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Side Chain Extension of Polypropylene by Aliphatic Diamine and Isocyanate

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Summary: A post-reaction modification of polypropylene by which to obtain increased melt strength is by reactive extrusion of randomly functionalized PP with polyfunctional monomers. In this study, reactive melt processing of maleated polypropylene (PP-g-MA) with poly[methylene (phenylene isocyanate)] (PMPI), hexamethylene diamine (HMDA), and poly(propylene glycol)-bis-(2-propylamine) (Jeffamine D-400) was carried out. The resulting chain-extended PP-g-MA was confirmed by FTIR analysis. Its thermal and rheological properties were also measured. HMDA and D-400 react with both the carboxylic acid and anhydride form of MA. Though PMPI only reacts with the carboxylic acid of MA, PP-g-MA reacted with PMPI has higher gel content and storage modulus compared to PP-g-MA reacted with the amine. This is because of the higher functionality of PMPI and localized reaction between the isocyanate in PMPI and the carboxylic acid in PP-g-MA.

Keywords: amine; chain extension; isocyanate; maleated polypropylene; melt strength

Introduction

Polypropylene (PP), one of the most widely used thermoplastics, possesses excellent properties, such as high melting temperature, high tensile modulus, low density and good chemical resistance. But PP has limitations in applications such as foaming, thermoforming and extrusion coating due to its poor melt strength. There have, therefore, been many attempts to overcome this disadvantage. The introduction of long-chain branching onto the PP backbone is one possible way in which the melt strength can be improved. Some types of post-reaction modifications have included increasing the melt strength of PP by introducing long-chain branching. Scheve et al.[1] tried to achieve this objective by irradiating a solid PP with high energy radiation. Many researchers, including Wang et al.[2], have shown that branching can be introduced by means of the recombination reaction in which PP reacts with polyfunctional monomers, having more than two double bonds, in the presence of peroxide. Another possibility is by the reaction between a randomly functionalized PP and polyfunctional monomers. In this study maleated polypropylene

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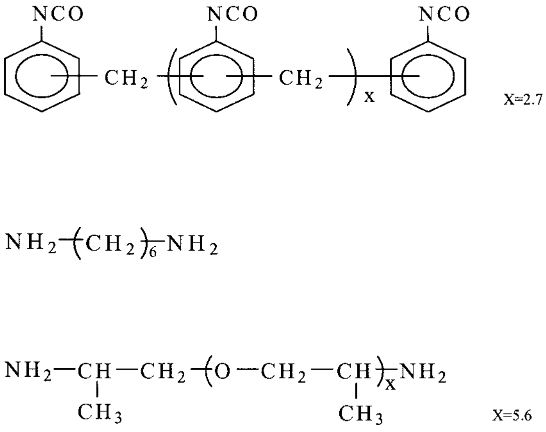
(PP-g-MA) was used as a randomly functionalized PP, as were two types of polyfunctional monomer: polymeric isocyanate (PMPI) and diamine (HMDA, Jeffamine D-400).

Experimental

Materials

PP-g-MA with a MA content of 2 wt% (Honam Petrochemical Corporation) was used. The weight average molecular weight was 23,000 g/mol and the polydispersity index 2.3. Poly[methylene (phenylene isocyanate)] (PMPI), hexamethylene diamine (HMDA), and poly(propylene glycol)-bis-(2-propylamine) (trade name Jeffamine D-400) were used as chain extenders. The chemical structures of the chain extenders are shown in Figure 1.



$NH_2-(CH_2)_6-NH_2$

$NH_2-CH(CH_3)-CH_2-(O-CH_2-CH(CH_3))_x-NH_2$

Figure 1. Chemical structures of the chain extenders used in this study.

Sample preparation and purification

PP-g-MA and chain extenders were reacted in a small Mini Max mixer at 175^0C for 10 minutes. The shear rate was 5 s^{-1}. One gram of PP-g-MA was charged into a preheated mixer and sheared. After the charged polymer had melted, the chain extender was added. Samples with different molar ratios of the reactive group for each chain extender were produced. The molar ratios of functional groups and weight fractions of chain the extenders are listed in Table 1. All the samples were purified by extracting the reaction product in the form of powder for 48 hours with an appropriate solvent. The polymers reacted with PMPI were purified by Soxhlet extraction with boiling acetone, and the polymers reacted with HMDA and D-400 with boiling methanol. After extraction, the polymers were washed with water and dried for 6 hours at 60^0C in a vacuum oven.

Table 1. Molar ratios of functional groups and weight fractions of chain extenders.

	Sample name	Molar ratio of functional groups[a)]	Weigt fraction[b)] (wt %)
PMPI	PMPI 1/4	1/4	0.39
	PMPI 1/2	1/2	0.78
	PMPI 1/1	1/1	1.56
HMDA	HMDA 1/4	1/4	0.30
	HMDA 1/2	1/2	0.59
	HMDA 1/1	1/1	1.18
D-400	D-400 1/4	1/4	1.02
	D-400 1/2	1/2	2.04
	D-400 1/1	1/1	4.08

[a)] [NCO]/[MA] for PMPI, and $[NH_2]$/[MA] for HMDA and D-400

[b)] Weight ratio of chain extender to PP-g-MA

Measurements

FTIR analyses were done using a Jasco FT/IR-480 plus. Thin films for FTIR measurement were made by pressing at 200^0C. Thermal properties of 5-10 mg samples were studied by differential scanning calorimetry (DSC), using a Seiko Extar 6000 DSC. The temperature scanning rate was

10 ^{0}C/min for both heating and cooling steps. Gel content was measured according to the ASTM D2765-84 method. Rheological properties were measured using an ARES rheometer of Rheometric Scientific, Inc. A parallel plate was used, and the gap size was 1mm.

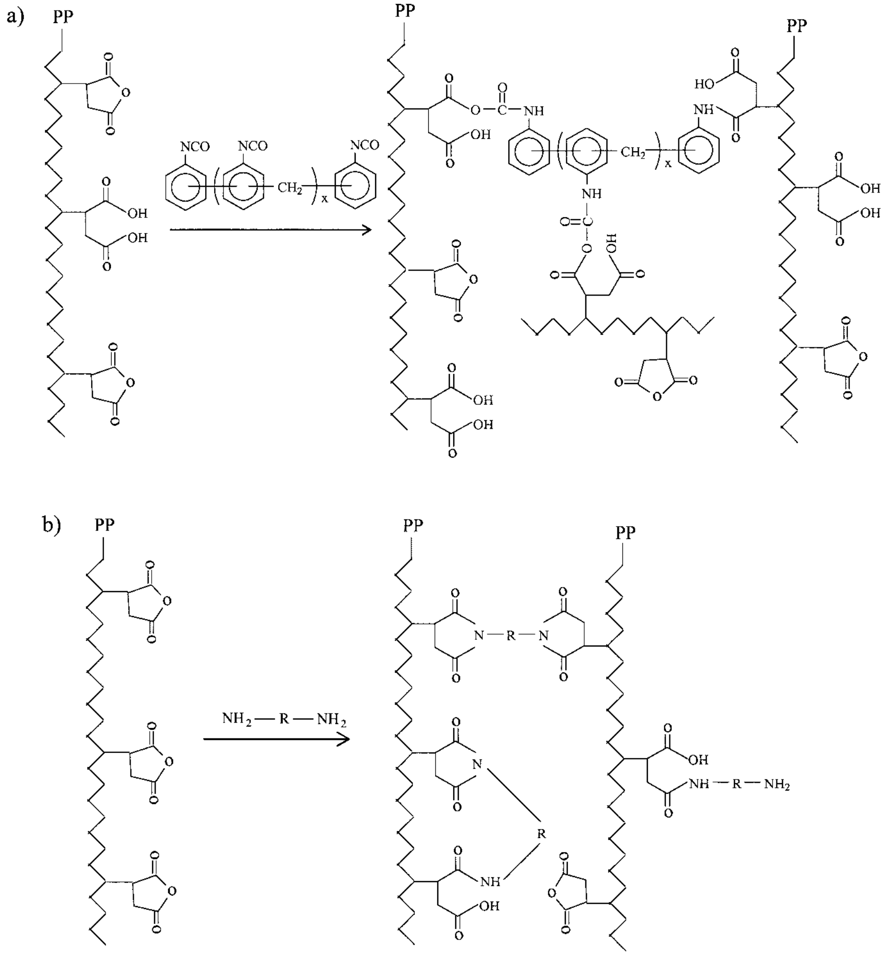


Figure 2. Simplified reaction mechanisms of reaction between a) PP-g-MA and PMPI, and b) PP-g-MA and primary diamine.

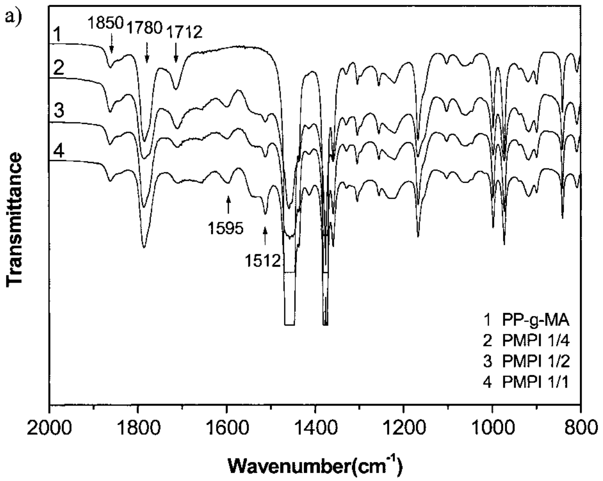
Results and Discussion

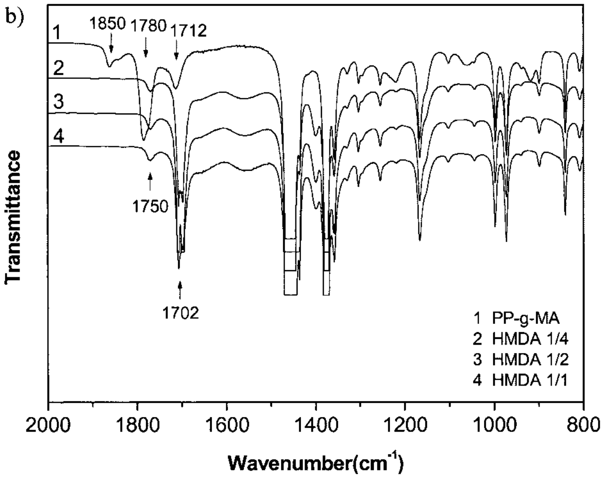
Chemistry

Some portions of MA in PP-g-MA exist in the form of anhydride and the others in the form of hydrolyzed free acid. As it is reported that an isocyanate group has good reactivity with carboxyl and hydroxyl groups, PP-g-MA can be chain-extended by reaction with PMPI[3]. The reaction mechanism of an isocyanate with a carboxyl group is shown in Figure 2a. In the case of the reaction between an isocyanate and a primary amine, the former can react with both the anhydride form of MA and the hydrolyzed free acid form of MA, to form an imide ring through the reaction mechanism shown Figure 2b.[4-5]

FTIR analysis

FT-IR spectra of chain-extended PP-g-MA and unreacted PP-g-MA are shown in Figure 3. The FT-IR spectra indicated that the MA in PP-g-MA exists in the forms of anhydride (1850 and 1780cm^{-1}) and hydrolyzed free acid (1712cm^{-1}). For samples reacted with PMPI, a decrease in intensity for the absorption peak at 1712cm^{-1} is observed, with the appearance of new peaks at 1595 and 1512cm^{-1}. Further, the intensity of these new peaks increases with increasing PMPI content. These new peaks indicate that an urea linkage was formed by the reaction between hydrolyzed free acid in the MA and isocyanate group in the PMPI. No change in the intensity of the peaks at 1850 and 1780 cm^{-1} means that isocyanate group did not react with the anhydride form of MA. For samples reacted with HMDA, characteristic peaks of MA at 1850, 1780cm^{-1} and 1712cm^{-1} disappear and new absorption peaks at 1770 and 1702cm^{-1}, that may be corresponding to the carbonyl group of the amic acid or imide, appeared. In the spectrum of samples reacted with D-400, the changes in characteristic absorption peaks of MA are similar to those of the HMDA series. Although characteristic peaks of MA still remain in the spectrum of D-400, absorption peaks at 1770 and 1702cm^{-1} increase with an increasing amount of D-400. Yet another new peak, at 1104cm^{-1}, attributed to the C-O-C stretching, increases with D-400 content.


a)
1
2
3
4
1850
1780
1712
1595
1512
Transmittance
1 PP-g-MA
2 PMPI 1/4
3 PMPI 1/2
4 PMPI 1/1
2000
1800
1600
1400
1200
1000
800
Wavenumber(cm^{-1})


b)
1
2
3
4
1850
1780
1712
1750
1702
Transmittance
1 PP-g-MA
2 HMDA 1/4
3 HMDA 1/2
4 HMDA 1/1
2000
1800
1600
1400
1200
1000
800
Wavenumber(cm^{-1})

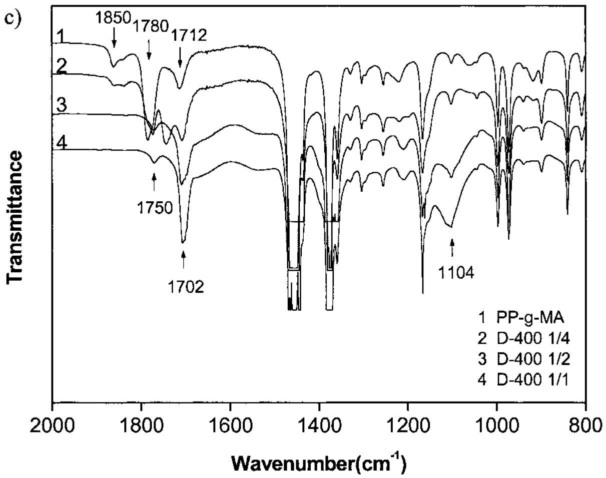


Figure 3. FTIR spectra of PP-g-MA and PP-g-MA reacted with a) PMPI, b) HMDA, and c) D-400.

Thermal properties

In Table 2, melting temperatures and ΔH_m of all samples measured by DSC are tabulated. Unreacted PP-g-MA has two melting points: 148.88 ^{0}C and 154.52 ^{0}C. Melting temperatures of all chain-extended samples are lower than the melting temperature of PP-g-MA, and reduced ΔH_m values are measured. Although PMPI only reacts with carboxylic acid, the decrease in ΔH_m is high even at the lowest molar ratio of PMPI. These decreases in ΔH_m for PP-g-MA reacted with PMPI are attributed to the high gel content, shown in Table 2. The average functionality of a PMPI molecule is 4.7 and is higher than those of amines used in this study. The reaction between PMPI and PP-g-MA can be localized, since the maleic anhydride group is hydrolyzed in local areas where moisture is present, and PMPI can only react with the carboxylic acid form of MA. Hence, PP-g-MA reacted with PMPI has higher gel content than PP-g-MA reacted with amine at the same molar ratio. For amine-extended samples, with increasing amine content, gel content increases and ΔH_m decreases.

Table 2. Thermal properties and gel content.

	T_{m1}	T_{m2}	ΔH_m	Gel content
	°C	°C	J/g	wt%
PP-g-MA	148.88	154.52	94.45	0
PMPI 1/4		151.26	77.34	7.2
PMPI 1/2		150.96	77.97	21.4
PMPI 1/1		152.16	79.82	25.3
HMDA 1/4		149.98	82.46	2.1
HMDA 1/2	133.09	144.76	75.36	5.8
HMDA 1/1	132.93	143.55	71.10	22.1
D-400 1/4		150.20	92.78	1.2
D-400 1/2		145.84	81.04	2.6
D-400 1/1		146.26	77.71	15.7

Rheological properties

Chain-extended PP-g-MA with high gel content has very high normal stress under the conditions where rheological properties were measured, hence rheological properties could not be measured for samples with gel content greater than 10 wt%. Storage moduli of D-400 1/4 and HMDA 1/4 decrease with decreasing frequency at the high frequency range, but at the low frequency range a plateau region is observed. PMPI 1/4, having higher gel content, has a constant storage modulus over the entire frequency range measured, an indication of a crosslinked structure. Amine-extended

PP-g-MA with a molar ratio of 1/2 also has a plateau modulus.

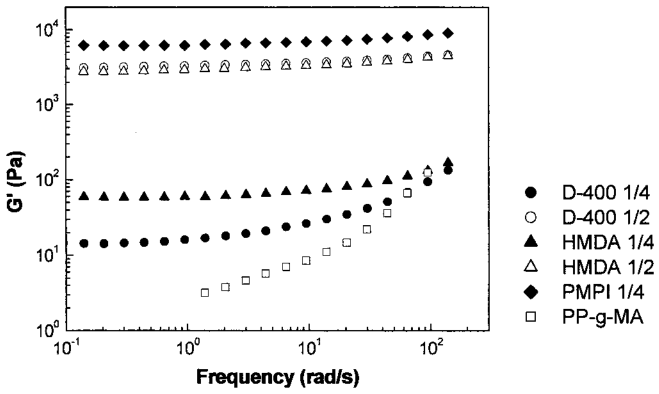


Figure 4. Storage moduli versus frequency at 270⁰C for chain-extended PP-g-MA and at 170⁰C for PP-g-MA.

Conclusions

PP-g-MA was chain-extended by reactive melt processing using polymeric isocyanate and a primary diamine. Isocyanate only reacted with the carboxylic acid form of MA and amine reacted with both the carboxylic acid and anhydride form of MA. With increasing initial amount of chain extender, gel content and storage modulus increased. Though PMPI only reacted with carboxylic acid, its high functionality and localized reaction lead to high gel content and high storage modulus.

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