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Modification of maleic anhydride grafted polyethylene with 1,4-diaminobutane in near critical propane

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Abstract

Granules of high density polyethylene grafted with 0.17 wt.% maleic anhydride (PEMA) were modified with an excess of 1,4-diaminobutane (DAB) by impregnation from near critical propane. After formation of amic acid groups, the excess of diaminobutane was extracted with a near critical propane–ethanol mixture (95/5 wt.%). Finally, the obtained PEMA–DAB was imidised quantitatively to the corresponding imide (PEMI) in the melt. The obtained PEMI showed no increased gel content with respect to the PEMA. The presence of primary amine groups was indirectly proven by selective extraction experiments. It appeared that PEMI samples had reacted with the anhydride groups of styrene-MA copolymer (SMA) during melt blending of SMA with PEMI, while the PEMA had not reacted. SMA/PEMI 80/20 blends consisted of a continuous SMA phase and PEMI droplets with a diameter of less than 1 μm. SMA/PEMA 80/20 blends showed a course morphology of PEMA strings in a continuous SMA phase. With this article we have shown that this new technique for the chemical modification of swollen HDPE particles in near critical propane has proven to be much better than the conventional modification in the melt, when it comes to avoiding crosslinking.

Keywords: Polymer modification; Supercritical and near critical fluids; Polyethylene

1. Introduction

The use of supercritical fluids (e.g. supercritical CO_2) has recently received much attention in polymer science, as this approach has several advantages compared with more conventional approaches. These fluids are of great interest for polymerisation [1–10], polymer modifications (such as chemical modification [11–13] and impregnation of additives into polymer matrices [14–18]), and extractions [19–22]. Conventional approaches for the chemical modification of polymers by solution processing techniques are neither economically nor ecologically feasible, because of the hazardous waste in the form of organic solvents, together with leftover monomer(s) and initiator(s). In addition, much energy is required to remove the solvents at the end of the process. An alternative and frequently applied method is the modification of polymers in the melt, but undesired side reactions may occur at these elevated temperatures. In this article we present a special example of a relatively new polymer modification technique in supercritical fluids. Supercritical CO_2 ($P_c = 72.9$ atm., $T_c = 31.1$°C), which is most frequently used, has the advantage that it is non-toxic, non-flammable and inexpensive. Supercritical propane ($P_c = 41.9$ atm., $T_c = 96.7$°C), although flammable, has proven to be useful for the solvation of high molecular weight polymers. Polymer granules may be swollen by supercritical fluids, thus allowing interpenetration of chemicals dissolved in supercritical fluids. This technique was applied by Howdle et al. [16] for the impregnation of polyethylene films using an organometallic complex as a spectroscopic probe. If a reactive additive is used instead, it is possible to modify functional groups attached to the polymer chain under very mild conditions, thus avoiding undesired side reactions. After modification is completed the solvent can be easily released by reducing the pressure and unreacted chemicals can be supercritically extracted with pure solvent.

This article discusses the modification of maleic anhydride grafted high density polyethylene (HDPE) with 1,4-diaminobutane (DAB) in near critical propane. The designation ‘near critical’ is chosen, because at 70°C and 300 bar one is operating beneath the critical temperature but still in the critical region [23]. In this critical region, the solvent power of a supercritical fluid can be related to the solvent density. At 70°C and 300 bar the reduced densities of the pure compound become liquid-like and the supercritical fluids begin to act like liquid solvents. At these chosen

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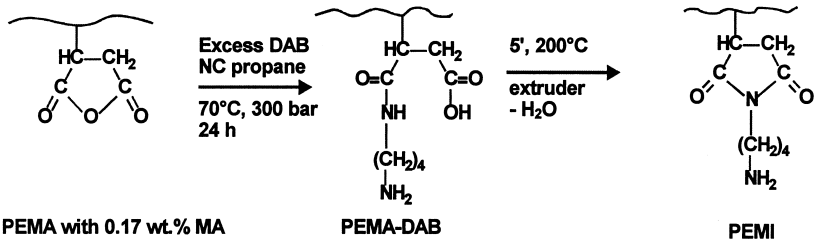

Scheme 1.

conditions, the highest solubilities are reached and the polymer particles swell to a large extent. Supercritical CO_2 is less suitable in this case, because the highly reactive primary amine groups may react therewith. In this article, the evaluation is limited to the compatibilising efficiency in polymer blends. In a future study, the manufactured amine-functionalised polyethylenes will be evaluated as adhesion promoting additives in laminates of two polymer materials.

2. Experimental

2.1. Materials

The melt flow index of the HDPE was 10 dg/min at 190°C. Maleic anhydride grafted HDPE and DAB were both purchased from DSM, and were used without purification.

2.2. Modification and extraction

Approximately 15 g of HDPE granules grafted with 0.17 wt.% MA (sample 1) was placed in an 850 bar autoclave. Subsequently, an excess of DAB was added (a nine-fold excess based on the weight percentage of MA). The impregnation of DAB was performed at 70°C and 300 bar (liquid propane pressure) for 24 h. The granules were divided into two portions; one portion was analysed as such by FTIR (sample 2) and the second portion was extracted to remove the unreacted DAB. The DAB modified PEMA was extracted several times by static extraction with a near critical mixture of 5 wt.% ethanol and 95 wt.% propane at 70°C and 300 bar for 4 h. After extraction, the reaction mixture was degassed at 50°C and 800 mbar for 3 h in a desiccator. The amount of DAB that had reacted with PEMA was estimated from the weight increase of the sample. This portion was also submitted to the IR-analysis (sample 3).

2.3. Imidisation and melt blending

The extracted PEMA–DAB, which was still in the amic acid form, was quantitatively imidised to PEMI in a twin screw-extruder at 200°C and 230 rpm for 5 min (sample 4). Extruded threads of SMA/PEMA 80/20 blends and SMA/PEMI 80/20 blends were obtained after mixing 0.9 g PEMA, respectively, 0.9 g PEMI with 3.6 g SMA in a twin screw-extruder at 230°C and 250 rpm for 5 min.

2.4. Materials characterisation

The melt viscosities and phase angles were measured with a Rheometric Scientific 800 (RMS 800) at 230°C. IR spectra were recorded on a Perkin–Elmer Sys. 1760 ×. The gel percentages of PEMA, PEMA–DAB and PEMI samples were determined as follows. Approximately 2 g of the samples were put in a basket with a pore size of 40 mesh and were treated with boiling xylene for 20 h. The non-soluble part of the polymer was dried under vacuum to constant weight. The weight percentage non-soluble HDPE was calculated, which corresponds to the gel percentage. The weight percentage nitrogen in PEMI was determined in triplicate by elemental analysis. The presence of primary amines was indirectly proven by selective extraction experiments. The morphology of the SMA/PEMA blends and SMA/PEMI blends was investigated by scanning electron microscopy using a Philips SEM 515 at 15 kV. The samples were broken at −196°C and the surfaces were etched with O_2-plasma at 10 W for 10 min. Subsequently, the samples were coated with a conducting Au/Pd-layer. The polymer blends were intermittently extracted with methylethylketone for 6 h, followed by drying for 72 h at 80°C in vacuum and 1 h at 180°C in vacuum and under a nitrogen flow.

3. Results and discussion

3.1. Sample preparation

In our investigation on the development of new technologies for the chemical modification of swollen polymer particles in supercritical fluids, HDPE grafted with maleic anhydride was modified with DAB in near critical propane. The obtained amic acid (PEMA–DAB) was thermally converted into the desired product (PEMI), as shown in Scheme 1.

3.2. Molecular characterisation

Molecular characterisations of PEMA, extracted PEMA–DAB and PEMI were obtained by means of FTIR

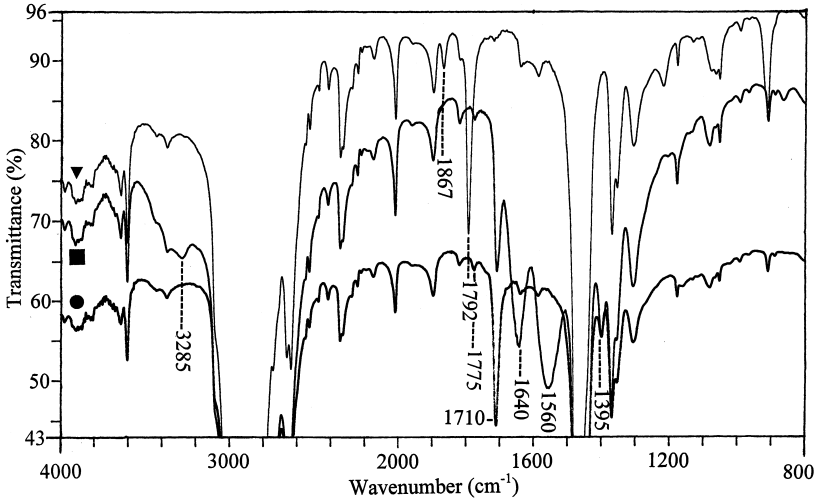

Fig. 1. FTIR spectra of samples 1, PEMA (▼), 3, extracted PEMA–DAB (■), and 4, PEMI(●).

spectroscopy. The FTIR spectra of samples 1, 3 and 4 are given in Fig. 1. The characteristics of the different sample numbers 1–4 are explained in Table 1. For sample 1, the IR spectrum is consistent with PEMA. The maleic anhydride absorption is observed at 1867 and 1792 cm^{-1}. The MA content of PEMA could be quantitatively determined by using a calibration curve developed at DSM Research and was found to be 0.17 wt.%. No maleic acid was observed. For sample 2, the non-extracted PEMA–DAB, no spectrum is given in Fig. 1. After extraction of sample 2 with near critical propane and subsequent drying, a weight increase of 0.24 wt.% DAB was determined by simply weighing the sample. This value is somewhat high compared with the expected weight increase of 0.15 wt.% if every single MA unit would have reacted with exactly one DAB molecule. Apparently some free diamine is still present, but obviously this was removed by degassing during the imidising step. For sample 3, the extracted DAB modified PEMA, broad bands were observed at 1560 and 1640 cm^{-1}, indicating the presence of amic acid. In addition, weak bands were found between 3500 and 3200 cm^{-1}, probably for primary and secondary amine groups of the amic acid. There are no indications for the presence of MA units. This figure also showed, that the formation of imides has already partially occurred (bands at 1775 and 1710 cm^{-1}). The FTIR spectrum of sample 4, the imidised PEMI, showed an absorption band at 1710 cm^{-1} corresponding to the imide. There are no indications for the presence of MA or amic acid in sample 4, although a small band at 1395 cm^{-1} can be observed which probably corresponds to the C–N vibration of PEMI.

Based on a MA wt.% of 0.17%, the calculated weight percentage nitrogen in PEMI is 0.048%, provided that one MA unit has reacted with exactly one DAB molecule. The measured weight percentage nitrogen in PEMI (sample 4) of 0.044 ± 0.006 wt.%, determined by elemental analysis, is an indication for the extent of reaction between MA units and DAB molecules. Although, in view of the relatively large error in the determination of the nitrogen content, no quantitative conclusions can be drawn, it seems that either the reaction was not entirely complete or that a small amount of DAB molecules has reacted with two MA units. The FTIR results, combined with the elemental analysis, point to an extensive transformation of the MA groups into primary amine groups. These results are also in agreement with the constant value of the gel content before and after the DAB modification (see Table 1), which was expected to increase if a significant number of DAB molecules would have reacted with more than one MA unit. The amorphous phase of the polymer granules is probably swollen to such an extent that the distance between the maleic anhydride groups becomes large enough to prevent crosslinking by the reaction of one DAB molecule with two MA groups. In addition, the mobility of the MA groups in swollen HDPE may be lower than in the HDPE melt, where crosslinking usually occurs (discussed later).

Table 1
Results of IR analyses and gel percentages of samples 1–4

Sample	Material	Treatment	IR-analysis	Gel percentage (wt.%)
1	PEMA	None	0.17 wt.% MA	1.1
2	PEMA–DAB	Excess DAB, non-extracted	Amic acid and DAB	0.9
3	PEMA–DAB	DAB extracted	Amic acid	1.2
4	PEMI	Sample 3 after imidisation	Imide	1.1

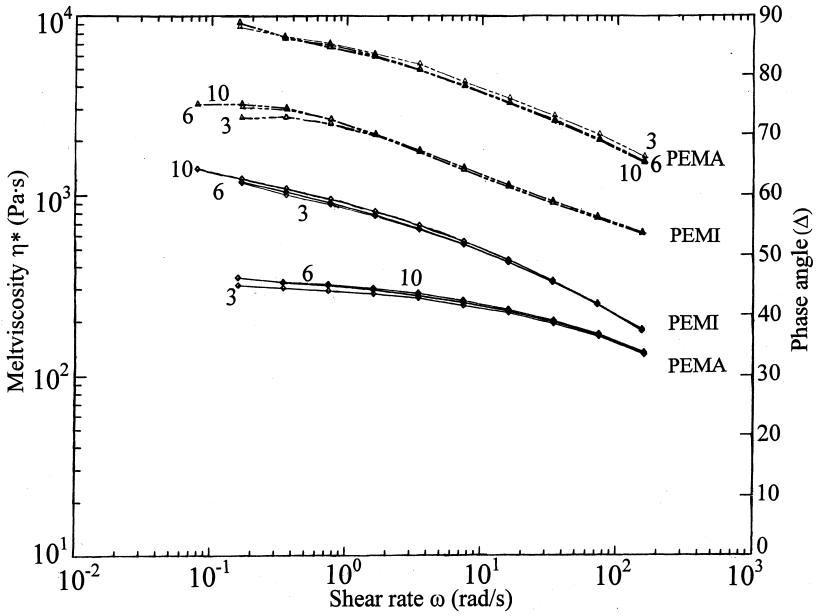

Fig. 2. Melt viscosities η^* (◇) and phase angles (Δ) of PEMA and PEMI at 230°C at 3, 6 and 10 min.

3.3. Near critical modification vs. melt modification

This new technique for the chemical modification of swollen HDPE particles in near critical propane has proven to be much better than the conventional modification in the melt as described hereafter. The DAB modification of HDPE grafted with 0.11 wt.% MA in a twin screw-extruder at 250°C with a twentyfold DAB excess, resulted in a weight percentage of 210 mg N kg^{-1}. However, if every MA group would have reacted with one amine group, a weight percentage of 320 mg N kg^{-1} polymer should have been found. As no MA groups were present, it is implied that the product has partially been crosslinked. In addition, a gel percentage of 4.3% was found instead of 1%, which can be reached with this new technique. This increased gel content also indicates that crosslinking had occurred even for a lower MA content than for the PEMA modified in near critical propane.

3.4. Melt viscosities

The melt viscosities of PEMA (sample 1) and PEMI (sample 4) are illustrated in Fig. 2. Although the gel percentages, given in Table 1, point to no significant crosslinking of PEMI (sample 4), the melt viscosity of the obtained PEMI is, especially for low shear rates, significantly higher than that of PEMA. This increase may possibly be ascribed to some long chain branching, which leads to an increase in

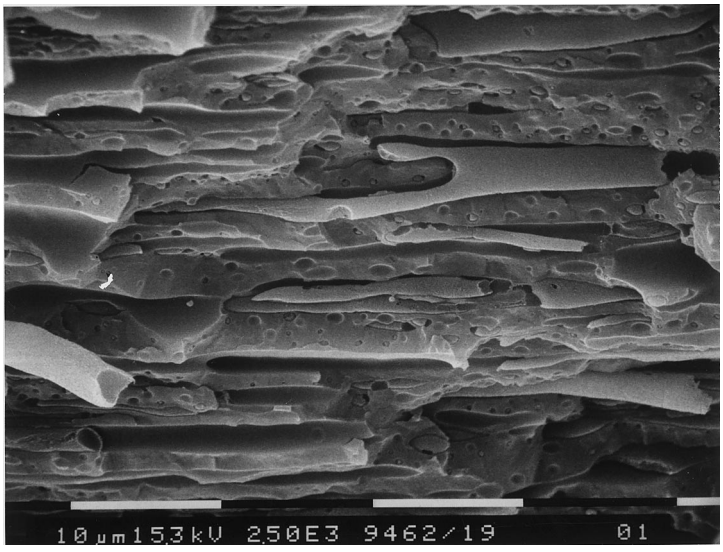

Fig. 3. SEM photograph of SMA/PEMA 80/20 blends. White bar represents 10 μm.

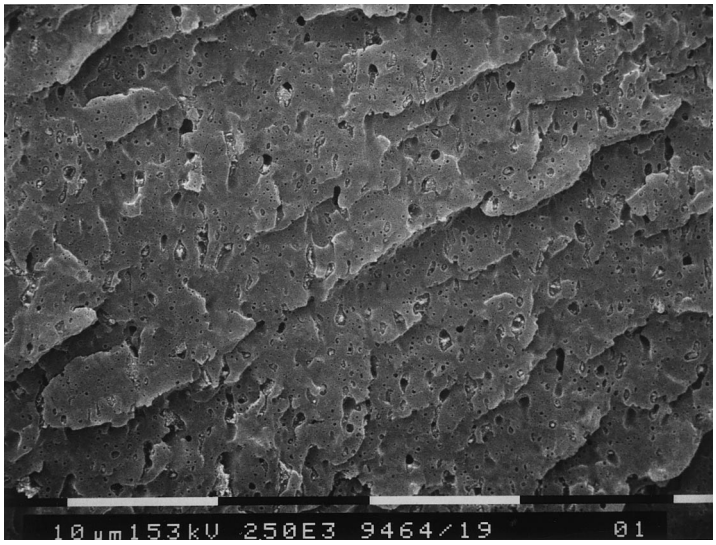

Fig. 4. SEM photograph of SMA/PEMI 80/20 blends. White bar represents 10 μm.

the molecular weight of HDPE and not to significant cross-linking. The observed increased elasticity (i.e. lower value of the phase angle) is also in agreement with some branching, which may be caused by the reaction of some DAB molecules with two MA units during the reaction in near critical propane (see also comments on the difference between calculated and measured weight percentage nitrogen), but may also be due to the transimidation reactions and/or reaction of HDPE grafted NH_2 groups with imide carbonyl groups attached to another HDPE chain. It is possible that these latter types of branching reactions only take place during heating of the sample before starting the measurement of the melt viscosity, and accordingly cannot be avoided. In the literature, long chain branching was observed as a decreasing phase angle with the increasing residence time in the melt [24].

3.5. PEMI as compatibiliser

One of the possible applications for PEMI could be the use as compatibilisers for polyolefin containing polymer blends. This was investigated for SMA/PEMA 80/20 and SMA/PEMI 80/20 blends. Using scanning electron microscopy the morphologies were visualised. In Figs. 3 and 4, photographs are shown for samples 5 and 6. From Fig. 3, it can be derived that the blend of sample 5 possesses a course and strongly oriented morphology. The threads are aligned in the extrusion direction. Fig. 4 shows a blend with a very fine dispersion of PEMI in the SMA matrix, with an average particle size of below 0.5 μm.

Table 2
Weight percentages of methylethylketone insoluble material in SMA/PEMA and SMA/PEMI blends

Sample	Blends ratios	wt.% of non-extracted material
5	SMA/PEMA = 80/20 (PEMA from sample 1)	19.3
6	SMA/PEMI = 80/20 (PEMI from sample 4)	27.8
7	SMA/PEMI = 80/20 (duplicate of sample 6)	27.2

It is known that the viscosity ratio of the continuous and dispersed phases influence the blend morphology [25]. To see whether or not the observed finer morphology of the PEMI based blend (from sample 4) is indeed caused by a compatibilising effect of the reactive PEMI as the compatibiliser, or by the viscosity effect, the blends were extracted with methylethylketone (selective solvent for SMA) to remove the SMA component. For sample 5 it was found that 19.3 wt.% of the total mass did not dissolve (Table 2). This corresponds well to the weight percentage PEMA in the blend, being 20%. Samples 6 and 7 yielded after extraction with methylethylketone, respectively, 27.8 and 27.2 wt.% as the insoluble residue, indicating that a chemical reaction had occurred between the reactive groups of the HDPE phase and anhydride groups of the SMA phase. It is obvious that the PEMI samples do contain functional amine groups, which are reactive with SMA anhydride groups. The finer morphology of the SMA/PEMI blends is presumably caused by the compatibilising reactions at the interface, and indirect evidence for the presence of amine groups in the PEMI sample is obtained. Further investigations will be performed in the future.

4. Conclusions

HDPE granulate with 0.17 wt.% MA was modified in near critical propane with excess DAB. In this way, the

anhydride functionalities of PEMA were to a large extend converted into the amic acid. Unreacted diaminobutane could be largely removed by means of extraction with a near critical propane–ethanol mixture. The obtained PEMA–DAB was quantitatively imidised to PEMI in the melt.

The melt viscosity of the obtained PEMI was higher than that of PEMA, and the PEMI sample proved to be more elastic. Both phenomena are probably due to long chain branching, which might be due to the reaction of some DAB molecules with two MA units. This may also take place during heating of the sample before starting the measurement of the melt viscosity as a result of reaction of amine groups of one HDPE chain with imide and/or carbonyl groups attached to another HDPE chain.

It was observed that the PEMI samples were reactive in the melt with the anhydride functionalities of SMA while the PEMA samples were not. PEMI turned out to be an efficient compatibiliser for SMA/PE blends.

This article has shown that modification of maleic anhydride grafted polyolefins in supercritical or near critical fluids is a promising technique for the manufacturing of non-crosslinked primary amine functionalised polyolefins, which was proven to be difficult by the modification in the melt. Even with a higher percentage of MA groups (0.17 wt.% MA using the 'supercritical modification' technique instead of 0.11 wt.% MA for modification in the melt) and a smaller excess of DAB, no significant crosslinking was observed because of the swelling of the polymer particles and the lower mobility of polymer chains which inhibits crosslinking. The modified polymers have a wide variety of possible applications, such as adhesion promoting polymers in multilayered films of polyethylene and polyethylene terephthalate, compatibilisers for polyolefin containing blends, and paint adhesion promoting additives for polyolefins.

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