charged to 100 ml of acetone. The o-MMT/ acetone mixture was homogenized under ultrasound for 1 h. In parallel, a prescribed amount of DCP was dissolved in 10 ml of acetone. Thereafter, the solution of DCP in acetone was added slowly to the abovementioned o-MMT/acetone mixture under continuous stirring. The mass ratio of the o-MMT and DCP was 1/1. The whole system was kept stirred for 3 h at room temperature before it was cast onto a polytetrafluoroethylene plate. The o-MMT confined DCP was denoted as DCP/o-MMT and was obtained after acetone was evaporated completely at room temperature. The DCP/o-MMT powder was then dried in a vacuum oven at 35°C for 24 h before use for subsequent free radical grafting reactions.

2.3. Melt Free Radical Grafting of MAH onto PP. The grafting reaction was carried out in a Haake batch mixer (HBI system 90) equipped with a mixing chamber and two rotors inside at 190°C for 7 min. The rotation speed of the mixer was at 65 rpm. The materials (MAH, PP powder, and (DCP/o-MMT) powder) were premixed and then charged to mixer simultaneously. For comparison a purpose, the same grafting reaction was carried out in a conventional manner; i.e., DCP was not preconfined in the o-MMT. The concentrations of DCP in each system were kept the same. After the grafting, PP-g-MAH products were dissolved in hot xylene and then precipitated in acetone. The precipitates were further washed twice with acetone to completely remove MAH residues. The washing steps were repeated three times more to remove DCP and MAH monomers and homopolymerized MAH oligomers. The purified PP-g-MAH products were dried in a vacuum oven at 80°C for 12 h for subsequent analyses.

2.4. Measurement of Content of MAH. The contents of MAH in products purified once and four times were measured by a chemical titration method described previously [17, 20].

2.5. Measurement of the Molar Masses of PP-g-MAH. The molar masses of PP-g-MAH samples were measured using a high temperature GPC of GPC V2000 Waters. A differential refractometer detector coupled with a "chromatography data station" provided by Digital was used for recording and

analyzing the signal. 1,2,4-Trichlorobenzene was used as the eluent. The samples were dissolved in 1,2,4-trichlorobenzene at 150°C, and the PP-g-MAH concentrations were in the range of 2.5–3.5 mg/ml. The injected volume was $200 \,\mu$ L, and the eluent flow rate was 1.0 ml/min. The whole measuring system was maintained at 150°C.

2.6. Characterization of o-MMT Dispersion. Characterization of o-MMT particle or platelet dispersion was carried out using transmission electron microscopy (TEM). For the TEM analysis, it was used a JEOL model JEM-1230 (Jeol Japan Inc.). As polypropylene is a soft polymer, the use of an ultramicrotome (RMC model MTXL) in cryogenic conditions was needed to cut samples for TEM analysis.

3. Results and Discussion

Figure 1 shows the dispersion of o-MMT particles or platelets in PP or PP and PP-g-MAH phase. Three types of samples were investigated: PP/o-MMT (without pretreatment) mixture blending in the Haake batch mixer without reaction (Figure 1(a)), PP/o-MMT/DCP/MAH mixture after reaction and purification, where DCP and o-MMT without pretreatment (Figure 1(b)), and PP/o-MMT/DCP/MAH mixture after reaction and purification, where DCP was preconfined in o-MMT (Figure 1(c)). The specific proportions are presented in Table 1. No matter whether it was pretreated, o-MMT could be dispersed homogeneously in the PP phase, but aggregation of o-MMT in dispersed phase could be unavoidable. Without pretreatment o-MMT mainly dispersed in PP as aggregation state (Figures 1(a) and 1(b)). But after pretreatment they could be dispersed in smaller sizes. And by pretreatment with ultrasound, the width of the MMT galleries became larger (indicated by circles). Trails 6, 16, and 21 had same PP/DCP/ MAH, the difference between trails 16 and 21 was that o-MMT used in trail 21 was not pretreated with acetone and ultrasound, so that the width of the o-MMT galleries was smaller than that with pretreatment, which was not wide enough for DCP to be dispersed in, thus trial 21 followed the similar reaction pathways to trial 6, and obtained similar grafting degree (Table 1, trails 6, 16, and 21).

Table 1 gathers the compositions of all the trials carried out in this work and selected characteristics of the products. There were two types of experiments: system 1 using the classical method: PP/DCP/MAH grafting system without o-MMT (No. 1–10); system 2 using o-MMT as nano-nreactors: PP/(DCP/o-MMT)/MAH grafting system (No. 11–20).

No matter in the classical system or in the PP/(DCP/o-MMT)/MAH system, MAH contents measured out by titration after one time washing were higher than that four times washing. And the higher the MAH content was the smaller the average molecular weight of the products. On the other hand, MAH contents in the PP/(DCP/o-MMT)/MAH system were always higher than those in the classical system.

To explain these phenomena, the PP-g-MAH grafting reaction mechanisms are exhibited as Figure 2, which was



FIGURE 1: TEM micrographs of PP/o-MMT of trials 0, 16, and 21. (a) Trial 0 (PP/o-MMT = 40:1 wt, o-MMT without pretreatment), (b) trial 21 (PP/o-MMT/DCP/MAH = 40:1:1:3 wt, o-MMT without pretreatment), (c) trial 16 (PP/(o-MMT/DCP)/MAH = 40:2:3 wt, DCP preconfined in o-MMT with the ratio 1:1 wt).

studied in detail by Shi et al. [17]. A primary free radical RO• formed by DCP may follow pathway (c), in which RO• reacts with a hydrogen atom of the polymer (PP), and preferentially a tertiary one, to form the corresponding macroradical PP•, or/and pathway (b), in which RO• reacts with an unsaturated monomer MAH to form a saturated free radical RM•. The latter would not participate in any grafting reactions because it can only undergo termination by dismutation (pathway (d)). However, RM• could homopolymerize to form MAH oligomers, or it can transfer the free radical to PP chain to form macroradical PP• (pathway (e)). Macroradical PP• formed from pathways (e) and (c) might suffer β -scission to form two shorter segments (pathway (g)) or might follow pathway (h) to form PP-g-MAH. As MAH can be dissolved in xylene and acetone and will be evaporated in a vacuum oven at 80°C, the first washing was used to remove the MAH monomer, as the method drying in a vacuum only could not remove the MAH

monomer completely [20]. However, it is inevitable that some homopolymerized MAH oligomers would be lost. It is obvious that no matter the classical method or using o-MMT as nanoreactors, homopolymerized MAH oligomers would be formed. As explained, in order to obtain PP-g-MAH, macroradical PP• should be obtained first. No matter what path macroradical PP• experienced, pathway (g) and/or pathway (h), they were parallel reactions. So, high grafting degree and low molecular weight existed at the same time.

Figure 3 compares the evolution of the grafting degree (measured out by titration after four times washing) in mass of MAH on PP-g-MAH and that of the number average molar mass of the PP-g-MAH, M_m as a function of the MAH content among the two grafting systems. When MAH used $\geq 2 \text{ g} (\sim 4.5 \text{ wt\%})$, the classical method would graft few MAH, less than 0.065%, onto PP chain. However, using o-MMT as a nanoreactor could improve the grafting degree by orders of magnitude. In the classical system, when MAH used were

Trial no.	PP (g):o-MMT/DCP (DCP) (g):MAH (g)	MAH%-1	MAH%-4	M_n (kg/mol)	M_w (kg/mol)
	Pure PP	_		62.1	252.0
0	$PP/o-MMT^{*} = 40:1$	_		_	—
System 1 (PP/DCP/MAH)					
1	40:(0.25):1	0.422	0.335	42.3	110.7
2	40:(0.50):1	0.458	0.277	43.8	113.9
3	40:(1.00):1	0.532	0.405	39.9	94.6
4	40:(1.50):1	0.528	0.212	50.0	122.5
5	40:(1.00):2	0.375	0.054	55.8	211.1
6	40:(1.00):3	0.367	0.029	61.8	221.4
7	40:(1.00):4	0.369	0.036	55.6	224.6
8	40:(0.50):2	0.375	0.032	53.2	155.8
9	40:(0.50):3	0.368	0.054	50.9	202.2
10	40:(0.50):4	0.377	0.061	46.6	170.5
System 2 (PP/(o-MMT/DCP)/MAH)					
11	40:0.50:1	0.471	0.378	47.2	113.1
12	40:1.00:1	0.510	0.349	42.2	118.7
13	40:2.00:1	0.599	0.576	36.2	93.7
14	40:3.00:1	0.578	0.533	38.0	98.3
15	40:2.00:2	0.494	0.454	46.3	135.1
16	40:2.00:3	0.438	0.266	41.1	128.3
17	40:2.00:4	0.399	0.137	51.5	194.0
18	40:1.00:2	0.394	0.137	55.7	189.1
19	40:1.00:3	0.399	0.119	55.3	162.4
20	40: 1.00: 4	0.382	0.079	49.9	187.9
System 3 (PP/o-MMT*/DCP/MAH)					
21	40:1:1:3	0.412	0.036		

TABLE 1: Compositions of all the trials carried out in this work and selected characteristics.

MAH%-1: MAH content measured out by titration after one time washing; MAH%-4: MAH content measured out by titration after four times washing; * o-MMT was not pretreated with acetone and ultrasound.



FIGURE 2: A simplified reaction scheme of the PP-g-MAH grafting system.

≥2 g (~4.5 wt%), though MAH contents after one time washing were stable in about 0.370–0.375%, but the contents reduced sharply during washing steps. This indicates that most of the MAH reacted formed MAH oligomers instead of grafted PP-g-MAH. And M_n of the products was almost larger than 50 kg/mol, which means seldom PP suffered chain scission. Thus, when concentration of MAH in the system were too high, free radical RO• would be easy to be caught by MAH following pathway (b) to form RM•, and then following pathway (d), meeting with another RM• disproportionation termination to become MAH again or pathway (f) to homopolymerize to form MAH oligomers. A small amount of PP• by pathway (c) or pathway (e) would be obtained, thus few chain scission or grafting reactions occurred. That is the reason why the M_n of the products were not much smaller than that of material PP ($M_n = 62.1$ kg/mol) and the grafting degrees were very low. On the other hand, in the PP/(DCP/o-MMT)/MAH system, the o-MMT nanoreactors would act as sustained-release capsules. They could slow down the rate of release of RO• from within the o-MMT galleries to the outside reaction volume occupied by the PP and MAH (Figure 4). Thus, the concentration of the RO• primary radicals in the



FIGURE 3: Comparison between the PP/DCP/MAH and PP/(DCP/o-MMT)/MAH grafting systems in terms of the evolution of the grafting degree and that of the molar mass of the PP-g-MAH as a function of the MAH content for a given DCP content.



FIGURE 4: A simplified reaction scheme of DCP homolytic fragmentation and diffusion in o-MMT.

grafting system outside of the o-MMT galleries was concomitantly lower. As the interactions between MAH and MMT surface were relatively strong (PP-g-MAH is often used as compatibilizer between PP and MMT in preparing PP/ MMT nanocomposites [21–24]), MAH would be enriched around o-MMT. Most free radicals in the grafting system were in the form of RM• (pathway (b)). However, as the instantaneous concentration in RO• in the system was low, the disproportionation reaction between two RM• radicals (pathway (d)) would be inhibited. At the same time, the chain transfer reaction (pathway (e)) became overwhelming, which enriches PP• concentration. And parallel reactions of chain scission (pathway (g)) and grafting (pathway (h)) would happen. This increased the grafting degree greatly but made the M_n lower. Obviously, we cannot guarantee that all the DCP were restrained inside the galleries of the o-MMT. DCP out of the nanoreactor would follow the same reaction pathways as in the classical system.

Figure 5 compares the evolution of the relative grafting degree of MAH and that of the number average molar mass of the PP-g-MAH, M_n , as a function of the DCP content among the two grafting systems. As MAH contents were not so high, increasing of DCP would increase radical RO•, and RO• would react with MAH (pathway (b)) or PP (pathway (c)); in the classical system, the former will increase the content of MAH oligomers, the latter will increase the content of PP•,



FIGURE 5: Comparison between the PP/DCP/MAH and PP/(DCP/o-MMT)/MAH grafting systems in terms of the evolution of the grafting degree and that of the molar mass of the PP-g-MAH as a function of the DCP content for a given MAH content.

which will follow pathway (g) or (h), and the grafting degree would be determined by the competition between the two reactions (pathway (b) and (c)). However, in the PP/(DCP/o-MMT)/MAH system, as MAH is enriched around o-MMT, most of RO• might follow pathway (b) to form RM• and then follow pathway (e) to (g) or (h), which was illustrated above.

4. Conclusions

In the reactive extrusion process of the free radical grafting of MAH onto PP, an important process in the polymer industry, too large content of MAH or DCP could not increase the grafting degree of MAH. o-MMT could be used as a nanoreactor to increasing the grafting degree. Both the strong interactions between MAH and MMT surface and the encapsulation effect of active species improved the grafting degree. With excessive MAH, o-MMT could decease the disproportionation reaction probabilities among RM• radicals but increase PP•, which would increase the grafting degree and reduce the M_n . However, without pretreatment with acetone and ultrasound, o-MMT had no benefit on improving the grafting degree, due to the narrow width of the o-MMT galleries, which could not form the encapsulation effect. A certain ratio of MAH and DCP is necessary to get the optimized grafting degree. Within the experiments in this work, when mass ratio among PP/(o-MMT/DCP)/MAH was 40:2:1, it could obtain the optimum grafting effect.

Data Availability

All data, models, and codes generated or used during the study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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