Michal Krištofič, Anna Ujhelyiová

Compatibilisation of PP/PA Blends

Department of Fibres and Textile Chemistry, Institute of Polymer Materials, FCHPT STU in Bratislava,

Radlinského 9, 812 37 Bratislava, Slovak Republic E-mail: michal.kristofic@stuba.sk

Abstract

Blending polymers is widely used for the preparation of new materials. The disadvantage of this application is that the polymer components are usually not compatible and the preparation of blends with suitable (mainly processing and mechanical) properties is not satisfactory. The use of a third compound, called a compatibiliser, is an effective way to ameliorate the end-use properties of the blend. Compatibilisers based on grafted or block copolymers are often used. The present contribution deals with the compatibilisation of polypropylene/polyamide blends with compatibilisers based on grafted or block polyole-fines.

Key words: polypropylene, polyamide, blend, compatibiliser.

is usually achieved by the addition of some additive to a major polymer. Combined modification uses chemically modified agents added to the major polymer forming a blend system. From the point of system stability it is suitable to add as an additive another polymer or agent with a high molecular weight.

The preparation of blends from commercial polymers is a well-known and easy way and is usually more effective and advantageous than the synthesis of new (co)polymers with suitable properties. The application of blends in industry is simultaneously cheaper, although it needs highly effective mixing of components.

The modification of non polar polypropylene with the aim of improving some its properties is often possible with a certain amount of another (polymer) additive. If more of a polar additive is used, the better the end-use properties usually are e.g. hydrophility, dyeability and electrostatic properties are gained; however, worse mechanical properties of the products modified are obtained. Polypropylene/polyamide (PP/PA) blends are interesting because both components are relatively cheap, with versatile advantageous properties, and are easily processable by melting. The compatibilisation of binary polymer blends can be made by the addition of a pre-made block or graft copolymer, segments of which have physical or chemical affinity with two immiscible homopolymers.

For improvement of the interfacial interaction as well as mechanical and other properties of PP/PA blends, compatibilisers e.g. block or grafted polyolefins are effective and frequently used. Polypropylene grafted with maleic anhydride (PPgMA) is usually used. Among others, the following compatibilisers: poly-

olefins, mainly polypropylene grafted with acrylic acid (PPgAA), polypropylene grafted with glycidyl methacrylate (PPgGMA), ethylene propylene random copolymer grafted with maleic anhydride or diethyl maleate (EPRgMA or EPRgDM), and styrene and maleic anhydride dual monomers and polystyrene-block-poly(ethylene-stat-butylene)-block-polystyrene, grafted with maleic anhydride (SEBSgMA), have been used with good results.

The modification of PP by the preparation of polypropylene/polyamide - PP/PA blends is interesting from an industrial point of view because it represents an economic and versatile method of modifying the basic properties of PP. This method effectively combines the thermomechanical properties of PA with the easy processability of PP [1].

The blends of incompatible polymers are usually characterised by the low dispersion of phases, high interfacial tension and poor adhesion. The addition of a compatibiliser, which interacts chemically or/and physically, favours compatibilisation during the compounding process. The compatibiliser itself can change the thermal characteristics of blend components and other end-use properties as well [2].

Ide and Hasegawa studied the effect of maleic anhydride grafted poplypropylene (PPgMA) on PP /PA 6 polymer blends. The structural stability and morphology of the blends were improved by PP-PA 6 grafted copolymers that were formed by the in situ reaction of anhydride groups with the amino end groups of PA 6 [3].

A new material with interesting thermal, structural and mechanical properties was also obtained if propylene/ethylene random copolymer (containing 6% eth-

he modification of polymers with the aim of achieving better properties thereof has been done for many years. This modification can be chemical, physical or a combination of both. The chemical modification consists in the preparation of new material by a chemical reaction. Physical modification ylene) with PA 6, in the presence of PP grafted with 1% of maleic anhydride, was used as the compatibiliser agent. The compatibilising effect was confirmed by measuring the decrease in interfacial tension between PP and PA 6 in the presence of PPgMA as a result of improved dispersion and adhesion between the phases [4].

Blends of PP/PA and PP/PA/maleic anhydride have been prepared using a twin extruder and fiber cutting, flying and mixing apparatus that directly commingles PP fibre and PA fibre. In the presence of a compatibiliser, a marked dispersibility of the polymer blends of PP and PA was observed, and mechanical properties were found to increase as a result of the improvement in interfacial adhesion and dispersibility. The properties of PP/ PA blends manufactured by two different pieces of equipment were shown to be similar in the case of melting both resins. However, particularly superior impact properties were obtained in blends not melting PA 6 fibers as a dispersed phase as compared to blends using maleic anhydride grafted PP i.e. PPgMA as a compatibliser [5].

The influence of PPgMA at the interface of immiscible PP/PA 6 blends was studied and the formation of a new copolymer at the interface between the domains and matrix was investigated. Characterisation of the interfacial copolymer was accomplished by carbonyl vibration of the imide group at 1674 cm⁻¹. The reduction in water absorption and the thermoanalysis experiments corroborated the imide linkage between the amino end groups of PA 6 and the carboxylic groups ogfPPgMA. The modification of the PA 6 particle size and the formation of the interfacial layer were characterised by microscopy and related to the reaction of the interfacial components [6].

The crystallisation and melting behaviour of polypropylene and PPgMA blends at different cooling temperatures was investigated. The blends of PP/PPgMA 50/50 show either single (at low cooling rate) or double (at rapid cooling rate) fusion endotherms depending on their previous crystallisation conditions. The double peaks correspond well to the melting points of pure PP and PPgMA, respectively, implying the separate melting of different lamellar crystals, while the single peak indicates the dominance of co-crystals in the blend system. A higher crystallisation temperature in the isothermal case and a

slow cooling rate in the non-isothermal case are favourable for the occurrence of phase separation between PP and PPgMA lamellar crystals. Isothermal crystallisation kinetics confirm that there is a correlation between the crystallisation rate and the resulting morphologies [7].

The crystallisation kinetics of PP and PPgMA are different and follow the Avrami behaviour at early stages with Avrami exponent 2.7 for PP and 3.8 for PPgMA. This difference is ascribed to their different crystallisation characteristics. The half crystallisation times of PPgMA and PP increase with the crystallisation temperature; but this occurs much more rapidly for PP than for PPgMA. The number of effective nuclei for PPgMA calculated from the kinetic parameters was almost ten times higher that for iPP. The diffusional activation energy of PPgMA was lower than that of PP, while the free energy of formation of a critical nucleos on the growing crystal surface was almost the same. From these results it can be concluded that PPgMA crystallises mainly via heterogeneous nucleation at all cooling rates examined, while PP crystallises via both heterogeneous and homogeneous nucleation, which is noticeable when the cooling rate is high. A small addition of PPgMA (equals to 0.2 wt.%) in the PP melt influences the crystallisation of PP, leading to a reduction in homogeneous nucleation at high cooling rates and to an increase in the number of effective nuclei. This means that PPgMA acts as a nucleating agent in the PP phase [8].

SEM and an image analyser were used for studying the morphologies of the fractured surface of blends PP/PPgMA/PA 12 = 65/10/25 and PPgMA/PA 12 = 75/25. The particle dimensions and its distribution of PA 12 dispersed phase in the compatibilised blends are much lower and narrower than those of the non compatibilised ones. Especially, most of the particles in the PPgMA/PA 12 = 75/25 blend are smaller than 0.1 µm. The PA 12 dispersed phase coarsens during annealing in the PP/PPgMA/PA 12 = 65/10/25 blend. The mechanism of the coarsening of the PA 12 dispersed phase is a coalescence process. The intense mixing between the PP component and the PA 12 component via the reaction of PA 12 leads to a change in the dynamic mechanical behaviour of the components. By dissolution of the polyolefin parts of blend PP/PPgMA/PA

12 = 65/10/25 it was confirmed that the precipitate has a lower PA 12 content than the feed, whereas the filtrate has a higher PA 12 content. From the PPgMA/PA 12 = 75/25 blend, the PA 12 content in the precipitate and the filtrate are the same as in the feed, implying that all the PA 12 has reacted with all the PPgMA in latter case but not in the former [9].

Blends of the PP matrix with 5-40 wt.% of pristine PA 66 pellets or recycled PA 66 fibres as the dispersed phase compatibilised with PPg MA showed good mechanical properties. In particular, the flexural modulus of the compatibilised blends is remarkably higher than that of the mechanical blends. All the intervals of compositions blends with PA 66 fibres give a higher modulus than corresponding blends with pellets. For explanation, a hypothesis was adopted that the structure of the PA 66 used coming from fibres or pellets may be different: the PA 66 fibres are made with oriented chains interacting through hydrogen bonds characterised by very small chain folded crystalline domains. It can be suggested that these interactions are active even at melting temperatures preserving. at least in part, an oriented structure with fine crystallites. Because the modulus of the single components PA 66 in fibres (3730 MPa) and in pellets (2810 MPa) are considerably different, the spinning of PA 66 gives oriented structures which may be preserved during processing and which improve the mechanical properties of a blend containing recycled PA 66 fibres [10].

In the blend 70 wt.% (PP+PPgMA) + + 30 wt.% PA 6 with different weight fractions of PPgMA, the formation of a new copolymer at the interface between the domains of PA 6 and matrix of PP was investigated. It was proved that a reaction between PA 6 and PPgMA occurs and that both components (PP and PA 6) exhibit miscibility with the PPgMA [11].

Industrial fibres obtained from (PP/PA6/PPgMA 70/30/2.5) have good spinnability and mechanical properties. The dyeing experiments showed that the dye uptake of fibres dyeable in an aqueous dyebath is excellent. The affinity of disperse dyes for the disperse fraction of PA 6 increases the dyeability of the new fibrous materials. The light, wet-washing (at 40, 60 and 90 °C) and dry—cleaning fastnesses of the new fibres are comparable to those of PET fibres [12].

The interfacial reinforcement between PP and PA 6 was investigated through in situ reactive compatibilisation at an elevated temperature using PPgMA. The fracture toughness between PP and PA 6 was influenced not only by the bonding temperature but also by the bonding time. The fracture toughness increased with the bonding temperature until 220 °C and then decreased at higher bonding temperatures, which could be explained by the two progressive occurrence of different failure mechanisms: first adhesive failure at the interface and later cohesive failure between chains. The fracture toughness increased with the annealing time, passed a peak, and then reached a plateau. The dependence of the fracture toughness on the bonding time could be also explained in terms of the two fracture mechanisms [13].

Polypropylene and polyamide blends 70/30 wt.% were studied with and without the addition of PPgMA at different levels: 1, 3, 5 and 10 wt.%. The isothermal crystallisation of the PA component is influenced by the presence of PP, reducing the crystallisation rate due to the diluent effect originated by this polymer. On the other hand the crystallisation rate of iPP in the blends is higher than the corresponding value for pure PP. This effect is higher in the blends without a compatibiliser. This behaviour is related to the nucleating activity by the PA component [14].

Ternary blends of PP, PA 6 and PPgMA as a compatibiliser with up to 50 wt.% of PA 6 were investigated. The blend composition and interfacial adhesion provided by the compatibiliser were two important factors that influenced the properties of PP/PA 6 polyblends. Sea and islands or co-continuous morphology was assumed to be present in the compatibilised polyblends containing a PA 6 dispersed phase greater than 30 wt.%. Polyblend polymers were successively melt spun into fibres, and DSC results showed that the dispersed and matrix phases in the fibre maintained a crystallinity comparable to or better than corresponding values for the neat fibres. The dispersed PA 6 phase contained fibrils oriented parallel to the axis and distributed throughout the cross-section of the fibre; however, they were more highly concentrated at the centre. Theoretical analysis showed that the PA 6 droplets coalesced together, leading to the development of fibrillar morphology [15].

PP fibres modified with polyamide 6 and PPgMA exhibit better dyeability, and it has high quality when dyed with disperse dyes in a bath without a carrier at 100 °C. In order to ensure the high quality colouring of blend fibres with respect to the processability of fibres (spinning and drawing), the optimum content of PA 6 is 25 to 30 wt.%. Compatibilised blend fibres PP/PA 6 70/30 have a polyfibrillar structure, of the matrix/fibrils M/F type, where the matrix is PP and fibrils are formed by PA 6 [16].

The effect of the concentration of the compatibilising agent, PPgMA, on the non isothermal crystallisation of molten blends of two semicrystalline polymers, PP and nylon 6, was studied and showed one or two crystallization peaks significantly affected by the presence of PPgMAH. The crystallization temperature of nylon 6 levels off as the concentration of PPgMA increases, whereas that of PP stays at a roughly constant temperature. These blends exhibited concurrent crystallization at the crystallisation temperature of PP [17].

Blends consisting of a PA 66 matrix (75 wt.%) and dispersed isotactic PP phase were prepared by extrusion with a PPgMA compatibiliser, one with a high content of grafted anhydride (2.7 wt.%, HAC) and one of low anhydride content (0.2 wt.%, LAC). HAC and LAC had a similar effect on the PP domain size and tensile properties at equal loadings, unlike the anhydride concentration dependency that had been reported for high PP content blends. As the compatibiliser loading increased from 0 wt.% to 7.5 wt.%, the skin/core injection-moulded morphology gradient diminished. The PP domain size decreased to less than 1µm, the tensile strength increased and the microscale deformation of the PP phase progressed from debonding to particle drawing and from debonding to fibril fracture. HAC and LAC are postulated to behave similarly because of sufficient reactivity with PA and similar surface coverage by HACgPA and LACgPA. Interfacial strength is postulated to increase with the decreasing particle size because of the increasing surface/volume ratio at relatively constant surface coverage [18].

Several other contributions [19 - 24] confirm the results mentioned above. Similar results were found by contributions studying the influence of other compatibilisers.

The effect of the addition of PA 12 and PP to blends was studied in [25]. DSC studies have shown that both compatibilisers (PPgMA and PpgAA) act on the crystallisation behaviour of the PP, causing different shifts in the peaks and the lowering of the crystallization enthalpy. The differences correspond to variations in the morphology; in fact, one can barely observe the existence of a second phase when PPgMA is added. Large differences are also seen from the rheological results, indicating that a more homogeneous structure may be obtained in the case of adding PPgMA. Mechanical properties were improved by the addition of both compatibilisers. Hence the effectiveness of the PPgMA is much larger than that of the PPgAA compatibiliser.

Uncompatibilised blend PA 6/PP 80/20 and the same blends compatibilised with PPgMA and PPgAA were compared after they were extruded, granulated and then reprocessed four times. At low residence times the hypothesised beneficial effect of the formation of new bridges between the two phases slightly improves the properties of the recycled blend, whereas with an increasing residence time and severity of the processing, the properties of the recycled blends tend to worsen. This is valid mainly for the uncompatibilised blend and for the blend compatibilised with PPgAA, while the blend prepared with PPgMA does not show any significant improvement. In the first two cases the morphology is characterised by the presence of some voids and the two phases are clearly distinguishable, while in the last case the two components are almost indistinguishable. In this case no improvement can be reasonably expected due to some increase in the copolymer bridges [26].

Graft side-chain liquid crystalline functional copolymers based upon acrylic acid-functionalised polypropylene PP (PPgAA) were assessed as compatibilisers for PP/LCP polyblend fibres. The compatibilisation effect observed was found to be dependent upon the liquid crystalline phase temperature range of the compatibiliser, with the most favorable being in a liquid state during melt extrusion and hot drawing, thus contributing a lubricatory effect to the blend and giving enhanced physical properties as a result [27].

Polypropylene grafted with glycidyl methacrylate (PPgGMA) as the compati-

biliser was used for the compatibilisation of PA 1010/PP blends. It was found that the size of the PP domains, tensile strength and impact strength of the ternary blends as well as the adhesion fracture energy between the layers of PA 1010 and PP were significantly dependent on the PPgGMA contents in the PP layer. The improvement in properties was attributed to the chemical and physical interaction occurring between PA 1010 and PPgGMA [28].

Different samples of PPgGMA (0.26, 0.33, 0.57 and 0.77 wt.% GMA) were used for binary and ternary blends of PA 1010, PP and PPgGMA. With an increase in the mixing time, the larger particle size decreased. Binary blends of PA 1010 with PPgGMA showed that the PPgGMA particle size decreased as the GMA content of PPgGMA increased. The resulting morphology was dependent on the GMA content in PPgGMA and on the miscibility of PP and PPgGMA. The copolymer formed by PPgGMA and PA 1010 is located at the interface between PP and PA 1010 and acts as a compatibilising agent which strengthens the adhesion between two phases. The more GMA content in PPgGMA, the stronger the adhesion between PA 1010 and PPgGMA [29].

The application of a compatibiliser brings better rheological, thermal, mechanical or other properties due to better adhesion of blend components. Chemical modification allows considerable adhesion advancement. Specific compatibilisers enable the direct bonding of modified iPP to polyamide PA in a reactive extrusion process [30].

The influence of the compatibiliser, a block copolymer, on the rheological behaviour of iPP/PA 6 blends was evaluated and the dual flow behaviour observed. The copolymer, acting as a lubricant, had an influence on the blend viscosity. At a low shear rate, the blend viscosity is higher than that of the matrix, while at a high shear rate the contrary was observed. The morphology of the blends is different in two domains, with a nodular morphology at a low shear rate and a laminar structure at a high shear rate. The copolymer was located at the interface and was supposed to dominate the nodular dispersed-phase behaviour [31].

The properties of PP and polyamide (PA) and PP/PA blends of different per-

centage composition with the addition of low molecular mass polyvinylpyrrolidone (PVP) and thermoplastic maleic anhydride (MA) were studied in [32]. PP/PA 6 blends with weight fractions equal to 70/30, 50/50 and 30/70 containing 2 wt.% of thermoplastic maleic anhydride and PA/PP/PVP (PP90% [PA 90%/PVP10%] 10%, PA/PP/PVP (PP80%[PA 90%/PVP10%] 20% and PA/PP/PVP (PP70%[PA 90%/PVP10%] 30% blends were processed. In the case of mechanical properties, while increasing the amount of polyamide in the blend compatibilised with MA, the tensile strength increases. In the investigation of water absorptivity, a significant increase in the value (while increasing the amount of the PA) was observed, whereas in the investigation of impact resistance, a significant drop in the value (while increasing the amount of the PA) was observed. The investigations highlight the possibility of manufacturing blends of PP and highly-hygroscopic polymers, such as PVP of low molecular mass used for the investigations and also its blend with PA 6. Based on the results, it was found that mixing PP with the previously prepared PA 6/PVP blend produces polymer material with higher elasticity and with a certain stability of the sorption properties [32].

The thermal and crystallisation behaviour of PP/PA 12 was investigated by Seno et al. The addition of 30 wt.% of PA 12 into PP improved the thermal stability of the blend. Compatibilisation had an extensive impact on the thermal stability of the blends. Maximum improvement in thermal stability was shown by the PA 12/PP 70/30 blend (since in this case the more stable PA 12 forms the matrix). Blend PP/PA 12 70/30 showed a minimum improvement in thermal stability as in this case PP was the matrix. The compatibilisation of 70/30 and 50/50 PA 12/PP blends did not affect the crystallisation and melting behaviour of PA 12 and PP. On the other hand, the enthalpies of crystallisation and fusion and, consequently, the percentage crystallinity of PA 12 in the PA 12/PP blends decreased remarkably with an increase in compatibiliser concentration [33].

The interfacial behavior of compatibilisers in polymer blends was investigated by Tao and Baotong. From an analysis of the literature and own experimental results they established that interfacial tension is a function of the concentration

of the compatibiliser and put forward a 'three-stage' physical model to account for the compatibilising behaviour of polymer blends. They also studied the effect of compatibiliser concentration on the size of the dispersed phase in binary incompatible blends and the relation between the interfacial area occupied by each compatibiliser molecule [34].

Superior impact properties were obtained when SEBSgMA was used as the compatibiliser in blends PA 6 and isotactic polypropylene, where PA 6 was the majority phase and PP the minority phase, with optimum PA/PP 80/20 and 10 wt.% SEBSgMA added. In cellular-like morphology the compatibiliser appears to form a continuous phase, while PA and PP form separate dispersions, PA - fine and PP - a coarse one. The mechanical properties indicated that, in fact, PA is also continuous, and the blend can be interpreted as possessing a modified semi-interpenetrating network (IPN) with separate secondary dispersion of PP. The coarser PP dispersion plays an essential role in impact modification. Binary blends of the compatibiliser and one blend component were also investigated. The same cellular structure was observed in the binary PA/SEBSgMA blends, and SEBSgMA again appeared to form the continuous phase when the elastomer concentration was at least 10 - 20 wt.%. By contrast, in PP/SEBSgMA only conventional dispersion of elastomeric SEBSgMA was observed up to 40 wt.% of the elastomer. The impact strength was improved and the elastic modulus lowered in both the PA/SEBSgMA and PP/SEBSgMA blends when the elastomer content was increased. A semi-IPN-like structure is formed in the binary, as well as in the ternary PA/SEBSgMA structures [35, 36].

Blends containing equal amounts of PP and PA 6 were prepared by extrusion mixing, using 5 wt.% of polystyrene-blockpoly(ethylene-stat-butylene)-blockpolystyrene, and modified by grafting with maleic anhydride (SEBSgMA) as compatibliser precursor. The blends were prepared by (A) one-step mixing of the three components, (B) mixing a preblend of SEBSgMA and PP with PA 6, and by (C) mixing a preblend of SEBSgMA and about one third of the total amount of PA 6 with PP and the rest of the PA 6. All of the blends contained dispersed PA6 domains surrounded by a separate interphase of the self-assembling compatibilising

polymer. The morphologies of blends A and B were similar and markedly different from that of blend C, which contained dispersed phase domains of two clearly distinguishable populations. The impact strength and elongation at break were lowest for C. The poor performance of blend C is due to the fact that a considerable fraction of the compatibiliser ended up in small well dispersed phase domains with a high weight ratio of the compatibiliser to PA 6 [37].

The utilisation of SEBS and SEBSgMA for the compatibilisation of blends of PA and PP is documented with similar results in another study by Ohlsson et al. [38].

The positive influence of compatibiliser SEBSgMA on PP/PA blends was also reported in [39]. The reactive blending of 70 vol.% PP and 30 vol.% PA 6 was performed in the presence of various amounts of succinic-anhydride elastomers which are immiscible with both blend components. The characteristic morphological feature of the resulting multiphase polymer blends was a continuous polypropylene matrix containing dispersed core/shell microparticles with a rigid PA 6 core and soft elastomer shell. The accumulation of the elastomer component at the polypropylene/PA 6 interface and reaction of the succinic anhydride of the elastomer with the amine-endgroups of PA 6 enhanced PA 6 dispersion and proved to be the key to unusual property synergisms. In contrast to the conventional soft maleic anhydride grafted EPM elastomer (EPMgMA), the stiffer maleic anhydride grafted SEBS (SEBSgMA) was much more efficient as a blend compatibiliser and gave PP/PA 6 blends with greatly improved strength and toughness without sacrifing stiffness [40, 41].

DSC, SEM and WAXD were used to study of the structure and compatibilisation of PP/PA 12 blends. The compatibilisation of maleated PP (PP-MA) and graft copolymer (PP-MAgPEO) of PP-MA and poly(ethylene oxide) (PEO) in PP/PA 12 blends was observed from the morphology or the fracture surface of the PP/PA 12 blends. The DSC results showed that there was nucleation between PP and PA 12, which was attributed to the unusual epitaxial relationship [42].

In polymer blends, the crystallisation of the dispersed semicrystalline component depends on the type and distribution of the nucleating heterogeneities and on the level of the dispersion. Either fractionated or coincident crystallisation may result. The morphology was controlled with 10 wt.% of four different commercial compatibilisers - PPgMA, SEBSgMA, EBAgFA and E-EAgMA - each leading to specific morphology and crystallisation behaviour. The compatibilised blends show more complex crystallisation compared with the corresponding binary blends. In the compatibilised blends the dispersed PA 6 seems to crystallise coincidently with PP, probably due to its small particle size. The crystallisation of PP takes place at a temperature above the bulk value at all compositions in blends compatibilised with PPgMA and in blends without a compatibiliser. By contrast, in blends compatibilised with SEBSgMA, EBAgFA and E-EAgMA, crystallisation takes place either at the bulk temperature or over the temparature range of 76 - 87 °C at the cooling rate 10 K/min. The amount of shift cannot be explained solely by the size of the PP dispersion [43].

Two types of elastomers grafted with maleic anhydride (MA), an ethylene-propylene random copolymer (EPR) and SEBS, were found to function both as impact modifiers and compatibilisers for PA 6/PP blends. The SEBSgMA material appears to be a better compatibiliser in comparison with the EPRgMA one, as judged by the degree of dispersion of polypropylene and the rubber in the blends. Toughness was greatest for blends where the PA 6 phase was continuous or cocontinuous and the rubber was well dispersed in it [44].

The one-step reactive blending process of ethylene-co-propylene copolymer EPM/PA 6 (20/80 and 80/20) was studied. In the presence of dicumyl peroxide, two monomers, diethyl maleate, DEtM and maleic anhydride, MA was used for the preparation of compatibilisers i.e. functionalized EPM. The thermal and morphology analysis showed significant improvement of the polyolefin/PA 6 blend compatibility using both compatibilizers; however, the presence of a large amount of functionalszed/branched polyamide renders the one-step process more complex and difficult to control [45].

The compatibilization effect was also investigated in PP(polyolefins)/PA 6(engineering plastics)/PS (styrene polymers) ternary blends. The results obtained indicated that, as a ternary blend com-

patibiliser, styrene (St) and maleic anhydride dual monomer melt grafted polypropylene [PP-g-(MA-co-St)] showed more effective compatibilisation in the PP/PA 6/PS ternary blend system than PPgMA, PPgSt and their mixture. The good compatibilizing effect of PP-g-(MA-co-St) can be explained by two mechanisms: one is the in situ formation of [PP-g-(MA-co-St)]-g-PA 6 copolymer at the PP/PA 6 interface, and the other is that it also contains styrene blocks, resulting in chemical affinity with PS and PP homopolymers [46].

The application of plastised starch (TPS) with biodiesel glycerol (TPSBio) or commercial glycerol (TPSCom), and their blends (PP/TPSPlas) into PP was studied. Blends of PP/TPSPlas were obtained by extrusion at the following composition rates: 95/5, 90/10, 80/20 and 70/30 of modified PP/TPSPlas. It was verified that there was no meaningful variation induced by the incorporation of TPSPlas into the melting temperature of the blends, when compared to pure PP. The addition of TPSPlas caused an increase in the crystallinity of PP, mainly for compositions 90/10 and 80/20 of PP/TPSPlas, probably due a morphological alteration such as crosslinking, which may have modified the molecular arrangement of the PP macromolecules by the presence of glycerol, which was also indicated by mechanical evaluations [47].

PP/ethylene-vinylacetate copolymer (EVAC) blend fibres were prepared in the presence of ethylene-propylene random copolymer (EPR) as a compatibilizer. EVAC copolymer contains 10.5 wt.% of vinylacetate and EPR contains 15.4 wt.% of ethylene. The amount of EVAC copolymer and EPR copolymer were 3.5 - 20.5 wt.% and 1.2 - 4.8 wt.% respectively. Sorptive properties of the modified PP fibres were positively and significantly influenced. The sorption of water vapour increases slightly with a higher amount of both additives. The dyeing ability of the modified PP fibres was improved as well. A higher amount of EVAC copolymer has a positive influence on the amount of fixed disperse dyes, as does the higher time of dyeing and the presence of a carrier in the dyeing bath. On the other hand, a higher concentration of the dye in the dyeing bath has a negative influence. The amount of EPR is not important nor the type of dyes examined [48].

The non-isothermal crystallisation kinetics of polypropylene, m-isopropenylα,α-dimethyl-benzyl isocyanate grafted PP (PP-g-m-TMI), and styrene (St), as a comononer, together with m-TMI grafted PP (PP-g-(St-m-TMI) were investigated using DSC at different cooling rates. The crystallisation rates of all samples increased with an increasing cooling rate. The relation of the half time of crystallisation $(t_{1/2})$ of the three samples was $t_{1/2}(PP-g-(St-m-TMI) < t_{1/2} (PP-g-m-$ TMI) < t_{1/2}PP, implying the introduction of St could effectively improve the degree of grafting of m-TMI, resulting in a crystallisation temperature increase, with the crystallisation rate being the the fastest. The Avrami and Ozava methods showed that the crystallisation neglected the secondary crystallization that followed primary crystallisation, but the Mo method successfully described the overall nonisothermal crystallisation process of all samples, where the crystallization rate of PP-g-(St-m-TMI) and PP-g-m-TMI were faster than that of PP. The activation energy (ΔE) for non-isothermal crystallisation determined using the Kissinger method confirmed the nucleating effect of St and m-TMU on crystallisation [49].

A reactive extrusion process was developed to obtain compatibilised A/B immiscible polymer blends. It consists in polymerizing a monomer of polymer A in the presence of polymer B. A fraction of polymer B chains initiates sites either at the chain end(s) or along the chain backbones, from which polymer A chains could grow. In the process, polymer A and graft or block copolymer of A and B were formed simultaneously, leading to in situ polymerized and in situ compatibilized A/B polymer blends. This paper shows the feasibility of conducting this process in a batch mixer using PP and PA 6. Thus ε-caprolactam was polymerised anionically in the presence of PP. A fraction of the PP chains bore 3-isopropenyl-α, α-dimethylbenzene isocyanate, which acted as growing centers to initiate PA 6 chain growth from the PP chains, forming a graft copolymer of PP and PA 6 [50].

Conclusions

This contribution deals with the preparation of binary polymer blends PP/PA and some ternary polymeric blends of PP/PA/ styrene polymers using a compatibiliser. Physically or chemically acting compatibilisers ensuring both good dispersion of a minor polymer in a major one and also the stability of their interactions, are effective.

As a basis, polyamides PA 6, PA 66, PA1010 and PA 12 were used. For this purpose, we studied the preparation and application of block, grafted or combined materials like polypropylene grafted with either maleic anhydride (PPgMA) or acrylic acid (PPgAA) or glycidyl methacrylate (PPgGMA), ethylene propylene random copolymer grafted with either maleic anhydride or diethyl maleate (EPRgMA or EPRgDM), styrene and maleic anhydride dual monomers and polystyrene-block-poly(ethylene-statbutylene)-block-polystyrene, grafted with maleic anhydride (SEBSgMA) with good results. Also mentioned are compatibilised blends of PP/PA with other additives like low molecular mass polyvinylpyrolidone or EVAC copolymer.

The influence of compatibilisation for better dispersibility, a more homogeneous structure, crystallization and thermal behaviour is evident, and many processing and end-use properties can be positively affected, such as the processability of the blend melt, the drawability of fibres, their polyfibrillar structure and mechanical properties, sorption properties (dyeability) etc.

For study of the compatibilised blends, mainly the evaluation of mechanical properties and the DSC method were used, as well as the SEM and WAXD methods.

Acknowledgment

The support of projects APVV 0226-06 and VEGA 1/0444/09 is appreciated.

References

- Karger-Kocsis J. Polypropylene: structure, blends, composites 2. Chapman & Hall, 1995, pp. 69-75.
- 2. Datta S, Lohse DJ. Polymeric compatibilizers B.1. Hanser, 1996, pp. 101-102.
- Ide F, Hasegawa A. Studies on polymer blend of Nylon 6 and polypropylene or Nylon 6 and polystyrene using the reaction polymer. *J. Appl Polym Sci* 1974; 18: 963-974.
- Beltrame PL, Castelli A, Canauz M, Canetti M, Seves A. Effect of an interfacial agent on the physicochemical characteristics of poly(propylene) poyamide 6

- blends. *Macromol Chem&Physics* 1995; 196: 2751-2756
- Yoon BS, Joang JY, Suh MM, Lee YM, Lee SH. Mechanical properties of PP/ PA 6 blends – effect of Manufacturing process and compatibilization. *Polymer Composite* 1997; 18: 757-764.
- Roeder J, Oliveira VB, Goncalves MC, Soldi V, Pires ATN. Polypropylene/polyamide 6 blends: influence of compatibilizing agent on the interface domains. Polymer Testing 2002; 21: 815-821.
- Kilwon Cho, Fengkui Li, Jaesung Choi. Crystallization and melting behaviour of blends polypropylene and maleated polypropylene blends. *Polymer* 1999; 40, 1719-1729.
- Yongsok Seo, Jinho Kim, Kwang Ung Kim, Young Chul Kim. Polymer 2000; 41, 2639-2646.
- Tao Tang, Zhongli Lei, Baotong Huang. Studies on the morphology and crystallization of polypropylene/polyamide 12 blends. *Polymer* 1996; 37, 15: 3219-3226.
- Sacchi A, Di Lando L, Pegoraro M, Severini F. Morphology of isotactic polypropylene-polyamide 66 blends and their mechanical properties. *European Polymer J.* 2004; 40, 8: 1705-1713.
- Roeder J, Oliveira RVB, Gonçalves M, Soldi V, Pires ATN. Polymer Testing 2002; 21, 7: 815-821.
- Seves A, Testa G, Marcandelli B, Bergamosco L, Munaretto G, Beltrame PL. Inducing Water Bath Dyeability in Polypropylenic Fibres by their Blending with Polyamide 6. Dyes and Pigments 1997; 35, 4: 367-373.
- Yongsok Seo, Tran Hai Ninh. Enhanced interfacial adhesion between polypropylene and nylon 6 by in situ reactive compatibilization. *Polymer* 2004; 45, 25: 8573-8581.
- Campoy I, Arribas JM, Zaporta MAM, Marco C, Gómez MA, Fatou JG. Crystallization kinetics of polypropylene-polyamide compatibilized blends. *European Polymer J.* 1995; 31, 5: 475-480.
- Afshari M, Kotek R, Kish MH, Dast HN, Gupta BS. Effect of blend ratio on bulk properties and matrix- fibril morphology of polypropylene/nylon 6 polyblend fibers. *Polymer* 2002; 43: 1331-1341.
- Prchal V, Krištofič M, Lapčík, LJr, Havlínová B. Colouristic Properties of Blended PP/PA 6 and PP/PET Polymer Fibres. Fibres and Textiles in Eastern Europe 1997; 5: 48-50.
- Moon HS, Ryoo BK, Park JK. Concurrent Crystallization in Polypropylene/ Nylon 6 Blends Using Maleic.Anhydride Grafted Polypropylene as a Compatibilizing Agent. J. Polymer Science Part B

 Polymer Physics 1994; 32; 8: 1427–1435...
- Duvall J, Sellitti C, Topolkaraev V, Hiltner A, Baer E, Myers C. Effect of compatibilization on the properties of polyamide 66/polypropylene (75/25 wt/wt) blends. Polymer 1994; 35: 3948-3957.

- Nishio T, Yokoi T, Nomura T, Ueno K, Akagawa T, Sakai I. et al. U.S. Pat. 4,988,764, Toyota Jidosha, 1991.
- 20. Mashita K, Fujii T, Oomae T. US Pat 4,780,505, Sumitomo Chemical, 1988.
- Sakuma M, Kitano M, Sakaizawa M, Yagi Y, Yamamoto N, Yookokura T. EP 0235876 A3, 1987.
- 22. Gróf I, Durčová O, Jambrich M. Colloid Polvm. Sci. 1992: 22: 270-278.
- 23. Rösch J, Mülhaupt R, Michler GH. *Macromol. Symp.* 1996; 112: 141-150.
- Ikkala OT, Holsti-Miettinen MR, Seppälä J. J Appl Polym Sci 1993; 49: 1165-1174.
- Valenza A, Acierno D. Ternary blends of nylon 12/polypropylene/modified polypropylene: Influe/nce of fundtional groups of the modified polypropylene. Eur. Polym. J. 1994; 30; 10: 1121-1126.
- La Mantia FP, Capizzi L. Recycling of compatibilized and uncompatibilized nylon/polypropylene blends. *Polym De*grad Stability 2000; 71: 285-291.
- Miller MM, Cowie JMG, Brydon DL, Mather RR. Fibers from PP and LCP blends using compatibilizing agent. 3.
 Assessment of graft side-chain liquid crystalline compatibilizers based upon acrylic acid-functionalized polypropylene. *Polymer* 1997; 38: 1565-1568.
- Zhang Xiaomin, Yin Zhihui, Na Tainhai and Yin Jinghua. Morphology, mechanical properties and interfacial behaviour of PA 1010/PP/PP-g-MA. *Polymer* 1997; 38, 24: 5905-5912.
- Zhang Xiaomin, Li Gang, Wang Dongmei, Yin Zhihui and Yin Jinghua. Morphology studies of polyamide1010/polypropylene blends. *Polymer* 1998; 39, 1: 15-22.
- Lurz A, Amesoeder S, Ehrenstein GW, Nagel J. Chemical modification of PA 6/PP composites in two-component injection moulding processes. *Gummi,* Fasern, Kunststoffe 2006; 59, 7: 447-453.
- Germain Y, Ernst B, Genelot O, Dhamani I. Rheological and Morphological Analysis of Compatibilized Polypropylene/Polyamide Blends. *Journal of Rheology* 1994; 38; 3: 681-697.
- Gnatowski A, Koszkul J. Investigations of the influence of compatibilizer and filler type on the properties of chosen polymer blends. *J Mat Process Technol* 2005; 162-163: 52-58.
- Seno J, Sabu T, Biju PK, Koshy P, Karger-Kocsis J. Thermal degradation and crystallization studies of reactively compatibilized polymer blends. *Polymer Degrad. Stab.* 2008; 93, 6: 1176-1187.
- Tao Tang, Baotong Huang. Interfacial behaviour of compatibilizers in polymer blends. *Polymer* 1994; 35, 2: 281-285.
- Holsti-Miettinen RM, Seppäla JV, Ikkala OT, Reima IT. Functionalized Elastomer Compatibilizer in PA 6/PP Blends and Binary Interactions Between Compatibilizer and Polymer. *Polym. Eng. Sci* 1994; 34: 395 -404.

- 36. Holsti-Miettinen RM, Seppäla JV, Ikkala OT. *Polym Eng Sci* 1992; 32: 868-877.
- Ohlsson B, Hassander H, Tornell B. Effect of the mixing procedure on the morphology and properties of compatibilized PP/Polyamide blends. *Polymer* 1998; 39: 4715-4721
- Ohlsson B, Hassander H, Törnell B. Improved compatibility between polyamide and polypropylene by the use of maleic anhydride graft SEBS. *Polymer* 1998; 39: 6705.
- Gonzales-Montiel A, Keskula H, Paul DR. Prepr. ADSC Div Polym Mater Sci Technol 1994: 70: 194.
- Rösch J, Mülhaupt R. The role of Core/ Shel–Microparticle Dispersions in Polypropylene/Polyamide 6 Blends. *Polym Bulletin* 1994; 32: 697-704.
- Rösch J, Mülhaupt R.Prepr. ADSC Div Polym Mater.: Sci Technol 1994; 70: 193.
- Tang T, Li HY, Huang BT. Compatibilization and Structure of Poly(Propylene) Nylon 12 Blends. *Macromol Chem & Physics* 1994; 195: 2931-2945.
- Ikkala OT, Holstmiettinen RM, Seppala J. Effects of Compatibilization on Fractionated Crystallization of PA 6/ PP Blends. J. Applied Polymer Science 1993; 49, 7: 1165 -1174.
- Gonzales-Montiel A, Keskula H, Paul DR. Impact-modified nylon 6/polypropylene blends: 1. Morphology-property relationships *Polymer* 1995; 36, 24: 4587-4603.
- Coltelli M-B, Passaglia E, Ciardelli F. One-step functionalization and reactive blending of polyolefin/polyamide mixtures (EPM/PA6). *Polymer* 2006; 47, 1: 85-07
- 46. Dong Wang, Xu-Ming Xir. Novel strategy for ternary polymer blend compatibilization. *Polymer* 2006; 47: 7859-7863.
- Rosa DS, Bardi MAG, Machado LDB, Dias DB, Silva LGA, Kodama Y. Starch plasticized glycerol from biodiesel and polypropylene blends. Mechanical and thermal properties. J. Therm Anal Cal 2010; 102: 181-186.
- Krištofič M, Ujhelyiová A, Marcinčin A, Alexy P, Prchal V. Fibre-forming Polypropylene Modified by Copolymers of Ethylene. Fibres and Textiles in Eastern Europe 1997; 5: 51-53.
- 49. LiChun Ma, LiPing Li and ChuiGen Guo. Influence of m-isopropenyl-α,α-dimethyl-benzyl isocyanate and styrene on non-isothermal crystalloization behavior of polypropylene. *J. Therm Anal Cal* 2010; 101: 1101-1109.
- Cartier H, Guo-Hua Hu. A novel reactive extrusion process for compatibilizing immiscible polymer blends. *Polymer* 2001; 42: 8807-8816.
- Received 25.10.2010 Reviewed 26.03.2012

Technical University of Lodz Faculty of Material Technologies and Textile Design

Department of Clothing Technology and Textronics

The Department was established in 2009, combining the departments of: Clothing Technology and Automation of Textile Processes.

The Department offers research and cooperation within the following fields:

- physical and biophysical properties of clothing (modelling the microclimate under clothing packages)
- creating a basis for engineering fashion design (e.g. actions to improve design processes)
- unconventional structures of clothing with regard to use and manufacturing
 analysis of the operating conditions
- analysis of the operating conditions of machines for clothing production (e.g. optimisation of the gluing parameters process working conditions of sewing threads)
- creating analysis and design processes for the industrial production of garments
- basic problems of general and technical metrology
- instrumentation of measurements, the construction of unique measurement device and system
- measurement and control computer systems, including virtual instruments of the fourth generation
- textronics as synergetic connecting textile technologies with advanced electronic systems and computer science applied in metrology and automatics
- identification of textile and clothing objects with the use of advanced microprocessor measurement techniques
- modelling of objects and their computer simulation, methods of experimental research, especially experiment design of experiments and computer analysis of results

The Department is active in the following educational and scientific fields: textile engineering, pattern design, education of technology and information engineering, materials engineering, health and safety at work, and logistics.

For more information please contact:

Department of Clothing Technology and Textronics Technical Universiy of Lodz ul. Żeromskiego 116, 90-924 Łódź, Poland tel.: (48)(42) 631-33-21 e-mail: maria.kwiatkowska@p.lodz.pl web site: http://www.clotex.p.lodz.pl/