New Reactive Additives for Interface Modification in Multicomponent Polyolefin Systems

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Summary: New reactive additives were synthesised and used as interface modifiers in different multicomponent polyolefine systems. The synthesis was carried out in computer-controlled reactor by means of Diels-Alder reaction and condensation. These additives are capable of combining the benefits of dispersing and coupling agents. A part of the synthesised reactive surfactants have also synergistic effect in flame retardant systems. Their surface-active character facilitates the reactive compounding. The undesirable transport processes of stabilisers and components of flame-retardants in polyolefine systems could be effectively controlled by interface modification.

Introduction

Interfaces of multicomponent polyolefine systems play a key role in the formation of the structure-property relationship[1,2]. Not only the filled, reinforced systems but also the introduction of other functional additives, like flame retardants, require the modification of the interfaces[3,4]. Surfactants are mostly used to promote the homogeneous dispersion, while reactive modifiers improve the adhesion between the apolar polyolefine matrix and the polar inclusion[5]. In order to perform the coupling at the interfaces in line, the additives should find their right place during a short residence time in a compounding machine. For this purpose the reactive modifiers should also have surface-active character. The aim of this work was to utilise our earlier experiences for combining the benefits of surfactants, coupling agents and/or synergists of flame retardant systems[6,7]. The molecule structure of new reactive surfactants (RS) was considered suitable for this purpose[8,9]. Their synthesis under controlled conditions and applicability for improving the adhesion, photostability and flame retardancy are discussed.

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Experimental

HDPE: Stavrolen 276773, density: 0.960 g/cm^3 (Stavropolymer, Russia); PP: Tipplen K793 (TVK, Hungary), density: 0.9 g/cm^3, melt index: 0.7 g/10min (21.6 N, 230°C). Anionic surfactant (AS): Disponil AES 63, [alkyl-poly(ethylene-glycol)-ether-sulfate] (Henkel GmbH); Cationic surfactant (CS): N-hexadecyl pyridinium bromide (Caola, Hungary); Non-ionic surfactant (NS): Tegin 4100 palmitic/stearic acid glycerol ester (Th. Goldschmidt. A. G., Germany); Oleic acid 90% (Aldrich, Germany); Copper phthalocyanine pigment: Hostaperm green GNX (Hoechst, Germany); Maleic acid anhydride (MAA): analytical grade (Sigma Chemical Co. USA); Glycerol-mono-oleate (GMO): Tegomuls O (Th. Goldschmidt. A. G., Germany); Isomerised linolic acid: Nouracid AE 457 (AKZO Chemie GmbH, Netherlands); Flame retardant system: ammonium polyphosphate: Exolit 422 ($(NH_4(PO_3))_n$ (n=700) (Clariant Germany), and Pentaerythritol (PER), R.P. grade, ($C_5H_{12}O_4$); (Aldrich), ratio: 3/1.

Work of adhesion was calculated using the equations proposed by

Owens-Wendt[10]
$$W_a = 2\sqrt{\gamma_1^{d}\gamma_2^{d}} - 2\sqrt{\gamma_1^{p}\gamma_2^{p}}$$

and Wu[11]
$$W_a = -\frac{4\gamma_1^d\gamma_2^d}{\gamma_1^d+\gamma_2^d} - \frac{4\gamma_1^p\gamma_2^p}{\gamma_1^p+\gamma_2^p}$$

where W_a is the work of adhesion, γ^d and γ^p are the dispersive (d) and polar terms (p) of the surface free energy of the components 1 and 2. For the purpose of calculation, the surface free energies of the separate surfaces were determined using methylene iodide and water.

Direct adhesion measurements were performed between PE film (thickness: 20 µm) and $CaCO_3$ sheet (a polished section of a piece of calcite from OMYA SA, France). The films/sheets were treated with the interface modifiers, compressed and then the force of peeling was measured.

The polymer compounds were prepared by homogenisation of the components in the mixing chamber 350 of Brabender Plasti-Corder PL2000 with rotor speed of 50 rpm, at 200 °C. Sheets (100×100×3 mm) were formed using a laboratory compression moulding equipment.

Preparation of additives: the reactive surfactant (RS) was prepared on laboratory scale in an earlier described computer-controlled model reactor [12]. In these experiments a double-walled glass reactor was equipped with reflux condenser. A program unit of the software was used for measuring the heat flow of the process. The preparation of the additives was started with the addition of conjugated unsaturated fatty acid and maleic anhydride into the reactor. The computer raised the temperature, according to the recipe, to 50-120 °C. The product was characterised by FTIR, DSC and TG analysis. In course of the organic boroxo siloxane elastomer (OBSi) synthesis the torque of stirrer was measured by the current of the motor and an adsorbent column was applied in order to determine the evolved water continuously. After dosing the Si and B containing components the temperature of the reaction was controlled (see in Figure 2) at a constant stirrer speed of 100 rpm. The product was characterised by FTIR and DSC analysis.

UV measurements were performed in solutions of 10^{-5} mol/l concentration using HP 8452A Diode Array type spectrometer. The instrument used for accelerated photo-ageing, was Xenotest 450 type weatherometer (Original Hanau), (rel. humidity of 40 %, black plate temperature 43 °C). Textenser type tensile testing instrument (Text. Res. Inst. Hungary) was used for determining the mechanical properties (the drawing rate was 100 mm/min).

Results and Discussion

Model experiments on PE and $CaCO_3$ systems

The influence of non-reactive surfactants (S) on the work of adhesion of PE was calculated using the Owens-Wendt and Wu methods and compared with direct adhesion measurements. Three types of non-reactive surfactants: anionic (AS), cationic (CS), non-ionic (NS) and oleic acid were applied as interface modifiers. In the case of oleic acid the effects of physical and chemical treatment were compared as well. The calculated and measured results for PE and $CaCO_3$ systems are given in Table 1.

Table 1. Calculated (calc.) and measured adhesion between PE and $CaCO_3$ without and with interface modifiers.

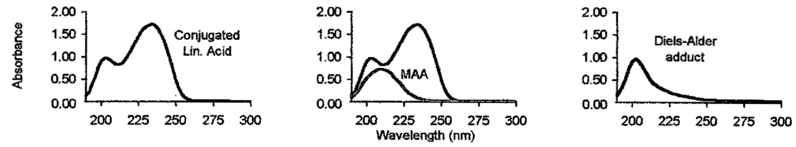
Surface 1	Surface 2	Work of adhesion (mN/m)		Direct adhesion measurements (N)
		calc. according to Owens-Wendt	*calc. according to Wu*	
Polymer (PE)	$CaCO_3$	76.7	89.9	2.6
AS on the polymer	$CaCO_3$	116.5	126.5	
CS on the polymer	$CaCO_3$	129.6	137.7	
NS on the polymer	$CaCO_3$	99.3	111.5	
Oleic acid on the polymer	$CaCO_3$	130.6	139.3	
AS on $CaCO_3$	Polymer	90.0	101.2	3.4
CS on $CaCO_3$	Polymer	85.1	97.1	3.3
NS on $CaCO_3$	Polymer	83.2	95.5	7.0
Oleic acid on $CaCO_3$	Polymer	86.5	97.8	3.5
Oleic acid on the polymer + Benzoyl peroxyde	$CaCO_3$			13.5

Based on the results given in Table 1 the following conclusions can be drawn:

- the reference values (see in row 1 of the table) are the lowest ones,
- the values calculated according the different methods does not differ significantly,
- the calculated W_a was higher when the treatment was applied on the polymer side,
- the W_a values show the difference between the untreated and treated surfaces in accordance with the direct adhesion measurements, but the effectiveness of the different treatments can not be predicted from the calculated values,
- the oleic acid ensures much higher adhesion when it is chemically bounded using initiator.

Syntheses and characterisation of new reactive interface modifiers

The good results of oleic acid in model experiments initiated us to synthesise reactive surfactants (RS). In line monitoring of the progress of reactions was performed using a computer-controlled reactor-calorimeter. Table 2 contains the chemical structure of the synthesised compounds, the process of the preparation and their functions in polymer systems. The formation of the new RS compounds takes place by means of Diels-Alder reactions, ester formation, addition and different condensation reactions. A part of the synthesised reactive additives have synergistic effect in flame retardant (FR) systems, these are denoted as SRS. An example for the synthesis in the computer-controlled reactor is given in Figure1.



I II III

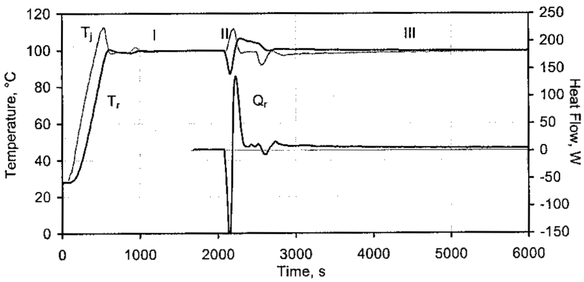


Figure 1. Change of characteristic values (Tr: temperature of the reactor, Tj: temperature of the jacket, Q: heat flow) during the synthesis of RS I and the UV spectra of the reactants and the products at different stages (I, II, III) of the process.

At the first part of the diagram the diene component was kept at constant temperature until 2000 s, then the dienofil (MAA) component was fed into the reactor, which melted and caused an endothermic peak on the heat flow curve. Just after this peak the exothermic effect of Diels- Alder reaction can be seen. The progress of the reaction was followed by UV spectroscopy as well. In the first spectra (I in Figure 1) the peaks belonging to the separate (at 200 nm) and the conjugated double bonds (at 230 nm) of diene component appear. The second stage is where the peak of MAA (at 210 nm) can be seen in the figure (II in Figure 1). The end of reaction could be determined by the disappearance of the peak characteristic to conjugated double bonds and MAA. This stage is shown in the third spectra (III in Figure 1). Example for the synthesis of a polymeric additive is shown in Figure 2. In this case the progress of the reaction could be easily followed through the on line information about the evolved water and the change of viscosity.

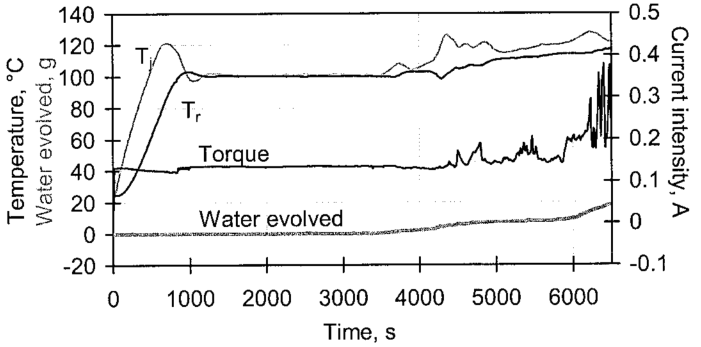
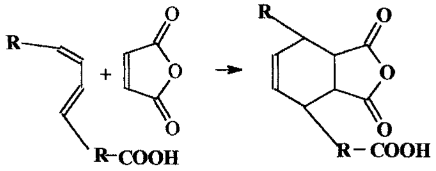
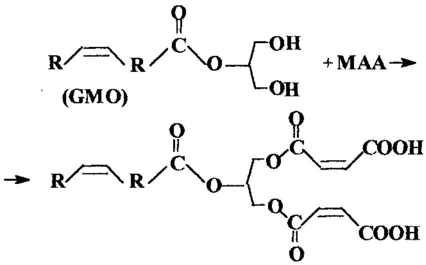
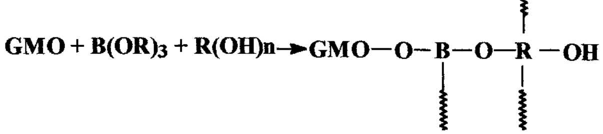
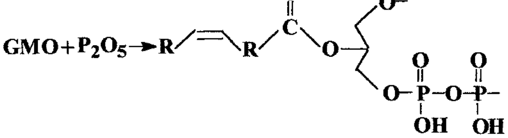
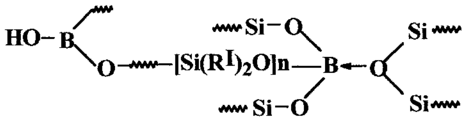
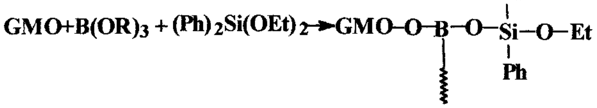


Figure 2. Change of characteristic values during the synthesis of OBSi in computer-controlled reactor (T_r,T_j are reactor and jacket temperature resp., torque is expressed by current of stirrer).

The synthesised reactive interface modifiers can be applied for pre-treatment of the additives of polymer compounds, but more advantageous is to utilise the technological benefits of reactive compounding. Due to the surface-active character of the additives they will find their right place at the interface before the reaction starts. RS I and RS II containing carboxylic or carboxylic-anhydride groups in the polar region and reactive double bonds in the apolar part, are capable of homogenising fillers in the matrix and of forming chemical bonds between the inclusion and matrix. The reaction of RS-s with polyolefine matrix was verified on model system by XPS (ESCA) surface analysis, while the reaction between the RS and filler was demonstrated by DSC. These results have been reported in details elsewhere[13].

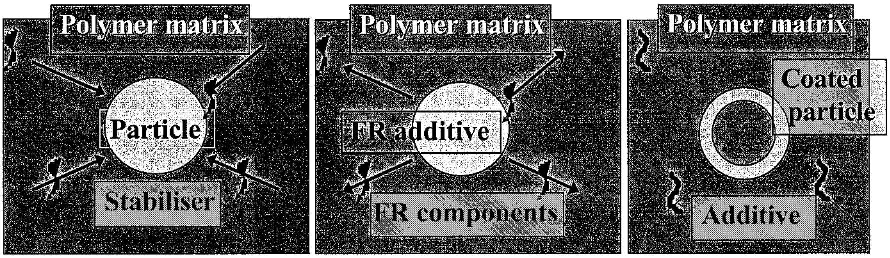
Table 2. The synthesised compounds.

Symbol	Formation of RS compound	Application
RS I	**Diels– Alder addition** 	Dispersing and coupling agent in particulate, and fiber containing compounds
RS II	**Ester formation by addition** 	Dispersing and coupling agent in particulate, fiber and polyamide containing compounds
RCRS	**Condensation**  $GMO + B(OR)_3 + R(OH)n \rightarrow GMO-O-\underset{\vert}{B}-O-\overset{\vert}{\underset{\vert}{R}}-OH$	Dispersing, coupling and rheology controlling agent in FR compounds
SRS I	**Addition** 	Dispersing, coupling and FR synergist agent in FR compounds
OBSi	**Condensation** 	Synergistic agent, glass forming precursor
SRS II	**Condensation**  $GMO+B(OR)_3 + (Ph)_2Si(OEt)_2 \rightarrow GMO-O-\underset{\vert}{B}-O-\overset{Ph}{\underset{Ph}{Si}}-O-Et$	Dispersing, coupling and FR synergist agent in FR compounds

The application of the interface modifiers is proposed in various types of blends, filled, reinforced, flame retarded polymers, for different purposes such as: controlling the dispersion[13,14], the rheology[14], the adhesion and structure at interfaces[8], mechanical properties (elongation at break, tensile strength, stiffness)[13], surface characteristics[15] depending on the structure and functional groups of RS-s. Here only two examples are reported to demonstrate the role of the RS-s in controlling the transport processes.

Transport processes of additives and their control by interface modification

The conscious design of an advantageous structure requires not only to understand the role of interfaces, but also to control the rearrangement of the components during whole lifetime of the materials, as it was recently demonstrated in the case of antioxidants[16]. The transport processes in the polymer system may deteriorate the originally good properties. We have investigated two examples as illustrated schematically in Figure 3. The first is the adsorption of stabilisers on the surface of filler or pigment particles that decreases the stability substantially (see in Figure 3a). The second is the migration of flame retardant additive components to the surface of products causing processing and aesthetic problems (see in Figure 3b, FR additive means the system given in Experimental).



a) adsorption of stabiliser

b) migration of flame retardant

c) restricted transport

Figure 3. Scheme of the undesirable transport processes and their control through modification of interface.

The concept of solving the mentioned problems by applying RS coating layer around the particles is shown in Figure 3c.

The photostability of PE film pigmented with Phthalocyanine green pigment decreases markedly (see in Figure 4, Pigm., Untreated) comparing to the same composition but without pigment (see in Figure 4, Unpigmented). By applying RS I the photostability of the PE film containing pigment improved in great extent as it is shown in Figure 4 (Pigm., RS treated). The photo-degradation process and mechanism of improvement has been discussed elsewhere[17].

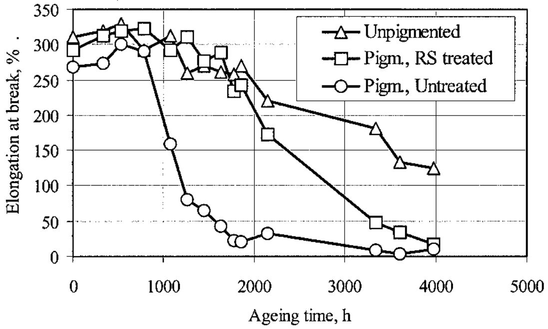


Figure 4. Effect of interface modification on photo-stability of PE pigmented with RS treated and untreated phtalocyanine green pigment.

Another example is the migration of additives in flame retarded polypropylene (FR-PP) systems. (The composition of the applied intumescent type FR system is given in Experimental, the total amount was: 30 %.) The migration of FR additives to the polymer surface was determined by extraction in water. The extracted amount is proportional to the conductivity of extracting water, which was measured by platinum electrode. Figure 5 demonstrates the drastic decrease of conductivity of extracting water due to modification of the interfaces within the flame retarded compound.

The interface modifiers, synthesised for flame retardants (SRS and OBSi, see in Table 2) are capable of improving their efficiency, thermal stability as well[14,15].

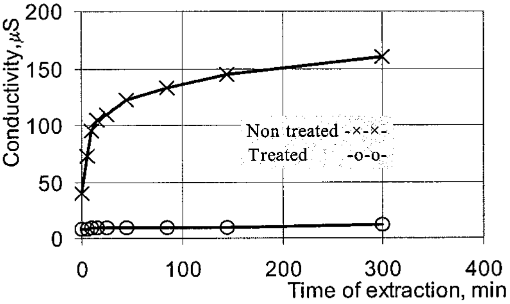


Figure 5. Effect of interface modification on hydrolytic stability of flame retarded PP .

Conclusion

Reactive interface modification of multicomponent polyolefin systems in a compounding machine require the use of surfactant type reactive additives that are able to find their right place during a short residence time. Model experiences confirmed the advantages of reactive long chain hydrocarbon compounds for modification of the interfacial layer. Various types of such additives have been synthesised by applying Diels-Alder and condensation reaction routes. Computer-controlled reactor promoted the accurate and reproducible synthesis of these compounds and offered a convenient in line way for monitring the progress of the reactions. The new additives combine the benefits of surfactants, coupling agents and/or synergists of FR systems. Photo-ageing and water extraction experiments confirmed the ability of reactive surfactants to control the transport processes in multicomponent polyolefine systems.

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