Plastic Waste Minimization: Compatibilization of Polypropylene/Polyamide 6 Blends by Polyalkenyl-Poly-Maleic-Anhydride-Based Agents

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ABSTRACT: The present article discloses the properties improvement in PP/PA 6 blends by new type experimental coupling additives. By the experimental agents especially the tensile properties could be improved. For example, the tensile strength and the elongation were 16.5 MPa and 4.4% without additive, which increased to 25.5, 20.1, 46.8 MPa and 8.1, 6.4, 8.6% in specimens containing polyalkenyl-poly-maleic-anhydride-amide, polyalkenyl-poly-maleic-anhydride-ester, and MA-grafted-low-polymer additives, respectively. DSC curves shows that compatibilizers influenced thermal properties of the polymer blends and reveal affecting of crystalline phase formation process in the blends due to the compatibilization step. Additives A and B rather leads to influencing of PA crystallinities. According to the SEM and FTIR analysis well separated polypropylene and polyamide phases was observed in case of specimens absence of additives but only one well distributed phase by the applying of the synthetized coupling agents. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 3028–3037, 2013

INTRODUCTION

Plastic market is one of the most prospective areas of structural materials, but the history of synthetic polymers is hardly more than 100 years. For example, the worldwide plastic production was only 1.5 million tones in 1950, which has exploded to nearly 300 million tones in 2010.[1–6] On the other hand the environmental friendly disposal of waste polymers is an unsolved problem yet. One possible way for the waste plastic utilization is the mechanical recycling, when new objects are shaping from the waste plastics. Mechanical recycling is applicable only in case when waste polymers are clear and selectively collected. However, the proper waste selection is often difficult due to very close polymer appearances.[5–12]

In polymer developments the blending of two or more polymers is a widely investigated area, but the multiphase polymer morphology generally leads to both poor chemical and physical interactions across the phases. Many researchers investigate the possibility of compatibilization techniques to increase the interfacial adhesion in polymer blends; generally in thermoplastics.[10–27] Market for thermoplastics is dominated by polypropylene

and polyethylene. Their costs are relatively low, around 80–90 euro cent pro kilogram. As advantageous property, both polypropylene and polyethylene have easy process ability, resilience and they are insensitive for moisture. The blending parameters of polyethylene or polypropylene with polyamide are a widely studied field, because theoretically a synergic combination of the polypropylene and polyamide properties should be resulted by this way. The problem is that the polyethylene/polyamide or polypropylene/polyamide blends are multiphase polymers therefore coupling agents are needed to improve the interfacial compatibilization. The compatibilization process is required to reach effective stress transfer between the phases. According to papers maleic anhydride or acrylic acid derivates are efficient compatibilizers, because hydrogen bonds, or even covalent bonds can be formed between the two polymers.[16,20–24] By the application of maleic anhydride or acrylic acid derivates proper interfacial bonds and load transfer mechanisms at the interphase can be reach.

The automotive application of polymers–polymer blends and reinforced polymers is a very rapidly increasing area. In the last decade the importance of polypropylene and its blends have been

Table I. The Main Parameters of Additives

Properties	A	B	C
Structure			
Type	polyalkenyl-poly-maleic-anhydride-amide	polyalkenyl-poly-maleic-anhydride-ester	MA-grafted-low-polymer
Appearance	white yellow	white yellow	golden yellow
Acid number, mg KOH/g	4.0	–	4.5
MA-content, mg/g	0.25	–	0.25
N-content, %	1.85	–	–
M_w	2660	3420	2100
M_n	1940	2750	1710
α	1.37	1.24	1.23

increasing especially in bumpers, seating, dashboard, car interior and exterior trim and lighting applications. Generally engineering plastics are used in polypropylene blends as reinforcing components. In those experiments polyamide and polypropylenes melt together to prepare blends, but it needs compatibilization to achieve satisfactory interfacial adhesion.[10,11,17,18,23,28–30] Good compatibility of polyamide/polypropylene blends could be reached by maleic anhydride grafted polypropylene, which resulted improved phase adhesion, or even organosilanes should be used as coupling agents for improvement of the interfacial adhesion.[17,18,23]

In our work, blends of waste polypropylene and polyamide have been prepared, their properties and the longer term uses have been investigated. The most important mechanical, physical, chemical and rheological properties have been followed by standardized methods, FTIR, SEC techniques. For improving the properties of polymer blends different experimental coupling additives (polyalkenyl-poly-maleic-anhydride derivates) have been used to reach stronger interfacial connection.

EXPERIMENTAL

Plastics

Plastics were obtained from waste sources; polyamide from automotive sector, polypropylene from automotive and packaging sector. Owing to their waste origin, plastics were the mixtures of different polypropylenes and polyamides. That is the reasons why the main properties of the raw materials are different from their typical values in technical datasheets of original polymers. PP and PA 6 have melt flow index of 0.9 g/10 min (230°C, 2160 g) and 45.5 g/10 min (230°C, 2160 g), tensile strength of 21.5 and 95.1 MPa, E-modulus of 940 and 3100 MPa, flexural strength of 22.0 and 121.4 MPa, Charpy impact strength of 14.5 and 8.5 kJ mm^{-2}, respectively.

Experimental Coupling Additives

New type experimental coupling additives were used to reach better interfacial connection between the polypropylene and

polyamide 6. The "additive A" and "additive B" marked coupling agents were the reaction products of α-olefin-succinic-anhydride intermediates with aliphatic alcohol and amide, while the "additive C" experimental coupling additive was synthesized by the reaction of α-olefins from by-products of polyethylene synthesis and succinic-anhydride. The main parameters of additives are shown in Table I. In case of the additives A and B, first the intermediate had been produced, then it was further reacted with aliphatic amide and alcohol, respectively. Intermediate was synthesized using maleic-anhydride and α-olefins in xylene solvent at 100–200°C, then the C_{18}-C_{25} α-olefin-succinic-anhydride intermediates have been reacted with aliphatic alcohol and amine in same solvent under nitrogen atmosphere using catalyst. At the end of the reaction procedure the products were purified by evaporation of the volatile components and filtration. More details about the coupling agent synthesis can be found in WO/2009/050526 patent. Regarding the chemical structure of the additives, "A" was polyalkenyl-poly-maleic-anhydride-amide, "B" was polyalkenyl-poly-maleic-anhydride-ester, while the "C" was maleic-anhydride (MA)-grafted-low-polymer. In the additive C synthesis, separated hydrocarbon fragments (C_{100}-C_{300}) from the by-products of polyethylene polymerization have been used for synthesis, instead of synthetic C_{18}-C_{25} α-olefins. As structures well demonstrate the additives A and B were half amide and half ester, respectively; therefore both of them have one reactive carboxyl groups in each monomer unit.

Each of the synthesized polymeric compounds has yellowish in their appearance. Owing to the —CONH— groups nitrogen content was measured only in case the polyalkenyl-poly-maleic-anhydride-amide coupling agents with value of 1.85%. The molecular weight distributions of additives have been measured by size exclusion chromatography method, which showed some differences in the molecular weight distribution curves. The highest weight and number average molecular weights could be observed in the polyalkenyl-poly-maleic-anhydride-ester agents
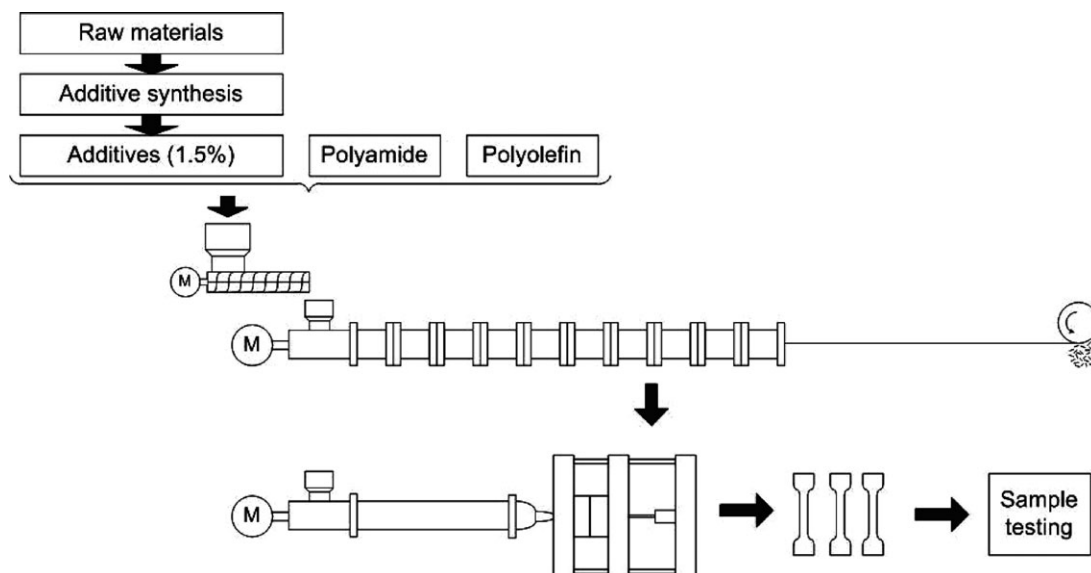
Figure 1. The process layout for the production of PP/PA 6 blends.

($M_w = 3420$, $M_n = 2750$), while the lowest in the MA-grafted-low-polymer ($M_w = 2100$, $M_w = 1710$). The polydispersity (α) values have followed the same order.

Sample Preparation

The specimens for testing made of polypropylene and polyamide have been manufactured according to the Figure 1. Prior to compounding, both polymers have been dried during 12 h at 80°C in an air circulating drying cabinet to avoid plasticization and hydrolyzing effects from humidity. Then 66.66 wt % PP and 33.34 wt % PA 6 were mixed in a laboratory extruder twin-screw (Labtech, Thailand) with 1.5 wt % in all cases and without experimental additives. The temperatures set in the 11 zones of the extruder barrel were 235, 235, 240, 245, 250, 255, 255, 260, 265, 270, 275°C from the feeder to the die. The screw speed was 50 rpm with feed rate of 1.5 kg hourly. The extrudate rod driven from the die has been quenched in cold water and then pelletized using a rotating knife.

The dog-bone shape specimens from polypropylene/polyamide blends were prepared by injection moulding (Arburg 370 C Allrounder 800-250). Before that procedure, the manufactured polymer blends have been also dried using same conditions as it was earlier mentioned (80°C, 12h).

Methods

To determine the tensile and three point flexural properties (mainly stress and extension) (MSZ EN ISO 527-1-4:1999, MSZ EN ISO 14125:1999) an INSTRON 3345 universal tensile testing machine was used. The temperature in the laboratory was 23°C and the relative humidity was 60% during the mechanical tests. Tensile tests were carried out at 80 mm min^{-1} crosshead speed. In case of investigation of flexural properties crosshead testing speed was 20 mm min^{-1}. Five independent samples had been tested in each case, then the mean value was calculated.

Scanning electron microscopy (SEM) was used to study the morphology of fractured faces of specimens and to follow the

possible interaction between the polymers and the additives. The applied apparatus was a Phillips XL30 ESEM instrument.

The coupling additives and the produced compounds were investigated also by infrared technique with a TENSOR 27 type FTIR spectrometer (resolution: 3 cm^{-1}, illumination: SiC Globar light, detector: RT-DLaTGS type) in the 400–4000cm^{-1} wave number range.

CEAST Resil Impactor was applied to measure Charpy impact strength of the produced samples according to MSZ EN ISO 179-2:2000 standard.

The melt flow index (MFI) of polymer blend has been measured according ISO 1133 method using 2160, 5000, 7260, 10,000 g loading and 275°C temperature.

Thermal properties were investigated by differential scanning calorimetry (DSC) using a Mettler Toledo DSC1 STAR System. Samples with a weight of $\sim$ 15 mg were placed in aluminium pans and constant heating and cooling rate of 10°C min^{-1} (line heating and cooling), nitrogen flow of 20 mL min^{-1} and the following heating programme were applied: running the first heating cycle from -30 to 245°C, keeping for 1 min and cooling to -30°C and keeping again for 1 min. Then the second heating cycle was applied up to 245°C.

RESULTS AND DISCUSSION

Tensile, Flexural Properties, and Charpy Impact Strength

The tensile properties of specimens have been measured by INSTRON 3345 universal tensile testing machine. In all cases same values of crosshead speed and other testing conditions were applied (e.g., humidity, temperatures, dimensions, etc.). Results are summarized in Table II. Tensile strength of waste polypropylene and polyamide was 21.5 and 95.1 MPa, respectively. Results demonstrate that the experimental additives could enhance the investigated properties, because all of the measured properties were better in the presence of additives, than those of

Table II. The Mechanical Properties of PP/PA 6 Blends with Different Coupling Additives and their Pure Components

	Properties	HDPE	PA	Without additive	Additive A	Additive B	Additive C
Before fatigue test	Tensile strength, MPa	21.5	95.1	16.5	25.5	20.1	46.8
	Elongation, %	9.2	6.5	4.4	8.1	6.4	8.6
	E-modulus, MPa	940	3100	850	1300	1200	1700
	Flexural strength, MPa	22.0	121.4	19.0	45.5	45.1	57.4
	Elongation, %	16.1	4.5	6.1	12.9	11.2	13.7
	E-modulus, MPa	850	3500	900	1400	1100	1900
	Charpy impact strength, kJ mm^{-2}	14.5	8.5	8.1	12.2	9.4	13.8
After fatigue test	Tensile strength, MPa	20.5	93	14.1	23.4	19.4	46.2
	Elongation, %	9.3	6.0	3.3	7.7	6.3	8.4
	E-modulus, MPa	960	3050	740	1250	1180	1710
	Flexural strength, MPa	21.4	119.5	17.4	44	44.8	56.4
	Elongation, %	17.0	4.4	5.2	11.7	10.4	13.1
	E-modulus, MPa	860	3300	780	1310	1040	1940
	Charpy impact strength, kJ mm^{-2}	14.6	8.1	7.5	11.7	8.4	14.1

their absence. The tensile strength and the elongation were 16.5 MPa and 4.4% without additive, while they were 25.5, 20.1, 46.8 MPa and 8.1, 6.4, and 8.6% when A, B, and C marked experimental additives have been added into the specimens, respectively. For the matter the E-modulus has followed same tendency; namely the best result was found by the appliction of MA grafted low polymer. The Charpy impact strength gives information about the behavior of specimens toward dynamical loading. Based on data, 8.1 kJ mm^{-2} Charpy impact strength of PP/PA 6 specimens without experimental additive could be measured, which were increased to 12.2 kJ mm^{-2} with additive A, 9.9 kJ mm^{-2} with additive B and 13.8 kJ mm^{-2} with additive C. Reletive comparison of the obtained results for PP/PA 6 compatibilized blends reveal that tensile strength, elongation, E-modulus, and Charpy impact strength increased about 25.0–187.5%, 45.5–95.5%, 41.2–100.0%, and 16.0–70.4%, depending on the additives, related to the additive free case, respectively. Results refer to better adhesion between the two immiscible phases by adding of the synthetized coupling compounds. The positive effects of properties (e.g., increasing in tensile strength) in the presence of comaptibilizers are explained with their chemical structure. Each compatibilizer had two main parts: a longer alkyl chain and succinic-anhydride group. Presumably the alkyl chain of the compatibilizers linked with the polypropylene main chain, while the polyamide chain could be linked with the reactive groups of compatibilizers (e.g., carboxyl groups). The flexural strength, elongation, and E-modulus of polyamide 6 raw materials were 121.4 MPa, 4.5% and 3500 MPa, respectively. Polypropylene had flexural strength of 22.0 MPa, flexural elongation of 16.1% and E-modulus of 8500 MPa. Similarly as it was earlier demonstrated, all properties were significantly lower without additives, than in their presence. Specimens proved flexural strength of 19.0 MPa, elongation of 6.1% and E-modulus of 900 MPa without coupling agents. The values of flexural strength and E-modulus were below than that of the original polypropylene, while the value of elongation has higher value than those of in case of pure polyamide specimens. The flexural strength of polymer blends was 45.5, 45.1, and 57.4 MPa in the presence of additive A, B, and C, respectively. The elongation was changed to 12.9, 11.2, and 13.7%, while the E-modulus 1400, 1100, and 1900 MPa by the before mentioned additives A, B, and C, respectively. It means that e.g., the flexural strength have been improved with 136.0–200.0%, the elongation with 83.3–124.6%, while the E-modulus with 22.2–111.1% by additives, related to the additive free polymer blends. It is important to remark that the best results have been given by the application of MA-grafted coupling polymer.

Fatigue Test

To investigate the longer use behavior of polymer blends, they have been pretested by periodic loading test: the injection moulded PP/PA 6 specimens have been periodically loaded (50,000 loading cycle) using 25% loading of maximal load at tensile test. Table II demonstrates the tensile properties, Charpy impact strength and flexural properties. The results of tensile test and Charpy impact test are graphically summarized in Figure 2.

The tensile strength of polyamide and polypropylene was 95.1 and 21.5 MPa before pretest. It was changed to 93.0 MPa (PA 6) and 20.5 MPa (PP) following the preloading test. To calculate the changes, 2.38% (PA 6) and 2.11% (PP) decreasing was found in tensile strength following the pretest, related to the original specimens. In tensile strength the relative change was −11.88% without additives; while −6.40, −3.00, and 0.43% in the presence of experimental additives "A," "B," and "C," respectively. Results reveal that the tensile strength was worsened due to pre-loading procedure, but the reduction was not as intensive in the presence of additives as in the case of pure PP/PA 6 blends. Moreover tensile strength increasing (0.43%) was observed in case of samples containing
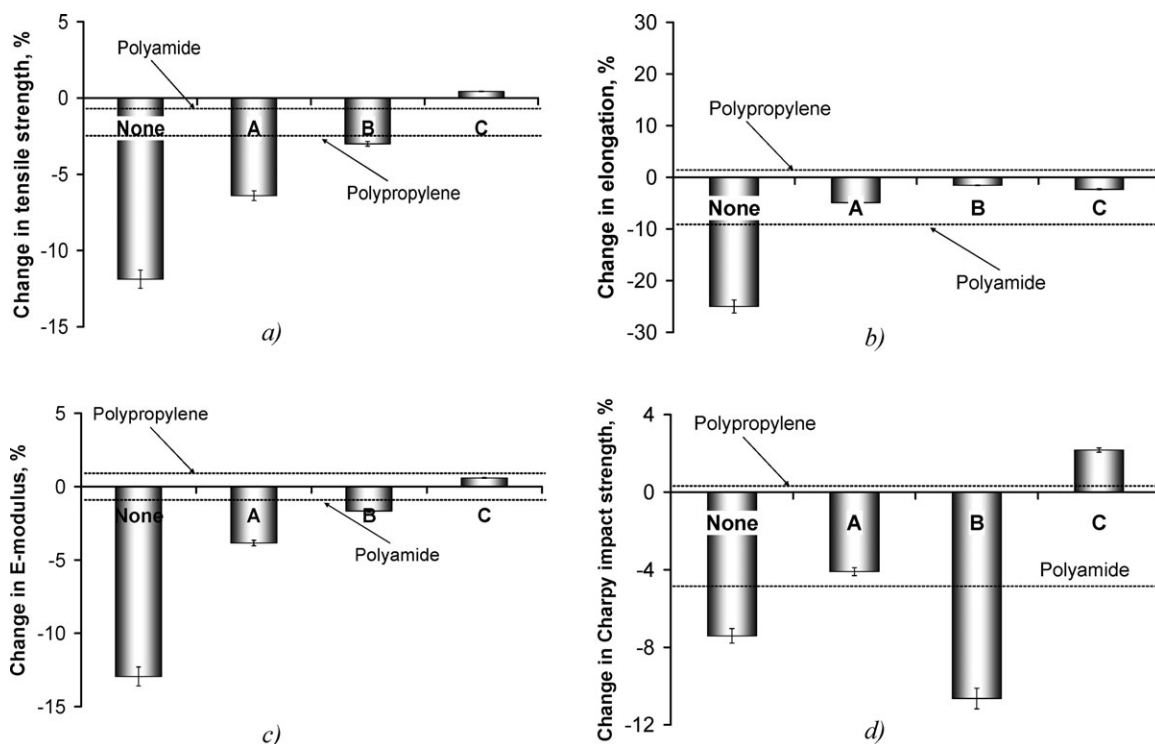
Figure 2. The results of tensile test and Charpy impact test (fatigue test) of PP/PA 6 blends with/without coupling additives and their pure components (a) Tensile strengths, (b) elongations, (c) E-modulus, (d) Charpy impact strengths.

additive C marked coupling agent. According to data similar results was found regarding both to the elongation and E-modulus. The pure waste PP has shown positive changes in elongation and E-modulus (1.09 and 2.13%), while the PA rather negative (−7.69 and −1.61%) due to pretesting. The most unfavorable effects was found when the two polymers had been blended without any coupling additives (−25.00 (elongation) and −12.94% (E-modulus)). That result referred to difficulties in the load transfer between phases of multiphase blends. By the using of experimental additives significant positive effects was found following the order of additives "A," "B," and "C." For example, the relative changes of E-modulus have shifted from −12.94% (without additive) to −3.85, −1.67, and 0.59% (with additives A, B and C, respectively). Generally, similar values of properties could be measured after the fatigue tests, than it was measured before that in case of PP/PA 6 blends contained additive "C." The results of Charpy impact data shows a bit different values as it was demonstrated earlier, because the worst results was found when the polymer blend contained additive "B" (−10.64%). It is also clear, that the best results could be measured in case of specimens made of waste polymers and additive "C" (2.17%). For that result the difference in the load distribution in case of static (tensile test) and dynamic (Charpy impact test) sample testing procedure could be blamed.

The flexural properties of PP/PA 6 blends are shown in Table II, too. The flexural strength of waste PA 6 and PP constitutes was 121.4 and 22.0 MPa, which changed to 119.5 and 21.4 MPa after the periodic loading. That means only 2.73 and 1.24% reduction of the property. The flexural strength of additive free PA 6/PP blend was 19.0MPa without pretest, which moved to 17.4 MPa after the cyclical loading test, so the flexural strength

decreased with 8.42% in consequence of the pre-testing. Similar results have been found both in elongations and E-modulus with relative change of −14.75 and −13.33%, respectively. Results well demonstrate that the deterioration in each property could be decreased by the applying of experimental additives and additives B and C provided the best results. For example the relative change in flexural strength was −2.22, −0.44, and −1.05% in the presence of additives A, B, and C, respectively. Following the same order the relative change of elongation was −9.30, −7.14, and −4.38%, while the E-modulus have changed with −6.43, −5.45, and +2.11%, respectively. Additives had advanced affect both to the tensile and flexural properties after the pretesting, for what their coupling property could be blamed. Owing to the linking of coupling additives both to the polypropylene and polyamide chains, the interfacial connection could be stronger between PP and PA 6. That is why the most mechanical properties were better in the presence of additives. However it is very difficult to answer that physical or chemical interaction is dominantly the reason for the better adhesion.

Rheological Properties
The melt flow index (MFI) is a widely used rheological data for thermoplastic polymers characterization. Moreover it is an indirect way for molecular weight determination. The higher the melt flow index, the lower is the molecular weight of the polymeric system. Melt flow index is a function of viscosity of the melted polymer at the testing conditions. The melt flow indexes of PP/PA 6 blends depending on different loading (or shear rates) are shown in Figure 3. Experiments have been taken at 275°C temperature with different loading (2160, 5000, 7260, and 10,000 g). Melt flow indexes were higher by increasing
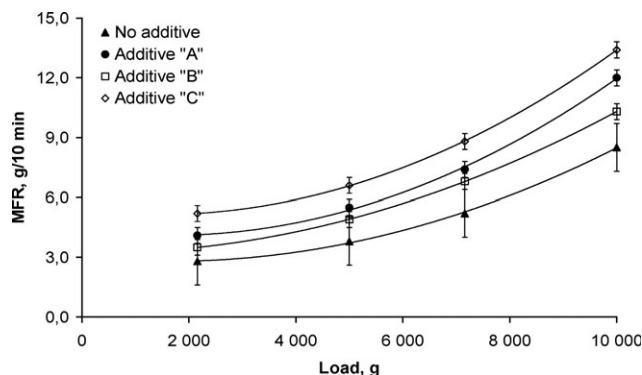
Figure 3. The change of MFI as functions of loading (or shear rates).

loading in each case. The lowest MFI values had been found when the polymer blend did not contain any coupling additives. In the other cases significantly higher values of MFI was observed; the highest one by the applying of MA-grafted low polymer. That result refers to the plasticizer effect of the experimental agents. On the other hand the plasticizer efficiency of coupling agents have followed the decreasing order of their molecular weights: additive "B," "A," and "C." As Table I demonstrates, the additive "C" had weight average molecular weight of 2100 g, while that of additive "B" of 3420 g. That is why the MA-grafted low polymer with the lowest molecular weight was able to plasticize the polymer blends in the highest degree.

Analysis by Fourier Transformed Infrared Spectroscopy

The chemical structures of the polymer blends and the possible interaction between the polymers and the experimental additives have been followed via Fourier transformed infrared analysis. Figure 4 shows the FTIR spectra of polymers absence and presence of additives. Typical absorption bands of both polyamide and polypropylene have found in the infrared spectra of untreated blend, while other characteristic chemical bond from polyalkenyl-poly-maleic-anhydride derivates could be recognize in additive containing PA 6/PP blends. The infrared absorption bands observed between 3000 and 2800 cm^{-1} occurred due to the C—H stretching vibration of —CH$_2$— and —CH$_3$ groups, which were four bands. The asymmetric ($v$asCH$_2$) and symmetric (vsCH$_2$) stretching vibrations of the —CH$_2$— groups resulted in absorption bands at wave numbers of 2926 and 2836 cm^{-1}, resp., while those of —CH$_3$ groups at 2962 and 2872 cm^{-1}, resp. Esters also gave infrared absorption around 1380 cm^{-1} ($v$asC—O—C). Around 1710 cm^{-1} bands with different intensities have been found, which were from the vsC=O in the five-member anhydride groups or carbonyl groups of esters. However, this is the typical range of the vsC=O vibration from amide group either. The problem is that very difficult to identify each band separately due to their overlapping. Other significant infrared bands have found around 1480 and 720 cm^{-1} caused by the mowing vibration (βsCH$_2$ and βasCH$_2$) of —CH$_2$— groups. The intensity of that band at 720 cm^{-1} was
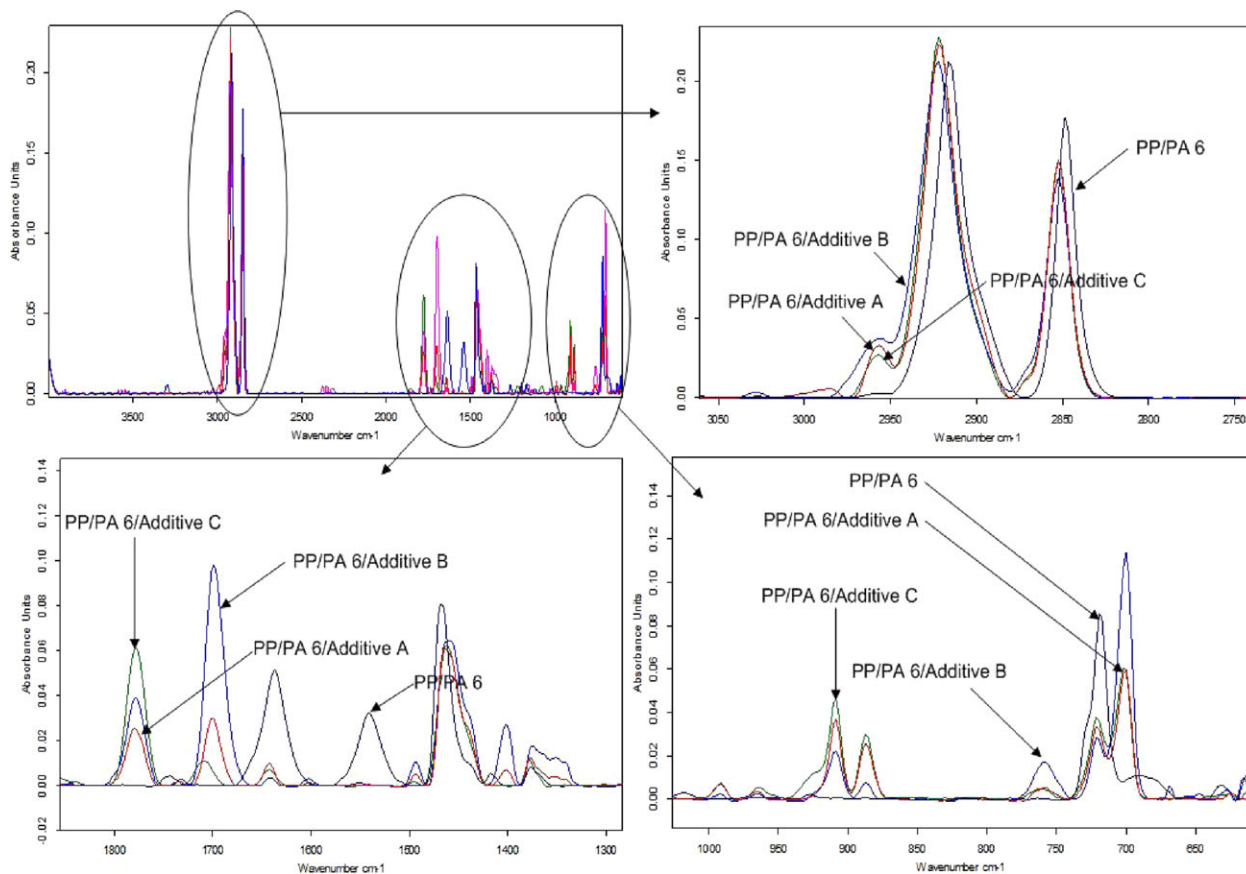

Figure 4. The FTIR spectra of PP/PA 6 blends with and without coupling additives. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
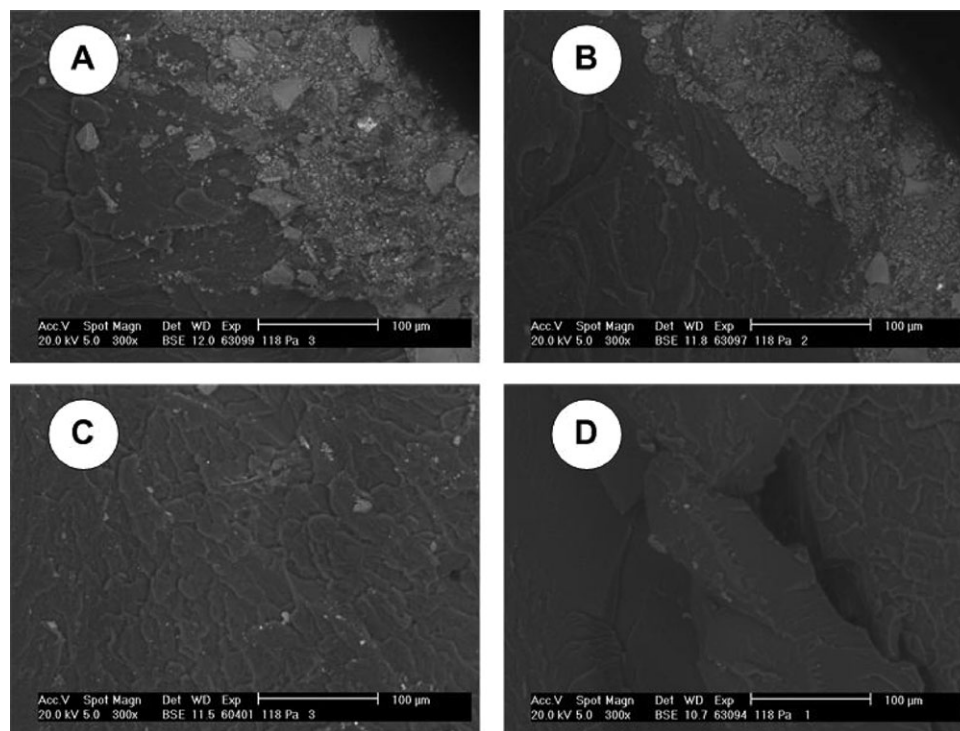
Figure 5. The fractured structure of PP/PA 6 specimens (A-without additive, B-with additive "A", C-with additive "B", D-with additive "C").

proportional to the length of the carbon chain. C—O—C stretching vibrations have given bands around 1150 and 1300 cm^{-1}. It is important observation that imide group caused absorption bands have also been found: at 1780 cm^{-1} (asymmetric imide C=O stretching) and 1730 cm^{-1} (symmetric imide C=O stretching). Both bands were the most intensive in the case of "C" coupling agents.

SEM and FTIR Analysis

The fractured structure of the specimens are shown in Figure 5 (a–d). The structure of polymer blend made without any additives are demonstrated in Figure 5(a), which represents two well separated parts. In all probabilities the immiscible phases are the cause for the weak mechanical properties. That theory have been described by others, who concluded that in case of PP/PA 6 blends the poor mechanical and other properties could be blamed with weak interfacial forces due to the immiscible phases.[12–19] In Figure 5(b–d) the fractured structure of additive containing blends are shown, where more homogenous phase was found. The possible scheme of coupling reaction are shown in Figure 6. The chemical structure of polyamide 6 contains nitrogen and oxygen besides carbon and hydrogen atoms. On the other hand the experimental Additive C has anhydride ring in each monomer unit. The anhydride ring plays role as bifunctional carboxyl groups and can react with the functional groups of polyamide chain, forming of new N—(C=O) chemical bonds. The new N—(C=O) chemical bond could be well recognized in the waveband range of 1780–1730 cm^{-1}. It is important observation that well separated new infrared band was found at 1780 cm^{-1} in the Figure 4, where the imide chemical group has given infrared activity. The Figure 7 shows the intensities of bands at 1780 cm^{-1} in case of different
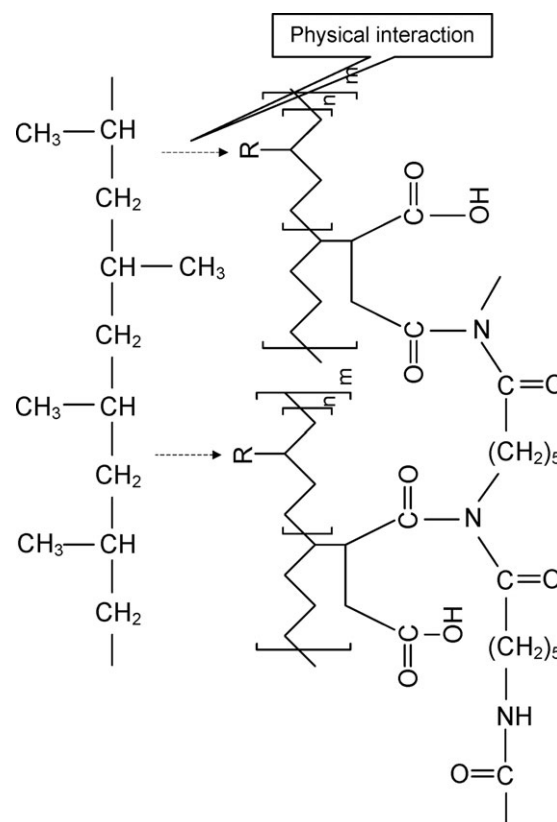

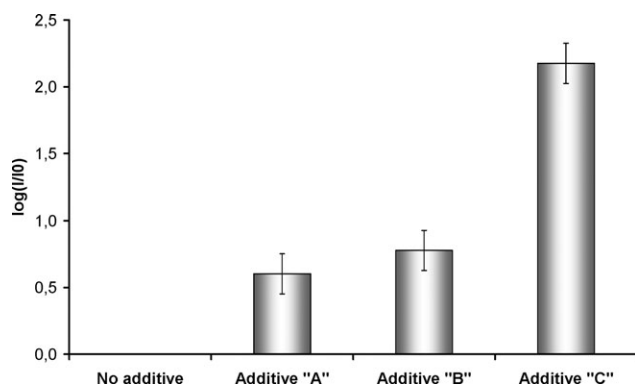**Figure 6.** The possible interaction between polypropylene and polyamide 6 chains.

Figure 7. The values of log (I/I_0) at 1780 cm^{-1} wavenumber in case of PP/PA 6 blends with and without coupling additives.

blends. Infrared activity was not found without additives at 1780 cm^{-1}. In case of PP/PA 6/Additive A and PP/PA 6/Additive B blends the investigated intensities was relatively low, while significant increasing has been demonstrated in the value of log(I/I_0) by the applying of MA grafted low polymer compatibilizer. The "I_0" is the intensity of incident light, while "I" is the intensity of transmitted light. Same new chemical should be take in all last three cases, but owing to steric reason the number of the new groups was the highest in the last case. As it was earlier discussed the additive "A" and "B" were half amide and ester, respectively. That is why the opened anhydride ring contained one carboxyl group and one amide or ester groups connected with long alkyl chain. Those long alkyl chains can cause for the steric hindrance when the new chemical groups should be formed. That is the reason for the lower intensity of infrared band at 1780 cm^{-1} occurred by the formation of new imide group. Because of the —NH— groups in additive A, the better compatibility was the consequence of both sterical effect and physical interaction. The ester group in the structure of additive A was unfavorable both from sterical and physical reasons, because there was less possibility for connection between the polyamide and the additive due to difficult bending of the side groups.

DSC Analysis

DSC curves are presented in Figures 8–10 and the results are summarized in Table III. First heating scan depicted in Figure 8 provide a clear evidence of glass transition temperature (T_g) related to PA 6 and melting of both PP ($T_{mPP} = 136.3°C$) and PA ($T_{mPA} = 219.8°C$). These values were expected for these polymer matrices. As it is presented above [Figure 5(a)] PP and PA create immiscible system, which is characterized by two individual T_gs. However, experimental setting disabled detection of T_g of PP that can be expected below −20°C. Thus, only T_g of PA (T_{gPA}) is visible at 48.2°C. The cooling scan (Figure 9) records crystallization exotherms with peaks at 188.4°C (T_{cPA}) and 111.6°C (T_{cPP}). The second heating scan (Figure 10) shows similar results like in the first scan unlike the fact that T_g was not detected due to specific behavior of PA 6, which has been described elsewhere.[27] Addition of compatibilizers influenced thermal properties of the polymer blends. For instance, T_g of PA 6 matrix was slightly reduced as well as T_{mPP} (Figure 8). The most significant change was observed in case of additive A

(drop of T_{gPA} from 48.2 to 41.1°C) and C (drop of T_{mPP} from 136.3 to 132.5°C). A behavior of polymer systems is strongly dependent on threir thermal history. Providing it is supposed be the same in case of all the samples, the results may reveal the interaction pattern of the additives used in the PP/PA 6 blends. While the additive A seems to be responsible for interactions predominantly with amorphous phase of the polymers (drop of T_g about 7°C), the additive C affects crystalline structure of PP, which leads to T_{mPP} reduction as mentioned above. In addition, a decrease in T_g (about 3.43°C) was also shown in this case. The results for the additive B can be classified between A and C, i.e., slight T_g and T_{mPP} reductions were observed from DSC results. The cooling DSC scans of PP/PA 6 systems without and with presence of the additives are depicted in Figure 9. It is clear that additives A and B affect crystalization process of both PP and PA 6 matrix when deformation and the peak shift to lower temperatures (about more than 10°C, see Table II) can be observed there. An accurence of a double crystallization peak (T_{c1PP}, T_{c2PP}) reveals presence of two various crystalline forms, which has been well known.[31] The cooling scan of the sample with compatibilizer C is more or less similar to the PP/PA 6 blend without additive. However, crystallization of PP was observed at significantly higher temperature (116.1°C) than it was noticed for noncompatibilized PP/PA 6 blend (111.6°C) in this case. The samples with standard thermal history in second heating scan (Figure 10) proves slight T_{mPP} reduction of compatibilized samples, especially for the blend with MA based additive C. The results obtained from DSC analysis reveal affecting of crystalline phase formation process in the blends due to compatibilization step. It could be concluded that using of additives A and B leads to influencing of PA crystallinities while the additive C causes changes mostly in PP domains due to its specific chemical properties. It is clear that resulting mechanical
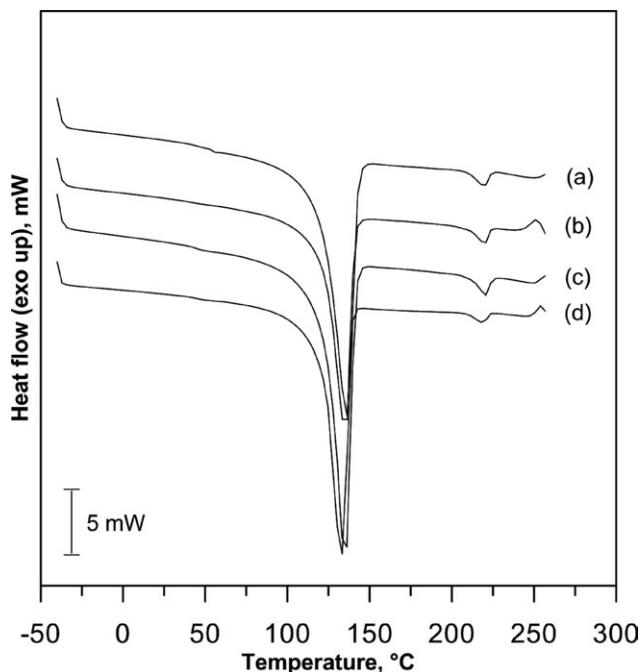

Figure 8. DSC curves of PP/PA 6 blend without (a) and with additives A (b), B (c), and C (d), first heating scan.
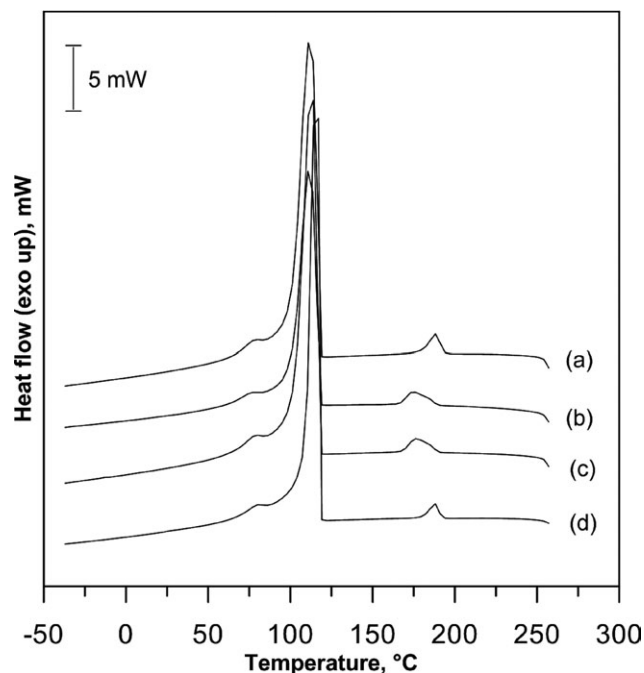
Figure 9. DSC curves of PP/PA 6 blend without (a) and with additives A (b), B (c), and C (d), cooling heating scan.

properties of the blends are governed by predominant matrix, PP, and its properties. From this point of view, additive C seems to be the most effective. This is in agreement with the results presented above. On the contrary, an importance of the additives A and B would be rising with increasing content of polar PA matrix in the blend.
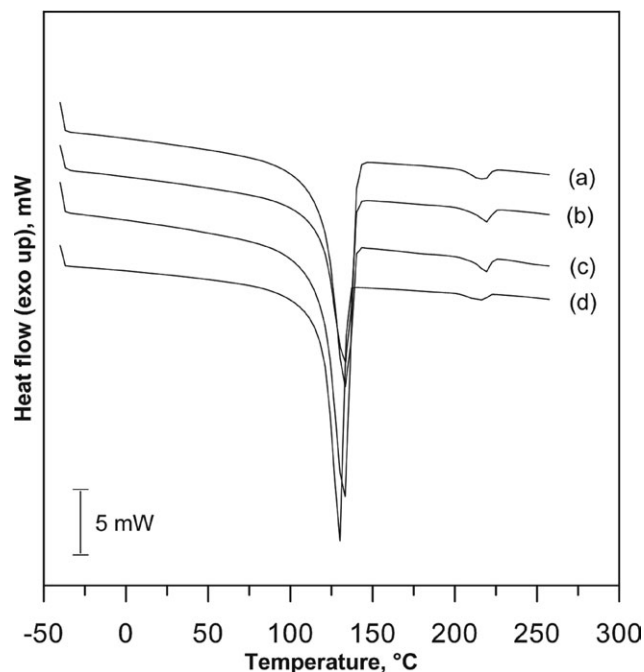

Figure 10. DSC curves of PP/PA 6 blend without (a) and with additives A (b), B (c), and C (d), second heating scan.

Table III. DSC Characteristics of the PP/PA 6 Blends with and without Coupling Additives

Sample	1st Heating scan						Cooling						2nd Heating scan			
	T_g (°C)	c_p (J g⁻¹)	T_{mPP} (°C)	dH_m (J g⁻¹)	T_{mPA} (°C)	dH_m (J g⁻¹)	T_{cPA} (°C)	dH_c (J g⁻¹)	T_{c1PP} (°C)	dH_{c1} (J g⁻¹)	T_{c2PP} (°C)	dH_{c2} (J g⁻¹)	T_{mPP} (°C)	dH_m (J g⁻¹)	T_{mPA} (°C)	dH_m (J g⁻¹)
PP/PA 6	48.16	0.161	136.3	146.4	219.8	4.34	188.4	5.64	111.55	150.47	89.5	9.13	133.5	152.15	217.8	4.54
PP/PA6/A	41.14	0.123	135	138.44	219.9	5.74	174.9	8.48	111.2	144.46	77.97	8.91	133.6	142.8	219.9	6.98
PP/PA6/B	44.73	0.11	135	142.39	220.6	4.55	176.39	6.39	112.9	149.45	79.84	9.35	132.8	148.81	219.4	4.63
PP/PA6/C	44.72	0.171	132.5	146.6	218.34	3.24	188.2	4.56	116.08	149.52	80.13	9.41	130.8	153.7	216.5	3.54

CONCLUSION

In this work blends of waste polypropylene and polyamide plastics have been prepared containing 1.5% experimental coupling additives. Additives were synthesized by the reaction of α-olefins and maleic-anhydride or they were its alcohol or amide derivates. Higher both tensile and flexural strength and E-modulus was found by the using of experimental additives. The efficiency of additives have followed the order of additive A, B and C. In case of flexural properties also the MA-grafted low polymer has the best properties in the reduction of incompatibility between the constituents of polymer blends. To investigate the long-term use behavior of polymer blends deterioration in the investigated properties was calculated without coupling additives (-25.00 and -12.94% relative changes), while significant positive effect was found by the additive using, following the order of additives "A," "B," and "C." New chemical bonds were proposed between the additive and the polymer chain. According to the morphology and FTIR analysis, well-separated PP and PA phases were found in case of specimens without additives and only one well-distributed phase in their presence. The long alkyl chains can cause for the steric hindrance when the new chemical groups should be formed, therefore lower intensity of infrared band at 1780 cm^{-1} occurred by the formation of new imide group. Because of the —NH— groups in additive A, the better compatibility was the consequence of both sterical effect and physical interaction. The positive effects of properties are explained with the chemical structure of comaptibilizers. Each compatibilizer had two main parts: a longer alkyl chain and succinic-anhydride group. Presumably the alkyl chain of the compatibilizers linked with the polypropylene main chain, while the polyamide chain could be linked with the reactive groups of compatibilizers (e.g., carboxyl groups). DSC results reveal specific activity of the investigated additives, which can be responsible for the observed compatibilizing effects.

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