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Grafting of Polyolefins with Maleic Anhydride: Alchemy or Technology?

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Summary: Nowadays, the process of maleic anhydride (MA) grafting and the application of MA-grafted polyolefins are viewed as mature technologies. The chemistry and technology of modifying apolar polyolefins with the polar and reactive MA either in solution or in the melt were already explored as far back as the 1950s. Commercial applications exploit the improved adhesion of polyolefins to polar materials, both at the macroscopic scale and on the microscopic scale. However, it is hardly recognised that, from a scientific point of view, grafting has still a strong resemblance to alchemy. Both process and application technologies have been developed in a trial and error fashion. Only in the last decade the structure of MA-grafted polyolefins has been elucidated and attempts to "look" inside the extruder during grafting were only recently successful. The first steps towards the development of sound chemical models are currently made. An overview will be given of the progress made in the various areas mentioned.

Keywords: extruder; grafting; maleic anhydride; NMR; polyolefin

Introduction

Grafting of maleic anhydride (MA) onto polyolefins is probably the classical example of free-radical grafting and of reactive extrusion.[1,2] In the 1950s both the first scientific papers and the first patents on MA-grafted polyolefins have been published and filed, respectively. The numbers of papers and patents amount roughly to 750 and 2000, respectively. A large number of companies (amongst others Atofina, Crompton, DSM, DuPont, Eastman, Equistar, Exxon and Mitsui) are grafting MA onto a variety of polyolefins, such as PE, PP, EP(D)M, EBM, EOM and SEBS, on a commercial scale. The total world production of these modified polyolefins is estimated at 150 kton/year. The price of these high-performance polyolefins is determined by the costs of the starting polyolefin, the MA graft content and the production technology.

MA-grafted polyolefins are usually obtained via a free-radical process using preferably as initiators, but also cationic or thermal („ene") reactions are possible. Preferably, MA grafting is

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performed in the melt, but also routes via solution, the solid state or the vapour phase (surface modification) are known and/or applied. The applications of MA-modified polyolefins are usually based on the enhancement of adhesion between apolar polyolefins and polar substrates (polyamides, polyesters, coatings, glass, inorganics, metals, and paper) either on the macroscopic level (co-extrusion, over-moulding and adhesives) or on the microscopic level (compatibiliser and dispersion and coupling agent).

It is frequently expressed that grafting of MA onto polyolefins is a mature technology and that all aspects are fully understood. However, it is the author's opinion that grafting of MA bears still a close resemblance to alchemy. The recent progress with respect to the (supra)molecular structure of MA-grafted polyolefins is hardly recognised. Reactive extrusion is a very complicated process, involving melting, dispersion, reaction, mass and heat transport etc., and is still performed as a black box process, i.e. the extrudate characteristics are directly interpreted in terms of the grafting recipe and the conditions. Application development of MA-grafted polyolefins is carried out via trial and error. The goal of this paper is to review the recent developments with respect to the production, the structure and the application of MA-grafted polyolefins.

Production

Recently, devices have been developed that allow sampling along the screw axis of a co-rotating twin-screw extruder in operation. About 2 gram of representative polymer melt sample can be taken within about 5 seconds.[3] A large series of MA grafting experiments has been performed, varying the polyolefin type (PE, EPMs and PP), the grafting recipe (amount of MA and type and amount of peroxide) and the grafting conditions (screw configuration and speed and temperature profile).[4,5] The MA graft content of the products was determined using FT-IR spectroscopy; rheometry and sol/gel extractions were applied to study cross-linking or degradation phenomena of the polyolefin backbone. Figure 1 shows that for a variety of grafting recipes the MA graft content follows a convex profile along the screw axis, independently of the polyolefin type used. The final MA graft content is determined by the MA dosage, the type and the amount of peroxide and the polyolefin composition. For PE and EPM copolymers it was shown that at 200 °C the MA graft content is not affected by the propene content of the polyolefin up to 60 wt.%, but then rapidly decreases to low values for PP. Thermal grafting, i.e. in the absence of peroxide, of these saturated polyolefins occurs hardly.

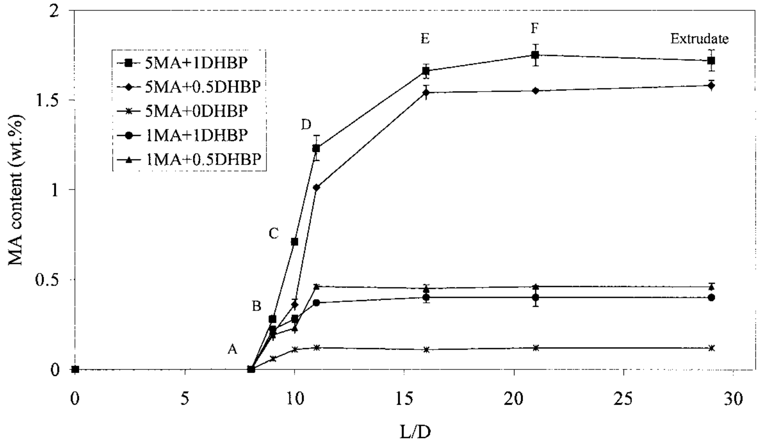

Fig. 1. MA graft content along screw axis as a function of grafting recipe [co-rotating twin-screw extruder: HDPE; DHBP: 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane; 5 kg/hr, 200 °C, 75 rpm].[4]

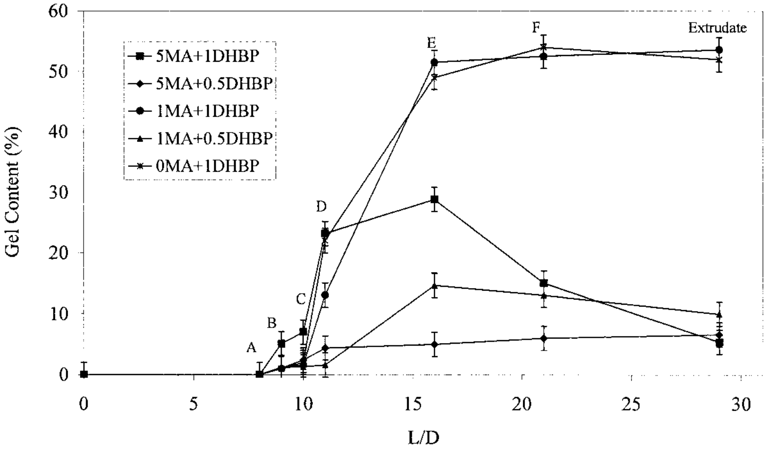

Fig. 2. Gel content along screw axis as a function of grafting recipe [co-rotating twin-screw extruder: HDPE, DHBP: 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane 5 kg/hr, 200 °C, 75 rpm;].[4]

In the case of PE, grafting of MA is accompanied by branching or cross-linking. As can be seen in Figure 2, the PE gel content is determined by the grafting recipe. Actually, the gel content may go through a maximum, which stresses the use of sampling devices for studying the grafting process or for its optimisation. For PP, grafting is accompanied by chain scission. For EPMs with intermediate compositions there is hardly a viscosity change, which is due to compensating effects of branching versus degradation.

In a semi-quantitative approach the experimental MA graft content along the screw axis can be correlated with the calculated decomposition of the peroxide. The latter is calculated using the Arrhenius' equation combining the melt temperature and residence time – both have been measured using the same series of sampling devices – along the screw axis. As for the MA graft content, convex profiles are calculated for the peroxide decomposition. Figure 3 shows that there is a fair correlation between the experimental MA graft content and the calculated peroxide decomposition.

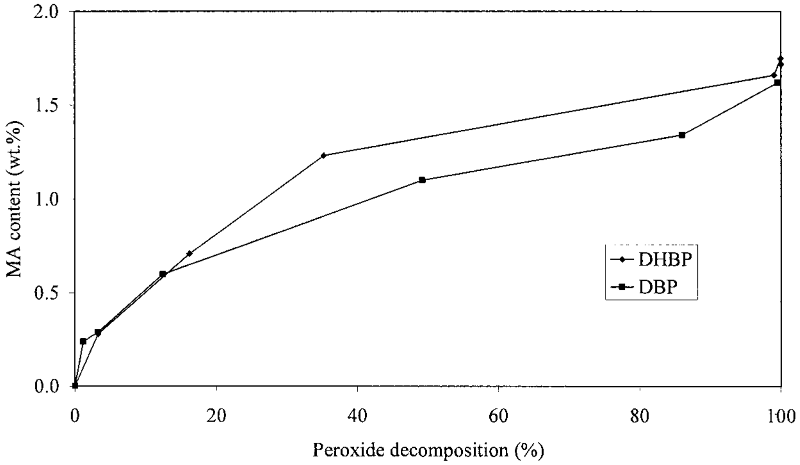

Fig. 3. Experimental MA graft content versus calculated peroxide decomposition [DHBP: 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane; DBP: di-tert-butyl peroxide] along the screw axis (co-rotating twin-screw extruder: HDPE, 5 kg/hr, 200 °C, 75 rpm).[4]

Clearly, this kind of studies results in true insight in the physico-chemical phenomena occurring within the extruder during MA grafting. Eventually, it should result in a quantitative process description and allow proper process optimisation.

Structure

With respect to the molecular structure of MA-grafted polyolefins, many suggestions have been made in the scientific literature, but few of them have experimentally been proven. A recent liquid-state ^{13}C NMR study on polyolefins grafted with ^{13}C-labeled MA in the melt and in solution has identified a series of graft structures as shown in Figure 4.[6,7] A series of low-molecular-weight alkylsuccinic anhydrides had to be synthesised to interpret the NMR spectra.[8] Only monomeric MA grafts have been demonstrated with the exception of HDPE grafted in the melt: mixtures of monomeric, dimeric and trimeric grafts are then formed. Grafting occurs only on secondary C-atoms in PE and ethene-rich EPMs and on tertiary C-atoms in PP and propene-rich EPMs. For EPMs with intermediate compositions grafting occurs both on secondary and tertiary C-atoms. Only saturated MA grafts have been demonstrated with the exception of PP grafted with MA: terminal MA grafts with an exo-cyclic unsaturation are formed as the result of PP chain degradation at a tertiary MA graft site: so first grafting, then β-scission. In summary, it can be stated that only a few of the structures suggested in the literature could be proven.

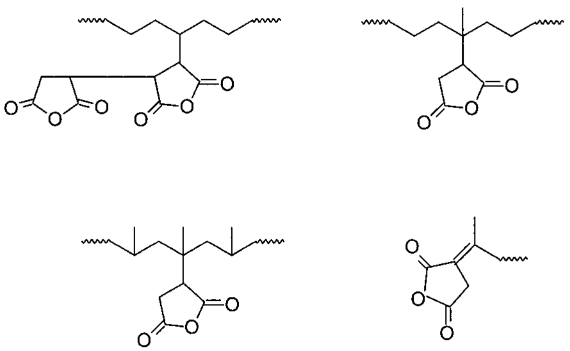

Fig. 4. Chemical structures of MA-grafted polyolefins (PE, EPM and PP).[6,7]

MS on MA-grafted alkanes (C_8 upto C_{30}), used as representative low-molecular-weight models for polyolefins, showed the presence of relatively large amounts of products with 2, 3 and even 4 MA grafts per alkane molecule.[9,10] Such multiple graft structures suggest the occurrence of intramolecular H-transfer (Figure 5). The formation of multiple MA graft structures may be enhanced when MA has not (yet become) dissolved in the polyolefin melt.

Finally, it has been shown using a variety of techniques that MA-grafted polyolefins have a tendency to form rigid, polar clusters (Figure 6), similar to those occurring in ionomers. The difference in polarity between the polar MA grafts and the apolar polyolefin backbones is the driving force for the formation of these MA-graft-rich clusters. It is enhanced by H-bonding, if hydrolysis of the MA grafts into maleic acid grafts has occurred. Dynamic and steady-state light scattering and fluorescence spectroscopy on solutions of EPM-g-MA in apolar hexane and polar THF have shown strong cluster formation in the former apolar solvent.[11,12] It was shown that for a particular EPM-g-MA sample, approximately 70% of the MA grafts is present as multiple grafts structures (cf. Figure 5).[13] SAXS of EPM-g-MA in the solid state has shown the presence of strongly scattering domains of 40 to 45 nm diameter. Upon increasing the MA graft content of EPM-g-MA the number of domains remains more or less constant, but the number of MA graft units per polar domain increases.[14] Finally, these MA-rich clusters (30 to 90 nm diameter) have actually been „visualised" via AFM on very thin EPM-g-MA films cast on mica.[15]

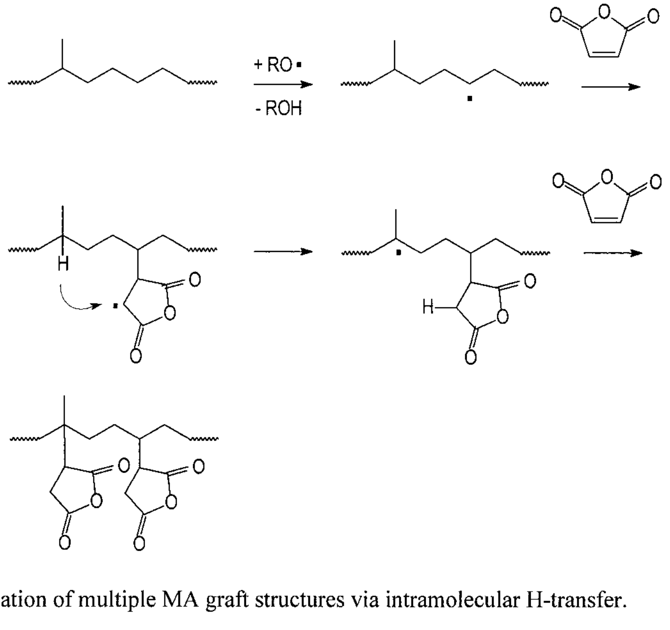

Fig. 5. Formation of multiple MA graft structures via intramolecular H-transfer.

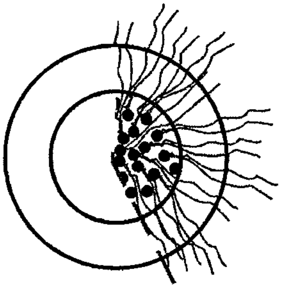

Fig. 6. Schematic representation of rigid MA-graft-rich domains in EPM-g-MA.

Applications

One of the major applications of EPM-g-MA is that as impact modifier of polyamides (PA).[16] Tough PA/EPM blends are usually produced via reactive blending, i.e. the compatibiliser is formed in-situ during blending via a reaction of the PA amine end groups with the grafted MA moieties. Using the sampling devices already mentioned, the changes in MA graft content, PA graft content and EPM particle size have been monitored along the extruder screw axis.[17] It was shown for a variety of PA-6/EPM-g-MA/EPM blends that all physico-chemical phenomena occur very fast upon melting of the PA-6 granulate in the first kneading zone. The residual MA graft content decreases to below 0.1 wt.%, the PA-6 graft content goes to a plateau value and the EPM particle size is reduced from mm to μm level (Figure 7). Further along the screw axis these quantities are not affected anymore. However, there is a continuous decrease of the PA-6 viscosity along the screw axis as a result of degradation.

Another typical application of MA-grafted polyolefins is that of adhesive between apolar and non-reactive polyolefins and polar substrates. In a recent study the adhesion between PA-6 and PP-g-MA was studied by determining the adhesion energy (E_{adh}) of sandwiches with a asymmetric double cantilever beam.[18] It was shown that E_{adh} is governed by diffusion of the MA-grafts towards the interface. XPS after removal of the non-grafted PA allowed the determination of the areal graft copolymer density (Σ). It was shown that E_{adh} is a linear function of $\log\Sigma$. Finally, it was demonstrated that the toughness of the interface is determined first by plastic deformation in the PP phase and ultimately by chain scission of PP blocks.

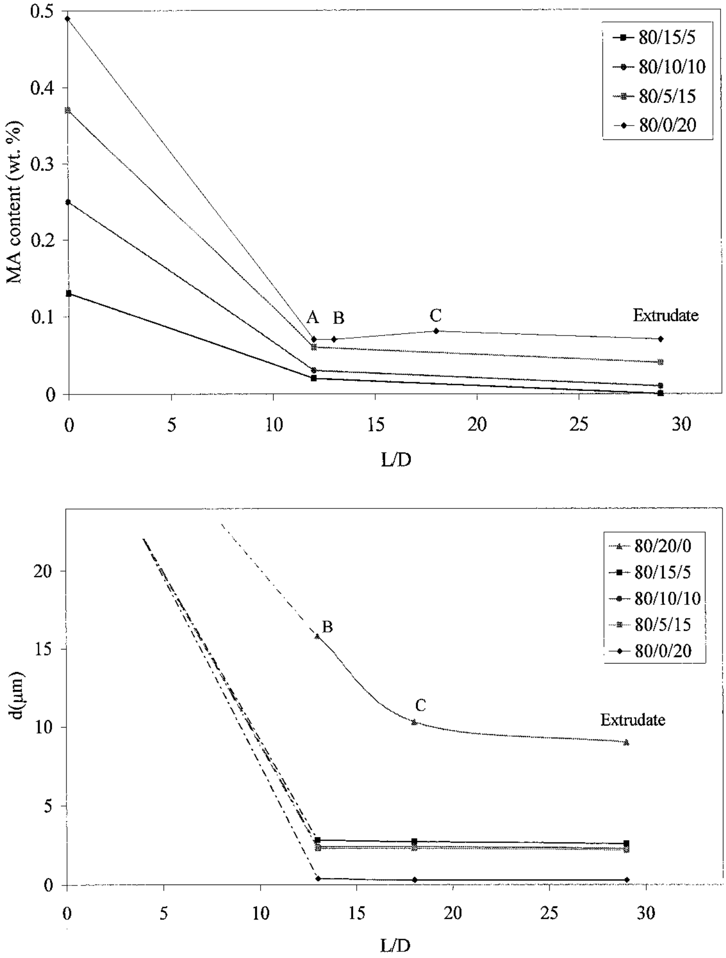

Fig. 7. Residual MA graft content of EPM-g-MA and average EPM particle size along screw axis for a variety of PA-6/EPM-g-MA/EPM blends (co-rotating twin-screw extruder: 6 kg/hr, 230 °C, 200 rpm).[17]

Concluding Remarks

From the results reviewed here it is clear that impressive progress has been made with respect to the production, the structure and the application of MA-grafted polyolefins. However, there is still a large number of questions to be addressed. An overview is given in Table 1, which is probably not exhaustive. Only, when more progress has been made in these areas, grafting of

MA onto polyolefins will be converted from alchemy to a true technology. Eventually, this should allow us to take maximum advantage of MA-grafted polyolefins.

Table 1. Questions related to MA-grafted polyolefins still to be addressed.

- Chemical structure/mechanism
  - identification/quantification of free-radical intermediates
  - intra/intermolecular H-transfer and termination reactions
  - kinetics
  - effect of polyolefin composition/tacticity ?
  - multiple graft structures in polymer system ?
  - clustering in melt ?
- Production
  - solubility/vapour pressure of MA in/above melt
  - effect of grafting recipe (MA dosage, type/amount of peroxide)
  - effect of residence time (distribution), temperature, rpm, screw lay out
  - process model, including chemical kinetics and mass/heat balances
  - low peroxide efficiency ?
  - strange maxima in MA graft content as function of recipe and conditions ?
- Application
  - study of interface
  - effect of (supra)molecular structure of MA-grafted polyolefin
  - relationships between interfacial structure and macroscopic properties
  - effectivity of monomeric MA graft vs. multiple MA graft vs. high-molecular-weight SMA co-polymer graft

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