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CHEMICAL MODIFICATION OF POLYMERIC HYDROCARBONS

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Abstract: Although polymeric hydrocarbons (PCH) carry no functions, they can be modified in many ways. Unsaturated PCH undergo addition reactions as hydrogenation, halogenation, epoxidation and thiol addition. Saturated PCH can be substituted with various functions, notably halogen and chlorosulfonyl groups. All PCH can be modified, by a grafting mechanism, with functional monomers as maleic anhydride. Some modified PCH play a major role in multiphase systems as blends, rubber-modified thermoplastics and thermoplastic elastomers. Attractive grafting procedures involve in-situ grafting in PCH/monomer solutions and during reactive blending processes.

INTRODUCTION

Since many years, polyolefins form the largest class of thermoplastic polymers with still increasing technical and economical importance. The annual production of polyolefins is expected to increase worldwide from presently about 55 Mio t to nearly 80 Mio t in 2005. Polyolefins are, similar to low molecular paraffins, relatively stable against chemical attack, which is one of the reasons for their good stability against environmental influences. But the poor chemical reactivity of polyolefins is also the reason why many investigations have been performed to modify the properties of polyolefins and to introduce reactive or polar groups into the polymer chains. The older literature is summarized in the book of Fettes1), whereas some more recent summaries give a survey of actual developments2-7).

Chemical modification of polymeric hydrocarbons (PCH) can be classified as follows:

Unsaturated PCH:
- Isomerisation
  - cis-trans
  - cyclization
- Addition Reactions
  - Hydrogenation
  - Halogenation
  - Epoxidation
  - Addition of Thiols

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- Saturated PCH:
  - Substitution Reactions
    - Halogenation
    - Chlorosulfonation
    - Oxidation
  - Addition Reactions
    - Functionalization
- Grafting of PCH:
  - Grafting "from"
  - Grafting "onto"

In the following report, some recent examples of chemical reactions of unsaturated and saturated PCH are described. In the second part, some developments in grafting of polymeric hydrocarbons are discussed.

REACTIONS OF POLYMERIC HYDROCARBONS

The chlorination of polyethylene is a long known process which can be performed in solution, in suspension or by direct reaction of gaseous or liquid chorine with polyethylene$^{8)}$. The degree of chlorination and the distribution of the chlorine atoms on the polymer chain depends strongly on the experimental conditions and results in a polymer which contains mainly three different monomer units:

$$-\left[CH_2-CH_2\right]_x-\left[CH_2-CHCl\right]_y-\left[CHCl-CHCl\right]_z-$$

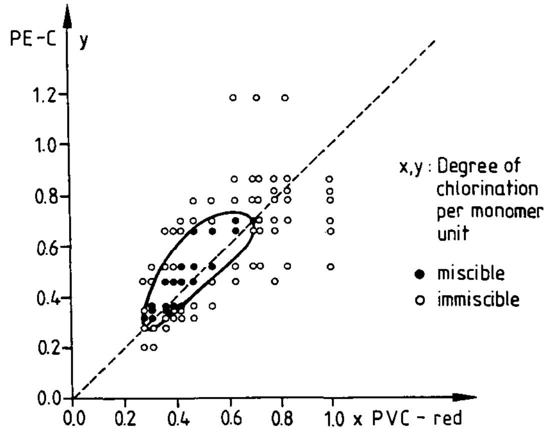
A much more well defined product is obtained by dechlorination of poly(vinyl chloride) with tributylhydridotin and azoisobutyronitrile as initiator. By this process a broad variety of copolymers of ethylene and vinyl chloride can be obtained$^{9)}$.

$$-\left[CH_2-CH_2\right]_n-\left[CH_2-CHCl\right]_m-$$

It is of interest that chlorinated polyethylenes which were obtained by these two methods are compatible only in a very small range of composition$^{10)}$ (Fig. 1).

As an example of addition reactions of unsaturated polymeric hydrocarbons the addition of 4-mercapto-acetamidodiphenylamin to EPDM may be discussed$^{11)}$. This thiol is a well know antioxidans for unsaturated polymers. It reacts in a Brabender plastograph in the mass temperature range of 140 to 180°C with EPDM where up to about 75% of the stabilizer can be added to the polymer. The applicability of this type of immobilization of an antioxidant to EPDM rubber was confirmed with cable sheating compounds crosslinked by electron irradiation.

Fig. 1: Miscibility in blends (1:1 w/w) of reduced polyvinylchloride (PVC-red) and chlorinated polyethylene (PE-C) at 30°C



One of the most important addition reactions of polyolefins is the functionalization by free radical induced addition of unsaturated monomers. There are many investigations on the reaction of maleic acid anhydride with polyethylene[12] or polypropylene (e.g.[7]). The reaction mechanism is rather complicated due to simultaneous chain degradation or crosslinking under the influence of the peroxide which generates free radicals. These side reactions can be avoided by choosing suitable peroxides, e. g. 2,5-dimethyl-2,5-di(tert-butyl)hexine-3, which can be used to graft up to 1 wt-% of maleic acid anhydride to polypropylene without degradation but with the disadvantage that toxic decomposition products of the initiator are formed[13] (Fig.2). Another problem is the discoloration of the reaction products by side products due to the polymerization of maleic acid anhydride. This undesired effect can be overcome by using substituted maleic acid anhydrides like citraconic acid anhydride. Depending on the type of free radical initiator up to 5 wt-% anhydride groups can be incorporated into polypropylene without colour formation[13]. The disadvantage is that this anhydride is much more expensive than maleic acid anhydride (Fig.3).

Fig. 2: Grafting of polypropylene with maleic anhydride (MSA) with the initiator 2,5-dimethyl-2,5-di-tert-butylperoxy - hexine-3

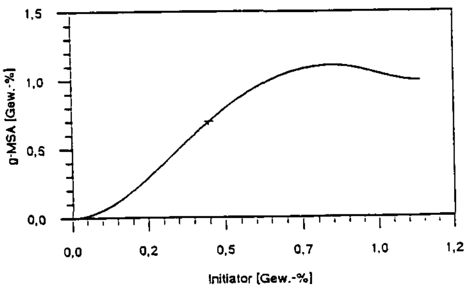
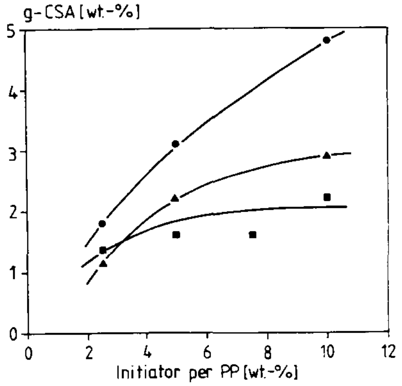
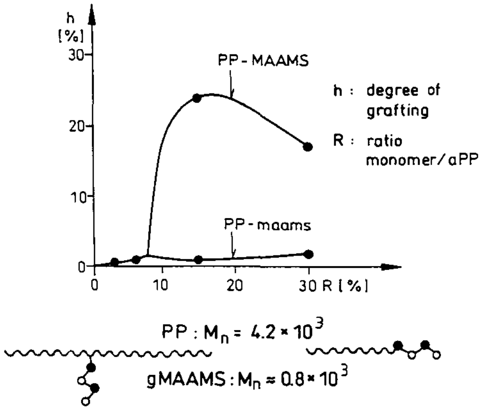


Fig.3: Grafting of polypropylene with citraconic acid anhydride (CSA), initiators tert-butylcumyl-peroxide (■ without, ▲ with silica) and 1,1-di-tert-butyl-peroxycyclohexane (●)



Due to its relatively low molecular weight and its good solubility, atactic poly(propylene) is a suited model for kinetic studies of maleination via free radical reactions in melt. Maleic anhydride was also grafted to atactic polypropylene with a mixture of maleic anhydride and α-methylstyrene (MS). Advantageous is that MS cannot homopolymerize at the high temperatures of melt reaction and that maleic acid anhydride and MS tend to copolymerize alternatingly to give colourless products. The kinetics of the grafting process is complicated by a phase separation of poly(propylene) and the monomer mixture which is caused by the special attractions between the two monomers. As a result, two grafted poly(propylene) products are obtained of which the major is only slightly but the minor is heavily grafted. The latter graft copolymer which is probably created in the interphases between phase domains carries about one grafted chain per poly(propylene) back bone chain approximately with three anhydride and five MS units[14] (Fig.4).

Fig.4: Heterogeneous grafting of maleic anhydride (MAA) and MS from PP: highly (PP-MAAMS) and weakly grafted chains (PP-maams) coexisting



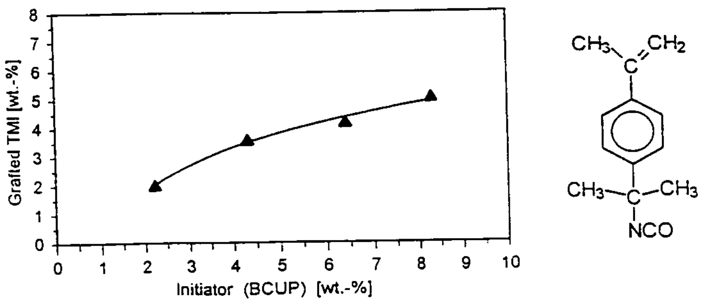


Fig.5: Modification of PP by m-isopropenyl-α,α-dimethylbenzylisocyanate (TMI) with tert-butylcumylperoxide (BCUP) at 180°C

As another possibility for introducing functional groups into polyolefins, the reaction with α-methylstyrene derivatives may be discussed. For example, m-isopropenyl-α,α-dimethylbenzylisocyanate (TMI) reacts with poly(propylene) in melt at 180°C in presence of tert-butylcumyl peroxide. Under these conditions up to about 5 wt-% of TMI can be incorporated into poly(propylene). The isocyanate groups of the obtained functionalized poly(propylene) can react for example with amines or with amino end groups of polyamides. Such grafted polymers can, for example, be used as compatibilizers for blends of poly(propylene) and polyamides[13] (Fig.5).

GRAFTING OF POLYMERIC HYDROCARBONS

PCH are useful blend components, both for their properties and their prize. Polyolefines as PE and PP have been blended with all large-scale thermoplastics and duroplastics, often simply as "prize diluents" but also to reduce polarity, enhance ductility or improve processability. PCH rubbers as polybutadiene (PB) or ethylene-propylene copolymers (EPDM) are commonly used as toughening agents for brittle thermoplastics[15].

Problematic is that PCH are strongly incompatible with virtually all other polymers. Unmodified, most of their blends are useless. They are invariably demixed, with ill-defined phase morphologies and weak interface adherence between the phases. To gain strength, the interfaces must be bridged by compatibilizers which are usually block or graft copolymers[16].

Low-cost strategies for polyolefine blends involve reactive blending. The compatibilizing graft copolymer chains are formed in situ during melt mixing[17,18]. Blends of polyolefines with other thermoplastics that consist of alkyl sequences, too, as polyamides or polyesters, are sometimes simply treated with peroxides so alkyl macroradicals are generated that couple in the interfaces via radical combination[16].

Unfortunately, the macroradicals degrade or crosslink the phases as well. Better results are obtained with two-stage reactive blending where the polyolefine macroradicals are first intercepted by maleic anhydride (or other functional monomers, see above). The functionalized polyolefine chains couple then in blends with suitably end-functionalized polycondensates as polyamides or polyesters in the interfaces via condensation[17,18].

Compatibilized blends thus produced contain the graft copolymer only in minor amounts, just sufficient to yield fine, stable phase morphologies. This suggests a question that has so far attracted little attention: can interface grafting, in processes of reactive blending, be adapted to yield pure graft copolymers? Recent model studies confirm this, with specific limitations[19]. Interface grafting in melts follows autoinhibitory kinetics. Graft copolymer chains that are generated in the interfaces evidently stay there, hindering further grafting, so the reaction can come to a halt. Complete conversion is indeed possible in a limited window of the chemical system parameters, but the graft copolymer product is usually bimodally composed of strongly and weakly grafted chains in coexistence.

Easier to control than melt blending processes are processes where polymeric hydrocarbons are grafted in monomer solutions. The prime example is high-impact polystyrene (HIPS) which is prepared by polymerizing styrene in PB/styrene solutions. In competition with homopolymer and graft copolymer formation, the system undergoes phase separation and matrix inversion. This yields in an unsurpassed variety of complex phase morphologies ranging from highly PS filled PB over the famous "salami" structures of commercial HIPS to micellar arrays in optically transparent PS[20]. At any stage, the process can be stopped or altered, which results in even more complex morphologies ("products by process"). Some of these structures are still investigated as to their potential.

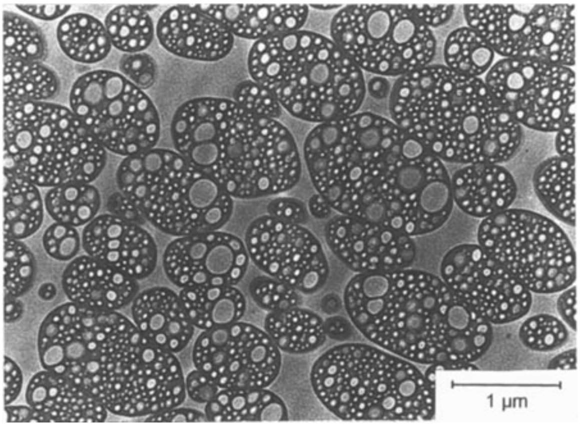
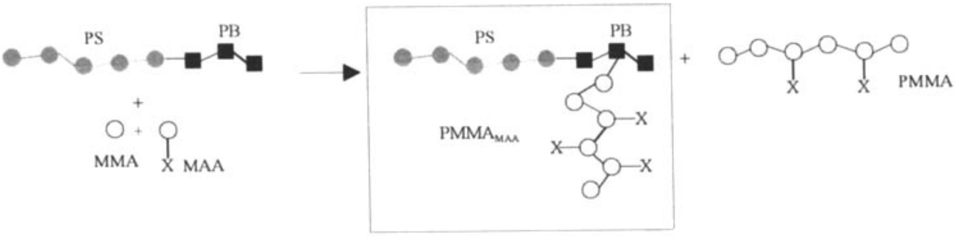


Fig.6: Graft copolymerisation of MMA on EPDM: salami masterbatch structure

The chemistry of this process can be changed considerably. In particular in the system EPDM/polymethylmethacrylate (PMMA), morphologies can be well controlled. The unique "salami domains" which convey impact strength to brittle polymer matrices, by mechanisms of crazing and cavitation, are shown in Fig.6. The single domains owe their stability and substructure to the graft copolymer (EPDMgPMMA) which forms a surface layer on the outside and micelles on the inside. As illustrated by Fig.6, these domains are packed in a surprisingly dense array. This is the stage just after the matrix inversion. It is known to be rheologically controlled, but why the domains do not coalesce although touching each other, is still not known. This concentrated "salami" morphology can be used as a masterbatch for impact modifying other thermoplastics.

A special class of copolymers results when the technique of polymerisation in polymer/monomer solutions is applied to block copolymers. This offers a simple route towards polymers with a three-block architecture. Grafting on the butadiene block of styrene-butadiene diblock copolymers (SbB) yields blockgraft copolymers which, unusual for graft processes, can be obtained with very little homopolymer by-product[21,22]. The blockgraft copolymer $\text{SbBgMMA}_{\text{MAA}}$ consists of three mutually immiscible blocks (PS, PB, PMMA_{MAA}: maleinated PMMA) and yields the three-phase microstructure shown in Fig.7. Advantageous about radical grafting is that a whole family of blockgraft copolymers can be produced from a single diblock copolymer. When the butadiene block is short, the products are almost equal to diblock copolymers. Indeed, $\text{SbBgMMA}_{\text{MAA}}$ behaves like a diblock copolymer SbMMA. But the chemistry of radical grafting is richer than the chemistry of anionic block copolymerisation: grafts can be random copolymers where special functions can be incorporated (as maleic anhydride in MMA_{MAA}).



The copolymer $\text{SbBgMMA}_{\text{MAA}}$ is a very versatile compatibilizer for polymer blends. Blends where one components each is miscible with the styrene block and the MMA graft are successfully compatibilized as well as blends with polyamides where the amino end groups couple with the maleic anhydride functions.

Similar blockgraft copolymers cannot be prepared from triblock copolymers SbBbS. Under the attack of peroxide radicals, part of the butadiene block is split. This does not change much in SbB diblock copolymers. But SbBbS triblock copolymers are severely degraded, being split into two shorter diblock chains.

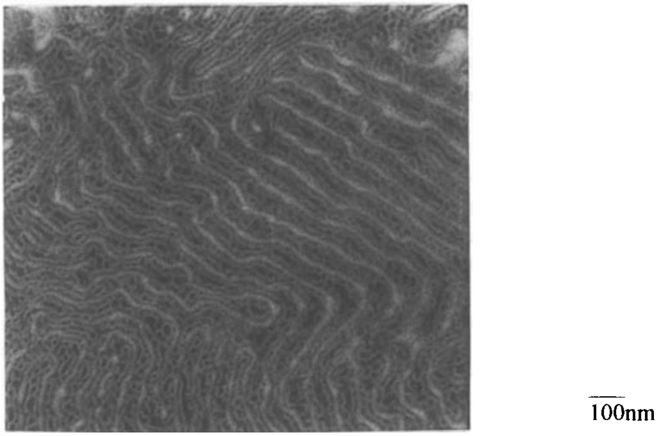
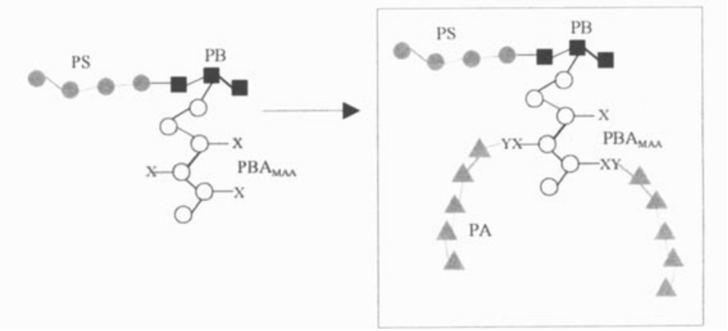


Fig. 7: Three-phase microstructure of the blockgraft copolymer SbBgMMA$_{MAA}$, styrene gray, butadiene black, MMA white

A novel type of stabilized polymer blends is established with blockgraft copolymers SbBgBA$_{MAA}$ with an elastomeric graft of maleinated butylacrylate. When the anhydride functions react with polyamide chains (PA), during reactive blending, a blockgraftgraft copolymer SbBg(BAgPA) results:



This copolymer has the structure of a thermoplastic elastomer. But it is also an efficient compatibilizer for blends PS/PA where it covers the interfaces so the BgBA center blocks form an elastomeric interface monolayer. Important is that these blocks are anchored in the two adjacent phases since the styrene block penetrates the PS phase and the PA grafts the PA phase. Under stress, this anchoring keeps the elastomeric interfaces from uncontrolled cavitation. Instead, the elastomeric interfaces induce profuse multicrazing and efficient toughening. This block graft copolymer thus combines the functions of a compatibilizer and an impact-modifier, rendering separate impact-modifiers in the two phases unnecessary.

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