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GRAFT MODIFICATION OF POLYETHYLENE WITH N-VINYLMIDAZOLE BY REACTIVE EXTRUSION AND COMPATIBILIZATION OF POLYETHYLENE/POLYPROPYLENE BLENDS VIA IMIDAZOL-CARBOXYL INTERACTIONS

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ABSTRACT

N-vinylimidazole monomer was grafted onto linear polyethylene in a small laboratory extruder with remarkably good efficiency. The amount of monomer in the reaction mixture — and thus in the product too — was limited by the use of polymer powder with absorbed monomer/initiator solution as input material.

The basically modified polyethylene produced this way was melt mixed with acrylic acid modified polypropylene. The interactions are of ionic character caused by proton transfer. It is remarkable that this mixture of the two modified polymers has a pronounced compatibilizing effect for polyethylene/polypropylene blends even in low concentrations.

INTRODUCTION

Radical initiated graft modification of various polymers, especially of polyolefines in processing devices (extruders) is already a well established industrial procedure [1], [2]. The extruders used for grafting have generally a specialized construction, are correspondingly expensive and very nearly unaccessible for experimental work.

We have published formerly the most simple description of the thermal decomposition characteristics of radical initiators under nonisothermal conditions [3]. The temperature domain of decomposition is determined by the Arrhenius parameters of the decomposition process and by the rate of temperature increase of the reaction mixture. For a strongly simplified ideal case (assuming perfect mixing and smooth, even linear temperature changes) it seems to be possible to regulate the temperature profile along the barrel and the rate of material transport in the extruder such way that the nearly complete decomposition of initiator coincides with the exit of material from the die. Approximating such conditions we grafted earlier successfully N-vinylpyrrolidone monomer onto polyethylene in a small laboratory extruder. This device has no separate input ports for monomer and other reaction components, thus, we worked with polymer powder/monomer/initiator mixtures and because of this, the amount of monomer was limited ($< 10\%$). Nevertheless, the efficiency of grafting was high except the region of very low ($< 2\%$) monomer concentrations [4].

The result of modification by the hydrophilic monomer was manifested by decrease of contact angle of water on the polymer surface, even at the lowest vinylpyrrolidone content (this indicates the relatively high concentration of pyrrolidone groups on the surfaces). The effectivity of vinylpyrrolidone grafting gave impetus to further investigations of reactive processing. As polyolefines are graft modified generally by acidic groups (acrylic, methacrylic acid, maleic anhydride etc.) we preferred the modification by the basic N-vinylimidazole monomer. This was motivated by the possible interactions of basic and acidic groups in mixtures of the correspondingly modified polymers.

MATERIALS

The polyethylene used through this study was a noncompounded virgin powder of a linear low density type 1-hexene copolymer produced by TVK, Hungary. This polymer is a rotational molding type characterized by melt flow index 3 g/10 min (190 °C, 2.16 kg) and density $d = 0.949 \text{ g cm}^{-3}$.

N-vinylimidazole monomer was an Aldrich product of 99 % + purity. It was used without further purification. The radical initiator dicumyl peroxide was supplied by Peroxid-Chemie GmbH, Germany.

The polypropylene was, similarly to the polyethylene, a TVK, Hungary product. The compounded commercial form is proposed for injection molding. This ethylene containing copolymer has the density $d = 0.900 \text{ g cm}^{-3}$ and MFI value of 12 g/10 min (230 °C, 2.16 kg). The acrylic acid modified polypropylene was a pilot plant product made by grafting the same grade of polypropylene. The product used by us had an acrylic acid content of 1.36 weight per cent.

EXPERIMENTAL

For our small-scale reactive extrusion experiments we used the same laboratory extruder as earlier [4]. This is a Haake Rheomex S type measuring extruder of 3/4" barrel diameter. For the grafting reaction it was equipped with an L/D = 25 ratio, 1:3 compression screw of the most simple construction. Three zones and the die section of the extruder were heated by separate control. The exit orifice was 3.55 mm (9/64") diameter, the extruded strand after cooling in tap water was pelletized.

The vinylimidazole content of the modified polymer samples was determined from microanalytically obtained nitrogen content data. Infrared spectra were registered with Unicam Mattson 3000 FTIR spectrometer on hot pressed polymer foils of 20-30 micrometer thickness. Melt viscosity of polymers was measured by Göttfert Rheograph 2002 capillary rheometer at 190 °C in the 10^4 s⁻¹ shear rate range. DSC measurements were made with a Mettler TA 4000 thermoanalytical system having DSC 30 measuring cell. For the thermomechanical investigations we used the same system with the TMA 40 measuring unit, the samples were 1 mm thick, 6 mm diameter circular plates.

Mixtures (blends) of polymers were prepared in a Brabender mixing chamber at 170 °C nominal temperature, 50 rpm mixing rate. From the mixtures 1 mm thick plates were pressed at 170 °C in a Fontijne SRA 100 hydraulic press. The test specimens cut from these sheets were measured on a Heckert FPZ 10 testing machine.

GRAFTING OF N-VINYLMIDAZOLE ONTO POLYETHYLENE

There are few publications referring to the free radical polymerization of N-vinylimidazole. The most informative is the paper of Bamford and Schofield [5]. The results of these investigations are, however, not applicable to the conditions of reactive processing. It was noted, of course, that at low monomer concentrations (as in the case of reactive processing too) the polymerization kinetics is normal and only high monomer concentrations result in degradative addition [5], [6]. We assumed that under conditions of reactive processing the behaviour of vinylimidazole will be similar to the vinylpyrrolidone studied by us earlier. We used the same initiator, dicumyl peroxide and, consequently, we applied the same throughput rate and temperature profile of the extruder as for the successful grafting of vinylpyrrolidone (rate 50 rpm, temperature settings 170/190/200/210 °C). In [4] it was discussed, how the extruder temperature profile and the linear material transport rate determine the rate of temperature increase of reaction mixture and how can the temperature domain of initiator

decomposition determined by this rate match the effective temperature domain of materials in the extruder.

As the laboratory extruder used has no injection ports, the reaction mixture was prepared in form of a relatively free-flowing powder mixture from polymer powder and liquid monomer, containing the dissolved initiator. The mixture of polymer powder and absorbed monomer was homogenized as it was possible manually. To have a free-flowing powder, the monomer content was kept low (< 5 weight %) in our experiments. The initiator concentration was constant in all experiments (0.15 weight % dicumyl peroxide in the reaction mixture).

The grafting reaction itself presented no problems at all. During the extrusion the torque measured on the screw was registered. It was found that the torque (i.e. the viscosity) of reaction mixtures is somewhat higher than of the pure polyethylene and shows small increase with growing vinylimidazole concentration. This small effect is caused probably by the combination termination of vinylimidazole radicals formed on polyethylene chains. This effect was investigated by melt rheometry too. At low shear rates ($\gamma_{ap} = 1.2 \text{ s}^{-1}$) the apparent viscosity determined by the Göttfert rheometer for the modified polymers was 1.4-1.6 times of the viscosity of the unmodified polymer. At high shear rates ($\gamma_{ap} = 115.2 \text{ s}^{-1}$) the modified polymers have 1.7-1.9 times the original viscosity, increasing with growing vinylimidazole content. These results are consistent with some molecular weight increase and branch formation on the polymer.

In the grafting experiments we used the minimum charge determined by the size and working conditions of extruder (approx. 200 g). Change of the feed composition during the continuous extrusion resulted in intermediate products as a consequence of mixing. Because of this, the first and last 25 % of the different charges were discarded. Remarkably is the high grafting efficiency (approximately 80 %) and the practical independence of efficiency from the monomer concentration used. This differs markedly from the behaviour of N-vinylpyrrolidone monomer [4]. The vinylimidazole monomer has high boiling point (192-194 °C) and, possibly, better solubility in molten polyethylene, thus, monomer loss by evaporation may be less important. Vinylimidazole graft data from nitrogen analysis and grafting efficiency calculated from these show that the data vary somewhat, maybe because of inhomogeneity, but generally correspond to an approximately 80 % efficiency. Grafted samples after extraction with isopropanol gave the same results indicating no or minimum homopolymer formation.

Table 1 Typical series of vinylimidazole extrusion grafting experiments. Polyethylene charge size 200 g, initiator 0.30 g dicumyl peroxide per charge. Extrusion parameters see text.

reaction mixture		product		efficiency %
<u>ml NVI monomer</u> 200 g PE	<u>mol NVI</u> 100 g PE	N % found	<u>mol NVI</u> <u>graft</u> 100 g PE	
3.0	0.01654	0.38	0.01374	83.1
		0.37	0.01337	80.8
4.0	0.02206	0.44	0.01594	72.3
		0.45	0.01631	73.9
6.0	0.03309	0.72	0.02634	79.6
		0.66	0.02409	72.8
10.0	0.05514	1.26	0.04696	85.2
		1.18	0.04386	79.5

The infrared spectra of the imidazole modified polyethylene (or the difference spectra with polyethylene, respectively) have characteristic absorptions at 663.5, 916.1, 1083.0/1110.0 and 1229.0 cm^{-1} . These correspond closely to published N-alkyl-imidazole absorptions (664.7, 908.1, 1077.7/1110.0 and 1231.2 cm^{-1}) [7]. We tried to correlate the integrated and normalized absorbance values determined on hot pressed foils of modified samples (between 1036-1175 cm^{-1} and 1177-1334 cm^{-1}) with the nominal imidazole content of these samples but the results were unsatisfactory and the experimental technique must be obviously modified.

Summarizing the results of the reactive extrusion experiments we can state that the grafting of vinylimidazole onto polyethylene can be realized with good efficiency. Practically no homopolymer formation takes place. Composition inhomogeneities of modified polymer are not unacceptable and are probably caused by the low homogenization efficiency of the small single-screw extruder used.

POLYETHYLENE/POLYPROPYLENE MIXTURES CONTAINING POLYMERS MODIFIED BY BASIC AND ACIDIC GROUP

Imidazole groups have relatively strong basicity as the non-bonding electron pair of the unsubstituted N atom is capable of hydrogen bond formation or, it can accept a proton with formation of imidazolium cation. Our goal was the study of the interaction between the basically modified polyethylene and polymers containing acidic groups. This interaction seemed to be especially important if the backbone polymers of the basic and acidic components were different, e.g. polyethylene and polypropylene. Thus, we choosed for our investigations acrylic acid modified polypropylene as acid-group-bearing component.

It is very well known that mixing of different polymers at the molecular level is exceptional and even such chemically similar types as polyethylene and polypropylene are incompatible. This is consequence of the low mixing entropy caused by the connectedness of the units of polymers [8]. Only strong specific interactions between groups of the two different polymers can assure in some cases a complete mixing. Generally, however, the result is even in presence of positive interactions not a molecular mixture but a compatibilized two-phase system.

Nevertheless, the importance of compatibilization is outstanding too, as the often poor mechanical parameters of simple mixtures may become interesting for practical points of view in result of the effect of a good compatibilizer. This would be very important in the reuse of mixed plastics of communal waste. Here the main components are the various types of the semicrystalline polymers polyethylene and polypropylene. A compatibilized blend of these, with acceptable mechanical properties, would be a valuable material.

For the immiscible polymer pairs the ideal compatibilizer is the diblock copolymer having halves chemically identical with the two immiscible polymers, respectively. Ideally, such a compatibilizer is located on the interface of the two polymers, the different halves interacting with the corresponding polymer phases. The detailed theoretical treatment of such systems is given in e.g. [9]. On the other hand, successful compatibilization can be the result of groupspecific interactions (e.g. acid-base interactions) too. Thus, partially sulfonated polystyrene and ethyl acrylate/vinyl pyridine copolymer were compatible because of the interactions of ionic groups formed by proton transfer [10].

Our compatibilization studies were made with the extrusion modified polyethylene containing 25 mmol imidazole/100 g polyethylene. The acidic component was polypropylene modified by acrylic acid (19 mmol/100 g polypropylene). Specimen preparation was described in Experimental. The samples were 50-50 % mixtures of polyethylene and polypropylene; in this series the content of modified polyethylene and modified polypropylene, respectively, was equal too, changing from 0 to 100 %. The interaction of the modifying groups was clearly visible on the IR spectra. The absorption at wavenumber 1710.8 cm^{-1} , characteristic in the spectrum of poly(acrylic acid) [7] was nearly absent in the spectrum of the mixture of modified polymers indicating the ionization of carboxylic groups. No other important changes were detected.

The melting and crystallization processes of the polyethylene/polypropylene mixture and of the 100 % modified polyethylene/100 % modified polypropylene mixture were studied by DSC. In the blend of the original polymers the melting peak of the polyethylene phase is at $129.5\text{ }^{\circ}\text{C}$ ($128.4\text{ }^{\circ}\text{C}$ for the second melting) and the enthalpy of melting is 175.8 J/g (185.4 J/g) corresponding to 60 % and 63.3 % crystallinity. Polypropylene melting peak was located at $165.1\text{ }^{\circ}\text{C}$ ($163.9\text{ }^{\circ}\text{C}$) and from the enthalpy changes 76.8 J/g (78.8 J/g) the calculated crystallinity was 47.1 % and 48.3 %, respectively. On the cooling curve there were no separate peaks for the two component, the single peak was at $114.6\text{ }^{\circ}\text{C}$ and the total enthalpy change 132.7 J/g was very near to the sum of the enthalpy changes of components.

Remarkably, the blend of modified polymers gave very similar results. The melting peak corresponding to PE was at $127.3\text{ }^{\circ}\text{C}$ and the PP peak at $159.2\text{ }^{\circ}\text{C}$ that is the melting point depression was significant, but not excessive. Similarly, the crystallinity determined for the PE phase was 59.0 % (58.0 %) and for the PP phase 47.6 % (49.4 %). The single crystallization peak was at $119.0\text{ }^{\circ}\text{C}$. Thus we stated that the extrusion modification of polyethylene lowered the melting point and the crystallinity, but the changes are less than expected. The same is true for the modified polypropylene. Moreover, in the mixture of the modified polymers no other significant change was to be observed by DSC. These results indicate that the ionic bonds formed between imidazolium and carboxylate ions are weak and at higher temperatures have no influence on the phase changes. Nevertheless, network formation by ionic bonds and the existence of a corresponding interfacial state cannot be excluded. This must manifest itself in the mechanical properties of mixtures.

The polyethylene/polypropylene mixtures of various modified polymer content were investigated by a thermomechanical measuring device. The sensor had 7

mm² surface and the force alternated between the values 0.025 and 0.125 N with a cycle time 12 s. Heating rate was 5 K min⁻¹. On the Fig. 1 the TMA traces of the mixtures containing A: zero, B: 50 % and C: 100 % modified polymers are depicted. In function of the temperature, the thickness of all samples initially decreases, above 70 °C increases and the elasticity grows. At the melting of polyethylene the sample A extends rapidly, in case of B a smoother transition is observable and in C only a break indicates the melting of polyethylene. It is remarkable, that the total expansion is to the melting of polypropylene nearly negligible for the mixture of modified polymers (sample C), whereas for the ethylene-propylene mixture (sample A) about 7 % increase of thickness was found.

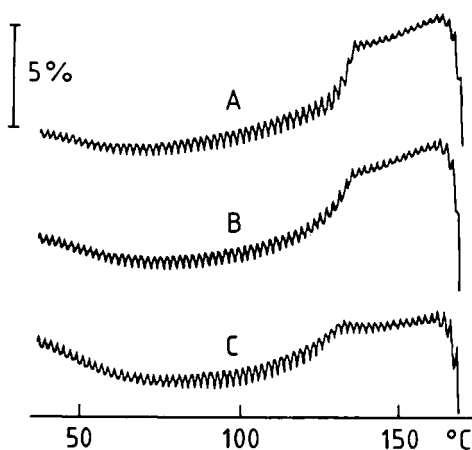


Fig. 1 TMA traces of 1:1 mixtures of polyethylene and polypropylene: effect of modified polymers (see text)

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To see the compatibilizing effect of the modified polymers, the mechanical properties of blends containing various levels of modified polymers were investigated. On the stress-strain curves well defined yield points were absent (with exception of the pure polyethylene/polypropylene blend; $\sigma_y = 13.5 \pm 0.4$ MPa, $\epsilon_y = 5.0 \pm 0.4$ %). Because of this, Table 2 contains only the values of elastic modulus E, tensile stress at break σ and elongation at break, ϵ .

The most interesting is the data series for the tensile stress at break, σ . Its value is nearly constant for blends with compatibilizer content between 13 % and 100 % and this constant value is at least 50 % higher than the breaking stress of the uncompatibilized polyethylene/polypropylene mixture. Elongation at break has generally low values through the series and shows only small increase with growing compatibilizer content. Strangely enough, the elastic modulus has the highest value at the lowest compatibilizer concentration (about 20 % higher than the modulus of the uncompatibilized mixture) and decreases such way, that the

Table 2 Mechanical properties of polyethylene/polypropylene blends containing various amounts of vinylimidazole modified PE and acrylic acid modified PP. Weight ratio of both unmodified and modified PE and PP is 1:1

modified PE + PP content weight %	E GPa	σ MPa	ϵ %
-	0.850 ± 0.072	12.3 ± 0.9	5.8 ± 0.5
13.2	1.037 ± 0.037	18.4 ± 0.7	6.4 ± 1.0
21.1	0.996 ± 0.043	19.0 ± 0.4	7.3 ± 1.1
31.6	0.896 ± 0.063	18.8 ± 1.1	6.6 ± 1.5
50.0	0.877 ± 0.040	19.5 ± 0.8	6.7 ± 0.7
100.0	0.851 ± 0.050	19.8 ± 0.8	9.1 ± 2.3

modulus of the blend of the modified polymers is practically the same as of the blend of pure polymers.

CONCLUSIONS

Polyethylene can be successfully graft modified with N-vinylimidazole by reactive extrusion. This modified polymer having basic imidazole groups was combined with acrylic acid modified polypropylene. Ionic bonding corresponding to salt formation (caused by proton transfer, indicated in IR spectra) results in the coupling of polypropylene and polyethylene sequences. One can suppose that these structures may have compatibilizing effect analogous to that of block copolymers. Mechanical properties of blends i.e. the breaking strength and its dependence on the compatibilizer concentration seems to be in accord with this model but for the detailed understanding of the effect further research is needed.

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