



In this study, grafting of PP using **I** in the presence of peroxide was carried out in a mixer. The amount of grafted isocyanate was determined and the thermal and chemical behaviour of the modified PP was investigated. The grafted material was used to improve the adhesion properties of PP-polyamide-blends as shown by SEM.

### Experimental

The reaction of isotactic PP (Hostalen PP N 1060, Hoechst AG) with TMI in the presence of *tert*-butyl cumyl peroxide (BCUP) was carried out in the mixing chamber of a Brabender Plasticorder at 180 °C (Tab. 1). After 10 min, the mixture was quickly removed from the chamber and cooled between two metal plates. For purification, the reaction mixture was dissolved in refluxing xylene and precipitated by cooling to room temperature. The precipitated polymer was washed with acetone and dried in vacuum at 120 °C.

Tab. 1. Reaction of 2 g TMI with 20 g poly(propylene) in the presence of *tert*-butyl cumyl peroxide (BCUP) at 180 °C; reaction time 10 min.

No.	BCUP (g)	TMI grafted (wt.-%)	Onset-temp. (°C)	m.p. (°C)	$\Delta H_m$ (J g <sup>-1</sup> )	$M_w/M_n$
0 <sup>a</sup>	0	0.0	151.1	164.0	98.0	398 400 / 85 600
1	0.5	1.8	149.5	152.1	91.3	130 100 / 41 500
2	1.0	3.6	142.6	150.4	76.2	59 700 / 19 800
3	1.5	5.4	138.6	146.4	78.3	80 100 / 23 500
4	2.0	6.8	134.8	143.5	72.8	84 500 / 26 000

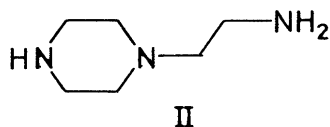
<sup>a</sup> Original material: Hostalen PP N 1060.

The amount of grafted TMI was determined by using two different methods: titration of the isocyanate with amines, and elementary analysis.

The titration is based on the reaction of the isocyanate group with octylamine to urea; excess octylamine was titrated with hydrochloric acid. The completeness of the reaction of octylamine with the grafted isocyanate was checked by FTIR spectroscopy. 0.2 g PP-g-TMI were heated in 50 mL of refluxing dried xylene. When the polymer was dissolved, 20 mL 0.05 M octylamine in xylene were added. After 1 h refluxing, the solution was allowed to cool and then sucked through a glass filter to remove the polymer. The purified solution was titrated to a yellow end point with 0.1 M hydrochloric acid in isopropanol using five drops of 1 % bromophenol blue in dimethylformamide as indicator.

Since the nitrogen content of PP-g-TMI was too low to be determined by elementary analysis with sufficient accuracy, the isocyanate groups of the graft product were reacted with a nitrogen-rich amine, i.e. 2-(piperazin-1-yl)ethylamine (**II**). The absence of

isocyanate bands in the FTIR spectrum confirmed that **II** had reacted completely with PP-g-TMI.



The thermal behaviour of the grafted polymer was examined by differential scanning calorimetry (DSC) with a Du Pont DSC 912 and a scanning rate of 10 K min<sup>-1</sup> under nitrogen atmosphere.

The molecular weight distribution of the grafted polymers was obtained with a Waters Millipore 150-C ALC/GPC gel permeation chromatograph at 130 °C using 1,2,4-trichlorobenzene as mobile phase and polystyrenes with known molecular weight distribution as reference.

The reactions with different nucleophiles in solution were carried out in xylene at 130 °C for 1 h. For that purpose, 1.0 g PP-g-TMI (5.0 wt.-% g-TMI = 4.6 mmol) was dissolved in refluxing xylene and a twentyfold molar excess of nucleophile was added. For the reactions in melt the molar excess was twentyfivefold. 20.0 g PP-g-TMI (1.0 wt.-% g-TMI = 0.99 mmol) were molten in the mixing chamber at 180 °C. The nucleophile was added in one step. After 10 min of kneading, the reaction mixture was quickly removed and rapidly cooled between two metal plates.

## Results and discussion

Fig. 1 shows the amount of TMI grafted on the PP backbone, measured by titration and elementary analysis. In the range between 2 and 5 wt.-% grafted TMI the results obtained by titration and elementary analysis are very similar. Differences are observed in the range above 5 wt.-%. Further experiments have proved that secondary amine groups like in **II** can also react with isocyanates, but the reaction is very slow. Thus, it is possible that in case of higher isocyanate concentrations the secondary amine group in **II** also has reacted.

The data of thermal behaviour of TMI-grafted PP are also listed in Tab. 1. The term 'onset-temperature' has been used here to describe the begin of the thermal effect [7]. The onset-temperature was determined by intersecting the extrapolated base-line with the tangent on the curve of the beginning thermal effect. The melting point (m.p.) is the minimum of the melting peak in the calorimetric curve. An increase of the amount of grafted TMI results in a decrease of the PP melting point, onset-temperature and heat of fusion,  $\Delta H_m$ . The molecular weights of PP (see Tab. 1) rapidly decrease during the reaction, but they are retaining at the same level with higher TMI content while the onset-temperatures of the polymers decrease linearly.

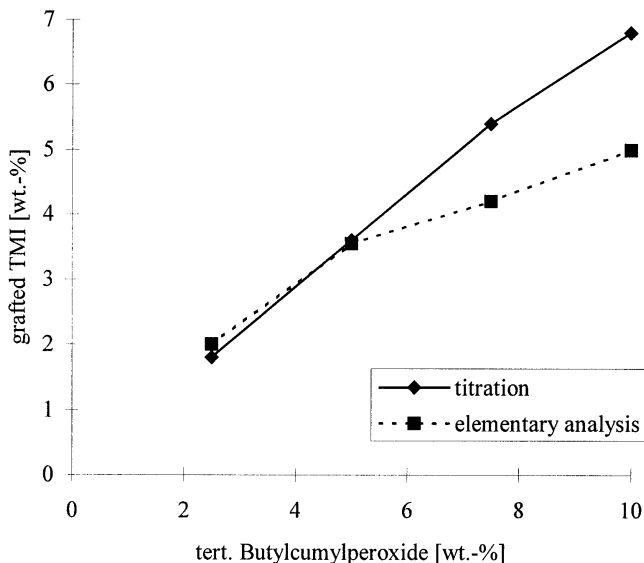


Fig. 1. Amount of TMI grafted on poly(propylene), depending on the peroxide content in the reaction mixture.

An explanation for these results is the hindered crystallization of the grafted polymers as indicated by the depression of the thermal data. A similar thermal behaviour was observed by Bradawidjaja et al. [8] who grafted maleic anhydride onto PP. They also found lower melting points for higher grafted polymers but no reduction in the heat of fusion.

The results of the reactions of the grafted isocyanate with different nucleophiles in solution and in melt are shown in Tab. 2. With strong nucleophiles like amines there is a reaction in solution and in melt. Weak nucleophiles like alcohols and thiols did not react in solution, but only in the melt at higher temperatures.

Tab. 2. Reaction of PP-g-TMI with different nucleophiles in solution and in melt (+: complete reaction; o: no reaction; (o): no complete reaction; /: not examined).

Nucleophile	Solution	Melt	Nucleophile	Solution	Melt
Octylamine	+	+	Dodecanol	/	+
Octadecylamine	/	+	BP-TMC <sup>a</sup>	o	(o)
Aniline	+	+	Dodecanthiol	o	(o)
Phenol	o	(o)	$\epsilon$ -Caprolactam	/	+
Ethanol	o	/			

<sup>a</sup> BP-TMC: 4,4'-(3,3,5-trimethylcyclohexylidene)diphenol.

Grafted PP is mainly used as compatibilizer in blends of PP and polyamides. These blends are used e.g. to improve the heat distortion of PP [9]. However, the mechanical properties like tensile and impact strength of PP-polyamide-blends without a compatibilizing coupling agent are poor [10]. For demonstration of the effect of TMI-grafted PP as coupling agent, PP-polyamide blends with 30 wt.-% polyamide 6 or 66 were prepared by kneading in a Brabender Plasticorder. The effect of the grafted polymer was investigated by SEM pictures of the fracture surface of test specimens. The diameter of the dispersed polyamide spheres can be used as a measure for the coupling efficiency of the blend components [11].

Fig. 2 shows, as an example, SEM pictures of the fracture surfaces. The distribution of the polyamide spheres in the blends with polyamide 66 is coarser than in blends with polyamide 6 but shows, in either case, an efficient coupling effect by decrease of the original diameter of the polyamide spheres. A further increase in the amount of TMI-grafted PP in the blends causes no further reduction of the diameter of the polyamide spheres.

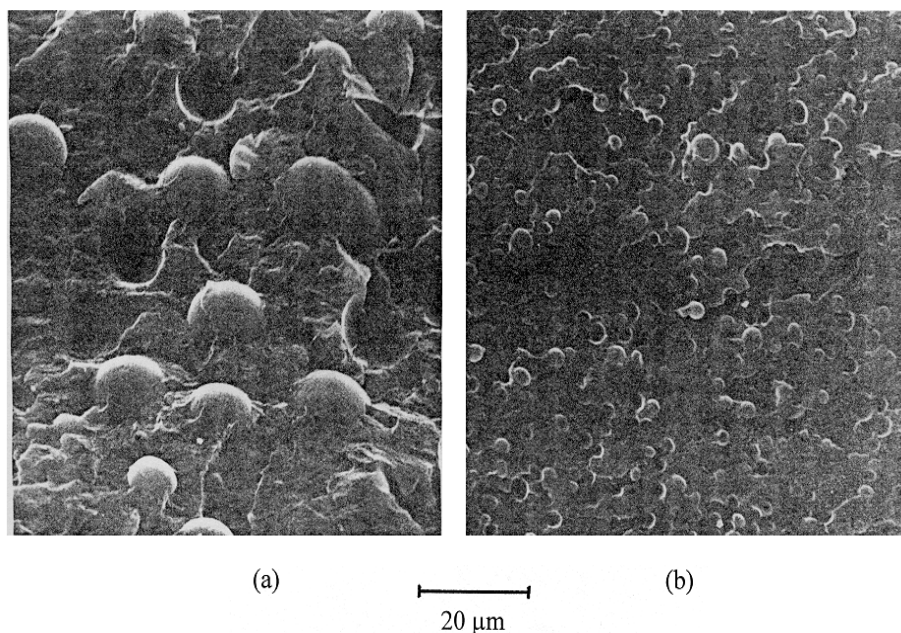


Fig. 2. SEM-picture of the fracture surface of composites of (a) poly(propylene) (67 wt.-%) with polyamide 66 (30 wt.-%) and TMI-grafted poly(propylene) (3 wt.-%) and (b) poly(propylene) (67 wt.-%) with polyamide 6 (30 wt.-%) and TMI-grafted poly(propylene) (3 wt.-%).

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