Mechanical and thermal properties of Polypropylene (iPP)-High density polyethylene (HDPE) binary blends

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Abstract

In this study, the mechanical and thermal properties of polypropylene (PP) and high density polyethylene (HDPE) blends in different mixture ratios are investigated. PP and HDPE 10 wt. % added blends are investigated by different tests; thermal analysis such as; melting temperature, crystalline temperature, crystalline energy, involved crystalline ratio, mechanical properties such as; Tensile strength at break, at yield and elongation at break) fitness and the impact resistance. PP and HDPE polymers are semi-crystalline, involving crystalline ratio for PP and HDPE 2.08 to 38.44 % and 4.66 to 62.80 respectively. For these homopolymer's crystalline phase and blends have two melting points, but they have only one crystalline temperature. The degree of melting and crystalline of blends is not different from the values of PP and HDPE. The tensile strength at the point of flow and breaking point are not varied according to the original homopolymer but the properties of strain at the breaking point are much weakened. Moreover, polymer blends at the value of non-bending, when the comparison make with the homopolymer, an improvement can observed 2.6 % by the increased ratio of HDPE and also the impact properties of the PP can be improved by adding more than 70 wt. % HDPE in to the PP.

Keywords - Polymer blends, binary blends, thermal analysis, mechanical properties

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1 Introduction

Polypropylene is a kind of thermoplastic of the polymer, which has very wide usage in industrial technology [1]. Besides this wide usage, Polypropylene has two negative properties in this applies, these are; not having effective resistance in lower degrees and high physical effects. To eliminate this situation, polypropylene (PP) is very often blended with various polymers [2-3]

Polyethylene is partially amorphous and partially crystalline [4,5]. Linearity of polymer chains affords more efficient packing of molecules and hence a higher degree of crystallinity. On the other hand, side-chain branching reduces the degree of crystallinity [6-8].

Polymer blends of technologically important materials whose properties have been studied at or near room temperature by many investigators [9-14]

Blending of different plastic resins has long been practiced in the manufacturing for various reasons including: (i) tailor-made blends to meet specific processing and performance requirements which cannot be satisfied by a single component; (ii) scientific interests; and (iii) financial incentives. One possible route of preparation of new materials is blending of two or more polymeric components with each other the final properties generally depend on the physical and chemical properties, as well as the morphology of the pure components, their portion in the blends, interactions among components and also processing routes [7-9]. These factors generally influence all physical properties.

Blending one polymer with another is a method of modifying the physical properties of a polymer in a desired manner. On the other hand, most recycled polymer is degraded due to the action of environmental agent on the finished product. Therefore, it is necessary to fully examine the thermal degradation of the blends in the presence of a recycled polymer in order to determine the thermal stability of the polymers and their blends [13-16].

In this study, Homopolymers (iPP and HDPE) and blends were investigated the mechanical properties (tensile strength at break, at yield and elongation at break), Stiffness, Impact resistance and thermal analysis (DSC and TG).

2 Experimental

2.1. Material

Polypropylene MH 418 and High density polyethylene S 0464 were used in this study. Nine blends (by increasing 10 wt. % in each other) prepared from polypropylene MH 418 (PP MH 418) and high density polyethylene S 0464 (HDPE S 0464); both them are homopolymers and have isotactic configuration, produced in Petkim Petrokimya A.Ş. Aliağa Complex were used in experiments. The supplier, density, and melt flow index (MFI) for the PP, HDPE homopolymers used to prepare the blends are listed in Table 1.

Table 1. Properties of PP and HDPE

Homopolymer	Supplier/grade	Density (g/cm^3, 23 °C)	MFI (g/10 min)	Test Method
PP	Petkim Petrokimya A.Ş./ MH 418	0.905	5.0	ASTM D1238
HDPE	Petkim Petrokimya A.Ş./ S 0464	0.964	0.35	ASTM D1505

2.2. Preparation of Polymer Blends;

PP was added to HDPE different ratios weight from 10 wt. % to 90 wt. % and 9 units sample prepared as 1 kg was weighed with balance having ± 0.1 wt. % sensitivity. All prepared polymer blends were loaded in EA/30 Amut Extruder was fixed the 190, 230, 250 ºC, respectively. All the homopolymers totally were melted and mixed homogenously, than the blend were produced which are 2±0.05 mm height and 10±0.1 mm width. All samples were coded between A1 and A11, as given in Table 2.

Table 2. Homopolymers and blends codes

Polymers	Blends Codes										
	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	A11
PP MH 418, wt. %	100	90	80	70	60	50	40	30	20	10	-
HDPE S 0464, wt. %	-	10	20	30	40	50	60	70	80	90	100

2.3. Equipments

2.3.1. Extruder and Equipment of the Tensile Testing

EA/30 Amut Extruder was used in the preparation of the blends. Tensile-relaxation tests are made by INSTRON 1114, 2-100 kg of Load Cell and head velocity 2 cm.sec^{-1}.

2.3.2. Olsen Non-Blending Test Equipment

The stiffness testing which determined the resistance to stiffness properties of material is done by Olsen non-blending test equipment having the capacity 3.46-6.91 kg.cm

2.3.3. Izod Impact Test Equipment

At the Izod tests, to prepare sample bands with Izod Impact and Notching Equipment are used the 60/326 type of injection moulding machine and correction bar.

2.3.4. Plaque Sample Preparation Equipment

At the preparation of samples, used equipment’s are heating press (230 ± 5 °C), Cooling press (30 ±

5 °C), press plaques, sample plaques and sample preparation moulds.

2.4. Mechanical Testing Measurement

2.4.1. Stress-Strain Tests

Sample plaques was prepared according to ASTM D-1238 and delayed 48-72 hour at the laboratory conditions. 3 testing samples were cut from plate at least 10 cm inner of it with the Dump-bell mould without any burr and air swell. The thickness of all the samples were measured from 4 places of the narrow parts of them with the micrometer having 0,01 mm sensitiveness and the smallest value written recorded as a thickness of the samples. 25 mm parts from the middle of samples was measured and marked for the % strain test.

The sample, which put into the upper chin, so that, is lying in between two chins. Extensometer foots are hold 25 mm space to the sample. After the under chin closed, the tension experiment is started automatic. The averages of all values calculated for the tensile strength at yield and break points, elongation at break point, stiffness resistance for every one recorded.

2.4.2. Stiffness Resistance

The test samples were prepared according to the ASTM D-747 with 2 mm thickness. It placed in a Laboratory conditions for 48 hours. Then, from these were cut the six-unit sample with mould the 12.07 x 63.5 x 2 mm dimensions. One of them was used to the pre-experiment. The thickness and width of samples about ±0.01 and ±5 mm sensitive measured by the micrometer and composing stick in laboratory.

The sample put into apparatus as a horizontally. About 27 mm of the sample is compressed and 30 mm part is left between compressed areas. The loading value against deviation read from loading scale and recorded. It takes average of the data.

2.4.3. Impact Resistance

The sample, in the 150 x 150 x 3 mm dimensions, prepared press machine in mould placed in a laboratory conditions for 72 hours. The preparing of the sample and pre-experiment makes then like mentioned. The thickness of samples measured about ±0.01 mm sensitive from least tree place and the smallest value recorded.

The sample was moved single-sided and was nicked in the 2.45 mm deep and 45 ° dimensions, which the shape is V. The sample was put into apparatus and the maximum degree recorded. The average of results was calculated.

2.5. Thermal analysis

Differential scanning calorimetric (DSC) analyses were carried out in a Shimadzu DSC-50 (Shimadzu, Kyoto, Japan) thermal analyzer in nitrogen atmosphere. The samples were heated from 25 °C to 200 °C at 10 °C min^{-1}, cooled to 25 °C at the same rate, and re-heated and cooled under the same conditions. Melting (T_m) and crystallization (T_c) temperatures and enthalpies were determined from the second scan. T_m was considered to be the maximum of the endothermic melting peak from the heating scans and T_c that of the exothermic peak of the crystallization from the cooling scans. The heat of fusion (ΔH_f) and crystallization enthalpy (ΔH_c) were determined from the areas of melting peaks and crystallization peaks.

The crystallinity of blends were calculated through the total enthalpy method; in all calculations, the heats of fusion at equilibrium melting temperature were 209 and 293 Jg^{-1}, for PP and HDPE crystals respectively [17].

$$(X_c) = \frac{\Delta H_f}{\Delta H_{crys}} x100$$

ΔH_f = Heat of fusion (J/g)

ΔH_{crys} = 100% crystal polymer crystallization energy (J/g)

(X_c) = Crystallinity (%)

The thermogravimetric analysis was performed with a Shimadzu TG model TGA-50. Heating rate of 10 °C min^{-1}was used. The sample weight was about 10 mg and all experiments were carried out in the under a steady flow of nitrogen or air atmosphere accordions to ASTM D-2117.

3 Result and Discussions

3.1. Mechanical analysis

The samples, the tensile strength at yield and at break points, elongation at break point, stiffness, and impact resistance values were given in Table 3. It was also illustrated as graphical in Figs 1-5.

Table 3. Mechanical properties of blends

Sample Code	**Tensile strength at yield (kg/cm^2)±10**	**Tensile strength at break (kg/cm^2)±10**	**Elongation at break (%) ±0.5**	**Stiffness**	**Impact resistance**
A1	332	236	689.0	8949	-
A2	340	332	12.8	9715	-
A3	320	321	5.9	8967	-
A4	309	311	4.0	10461	-
A5	290	288	2.5	9958	-
A6	296	290	2.0	10608	-
A7	224	239	1.3	10905	-
A8	264	264	3.5	10274	6
A9	298	219	8.9	10282	10
A10	290	99.5	38.9	11073	16
A11	278	263	981.0	10201	56

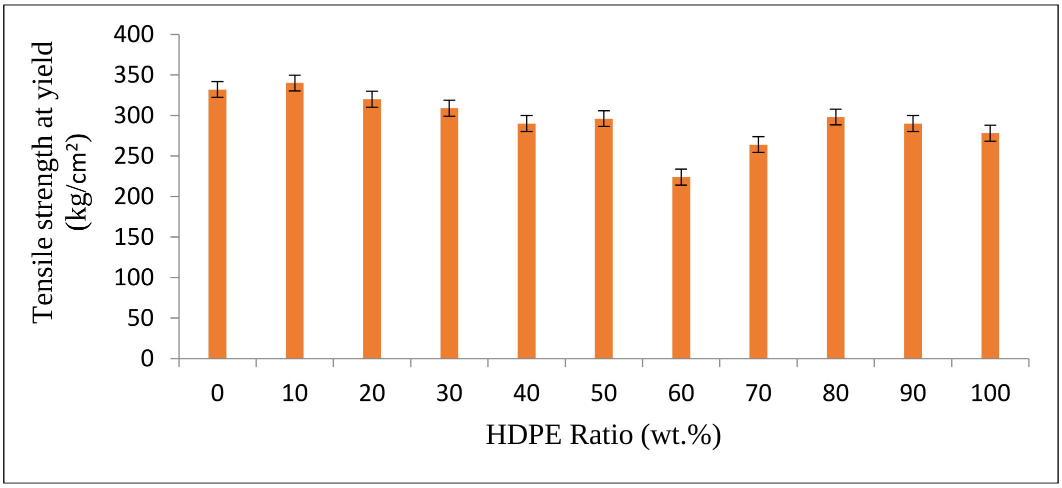

Figure 1. Tensile strength at yield values of PP + HDPE blends

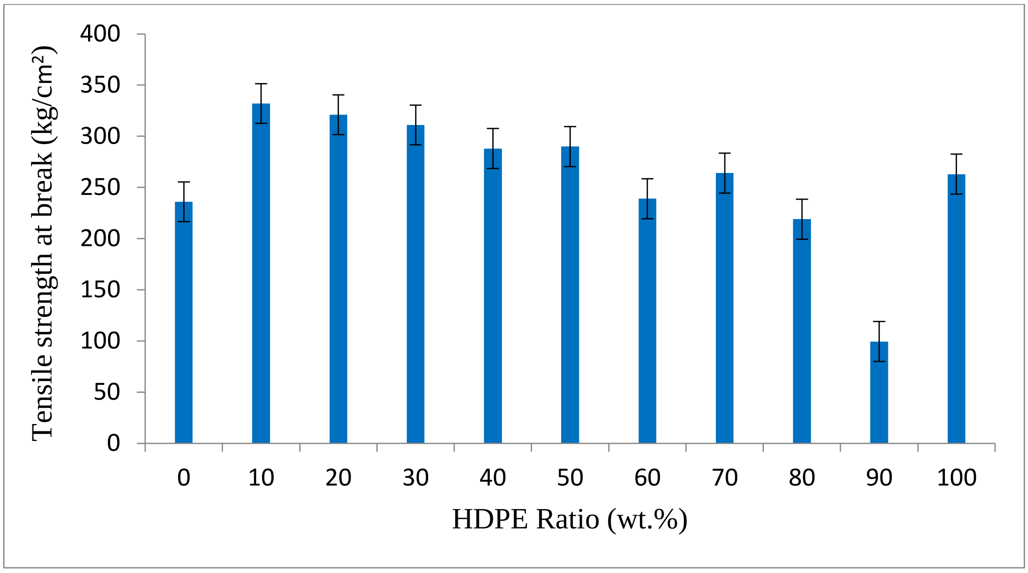

Figure 2. Tensile strength at break values of PP + HDPE blends

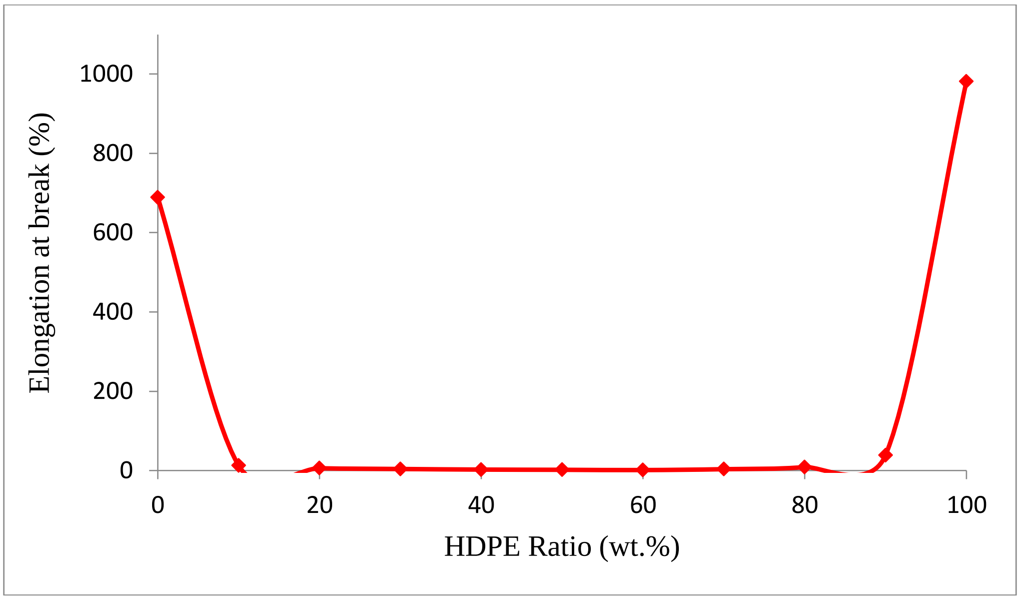

Figure 3. Elongation at break values of PP + HDPE blends

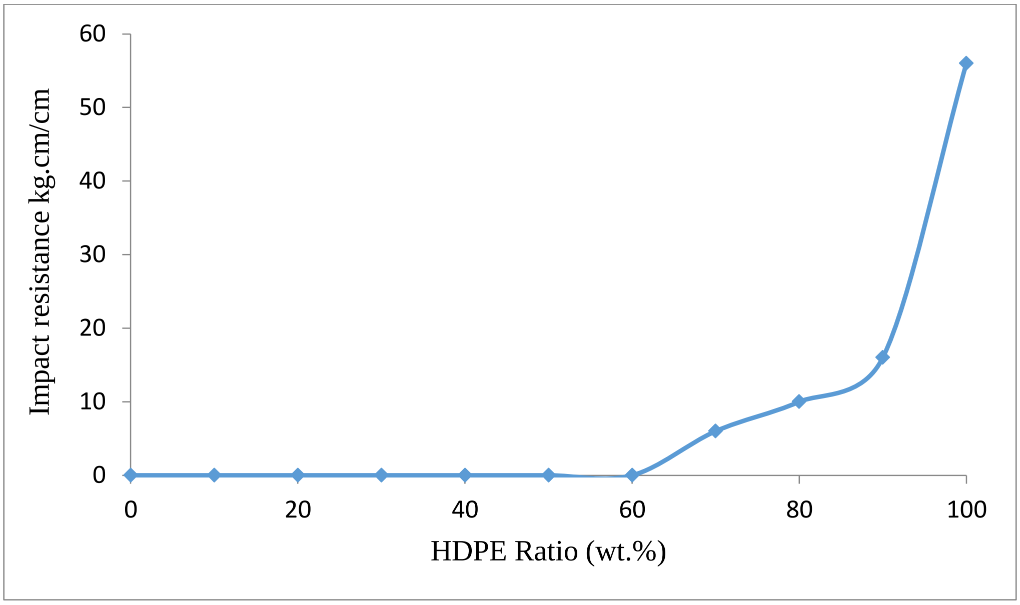

Figure 4. Impact resistance at break values of PP + HDPE blends

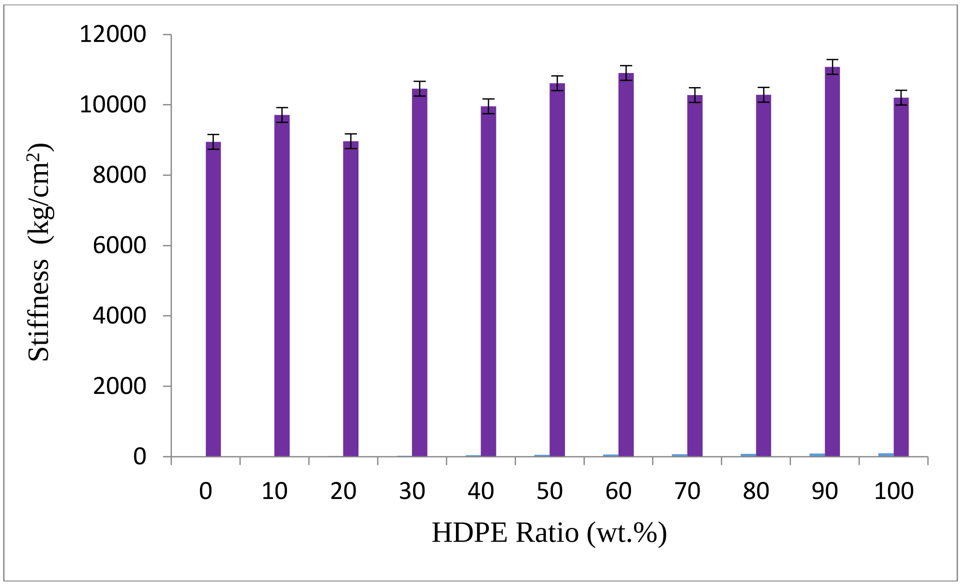

Figure 5. Stiffness values of PP + HDPE blends

As summarized in Figure 1, the tensile strength at break and yield decrease the increase of HDPE weight in the blend as compared to pure PP. Also, it can be seen that the tensile strength at yield in 70-90 % of HDPE weight improved some extent. On the other hand, impact resistant occurs an increase of HDPE weight in PP which has not any impact resistance. In figure 3 and 4, elongation at break and impact resistance values of blends and the HDPE ratios are shown. Also, by increase of HDPE in PP, the elongation of break values decrease. On the other hand in figure 5 with the increase of HDPE the stiffness of pure PP decreases.

3.2. Thermal Analysis

Thermal behaviors of PP and HDPE blends were examined by melting points (°C), crystallization points (°C), melting and crystallization energies (J/g), and % of crystallinity ratio (Xc). Obtained results are given Tables 4.

The results of DSC heating and cooling scans for homopolymer PP, HDPE and blends are shown in Table 4. Evidently, there is an endothermic melting peak in all heating scans, and there is a distinct exothermic crystallization peak in all cooling scans. The various melting and crystallization parameters which were determined from heating and cooling scans are shown in all homopolymer and blends, called Table 4.

Table 4. Thermal properties of blends

Melting (from second heating scans)					**Crystallization (from second cooling scans)**			
	PP		**HDPE**		**PP+ HDPE**		**PP**	**HDPE**
Sample Code	**T_m °C**	**ΔH_f (J/g)**	**T_m °C**	**ΔH_f (J/g)**	**T_c °C**	**ΔH_c (J/g)**	**Xc (%)**	**Xc (%)**
A1	164.84	80.34	-	-	116.66	83.98	38.44	-
A2	163.78	60.66	132.06	13.64	120	98.54	29.02	4.66
A3	164.06	46.69	132.99	41.4	121.11	118.24	22.34	14.13
A4	162.46	45.46	132.05	45.54	121.11	120.81	21.75	15.54
A5	163.68	41.46	133.09	45.6	121.3	116.38	19.84	15.56
A6	162.15	35.06	132.9	67.72	121.43	132.2	16.78	23.11
A7	161.64	25.07	133.49	100.1	121.54	153.02	12.00	34.16
A8	161.85	14.54	133.05	126.8	121.54	160.77	6.96	43.28
A9	161.55	6.43	133.71	151.6	121.71	169.89	3.08	51.74
A10	162.18	4.34	133.97	165.7	121.98	183.01	2.08	56.55
A11	-	-	134.42	184	121.87	183.69	-	62.80

According to Table 4, pure polymers have own melting point. However, it was showed that melting energy's changes a large of extent. On the thermograms of the blends, two melting points and a crystallization point were witnessed. The Melting points indicates that PP and HDPE kept their properties. Although, when the blends which were heated above melting point were cooled to crystallization, PP and HDPE were crystallized in same structure and at close a close value to HDPE's crystallization value thus it can be said the PP was crystallized in melted HDPE and only one crystallization point were found. The melting energy values of PP and blends appeared in this order: a fast increase, almost static and a fast increase; for blends and PP a fast decrease, almost static and a fast decrease. The melting energies of A3, A4, A5 specimens were seen that they were almost Table 4.

Starting of PP, Crystallization energies increased, stayed static (A3, A4, A5) and increased; it was seen that the highest value belongs to HDPE.

The TG data of blends have been taken under a steady flow of nitrogen (N_2) or air at singe stage heating rate as 10 °C /min to evaluate the kinetic and thermodynamic parameters.

The typical dynamic TG thermograms of PP/HDPE blends (100, 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90, 100 wt/wt.%) in a dynamic nitrogen atmosphere and in air are shown in Figs 6. HDPE being the most sTable, and PP the least sTable. The procedural decomposition temperature (initial T_i , and final T_f), char yield (% w_f) of blends at final temperature and temperatures of the maximum rate (T_{max}) are defined from DTG and TG curves corresponding to a single-stage decomposition reaction. The determined values of T_i, T_f, T_{max} and w_f are listed in Table 5. Both component and homopolymers are shown a single stage thermal degradation at temperature lower than about 500 °C.

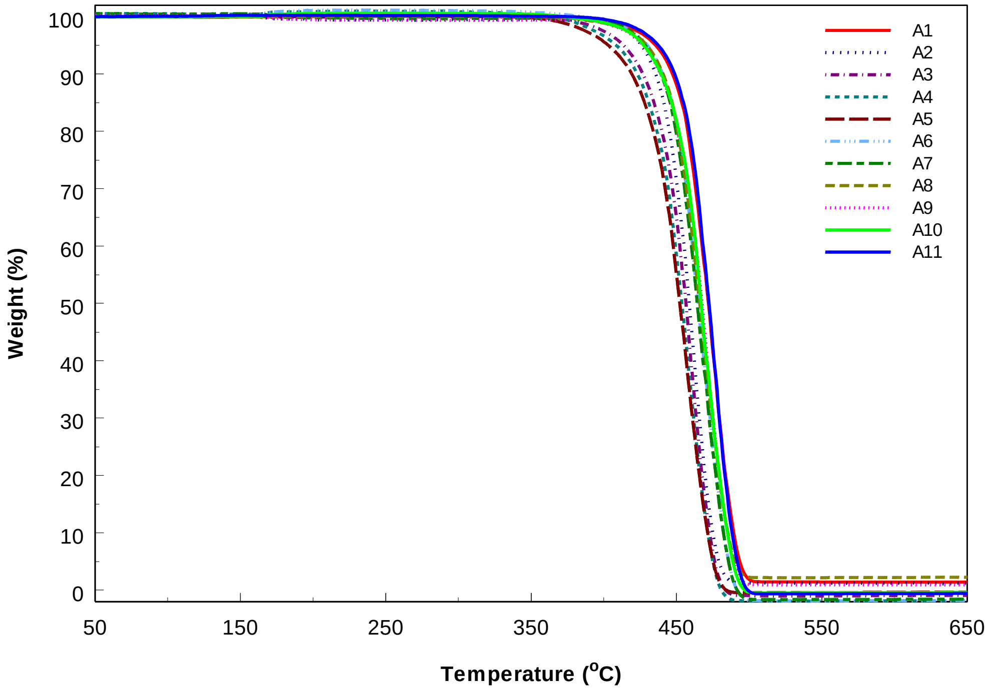

Figure 6. Weight fraction versus temperature for different composition of PP+HDPE blends

Table 5. TG data of PP+HDPE blends

PP+HDPE	Conversation (%)	T_i (°C)	T_{max} (°C)	T_f (°C)	Residue weight 400 °C	Residue weight 450 °C	Residue weight 500 °C	Char yield, % w_f
100/0	0.02-99.9	373.8	459.1	509.4	1.5	40.1	99.9	0.01
90/10	0.02-99.9	381.4	461.0	488.2	1.1	41.3	99.9	0.01
80/20	0.02-99.9	385.0	462.7	489.7	0.8	37.8	99.9	0.01
70/30	0.03-99.9	383.3	466.4	496.2	0.7	35.1	99.9	0.01
60/40	0.05-99.9	380.8	463.7	497.7	0.5	29.7	99.9	0.01
50/50	0.01-99.9	378.2	465.7	501.4	0.6	22.5	99.9	0.01
40/60	0.01-99.9	385.2	468.2	520.1	0.5	19.4	99.7	0.01
30/70	0.01-99.9	383.9	478.1	508.0	0.4	10.8	99.8	0.02
20/80	0.24-99.9	381.1	475.8	524.1	0.3	9.6	99.7	0.02
10/90	0.01-99.9	377.7	482.1	498.7	0.2	5.6	99.9	0.01
0/100	0.02-99.9	375.2	477.5	515.5	0.1	3.3	99.8	0.01

From analyzing non-isothermal TG curves of blends, it was found that they can behave as a pure polymer without residue weight, can described by a single wave characterized by one activation energy, degrade mainly between 375-520 °C, that the thermal degradation of PP took place most rapidly and, increasing in the stability of PP with further addition of HDPE. Also, initial weight loss is found to be very small.

4 Conclusion

In this study, the thermal and some mechanical properties of polypropylene MH 418, High density polyethylene S 0464 and of their nine different blends investigated. Obtained results are followed:

- PP and HDPE are semi crystalline polymers, with crystalline phases of 4.66 to 38.44 % in PP and 4.66 to 62.80 % in HDPE.
- Tensile strength values at yield and break point of nine polymer blends were not changed in respect of homopolymers, but, elongation at break values were very poor from the original homopolymer values.
- The stiffness values of blends were improved with the increasing of HDPE concentration up to ~2.6% in the blends; this improvement gives movable plastic products manufacturing application for the blends.
- Poor impact resistivity of PP was improved higher than 70 wt. % of HDPE content in the blends; this situation gives low temperature application to related blends.
- Thermal analysis of blends showed two melting points peaks, which are characteristic of PP and HDPE. Obtained single crystallization points peaks of the blends show that PP segments crystallized in molten HDPE segments [18]. According to these results, we can conclude that all blends are immiscible with two phases; but, it is possible to make compatible by using suitable plastic processing technique and material [19].

In terms of mechanical and thermal properties PP and HDPE blends can be used in industrial areas was seen partly instead of each other.

5 References

[1] Şirin, K.; Balcan, M. Mechanical properties and thermal analysis of low density polyethylene+polypropylene blends with dialkyl peroxide. Polym. Advan. Technol. 2010; 21(4), 250-255.

[2] Şirin, K.; Doğan, F.; Çanlı, M.; Yavuz, M. Mechanical properties of polypropylene (PP)+high-density polyethylene (HDPE) binary blends: Non-isothermal degradation kinetics of PP+HDPE (80/20) Blends. Polym. Advan. Technol. 2013; 24(8), 715-722.

[3] Şirin, K.; Beşergil B. Celal Bayar Üniv. Science Institute. Master thesis, Manisa, 2000.

[4] Beşergil, B. Polymer Chemistry, Gazi kitabevi, Ankara, 2004.

[5] Abshire, A.D. SDI International Polymer Blends, Menlo Park, Report Nummer: 175, 1986

[6] Paul, D.R., Newman, S., Polymer Blends, pp 19, Academic Pres, New York, Vol:1; 1978

[7] Olabisi, O.; Lyod, M.R.; Montgomery, T.S. Polymer-Polymer Miscibility, Academic Pres, New York, 1979; 123 pp.

[8] Varlet, J.; Perez, J.; Vassoille, R.; Vigier, G.; Glotin, M.; Cavaille, J. Microstructure and mechanical properties of isotactic polypropylene (iPP)/polyamide 12 (PA12) blends J. Mater Sci. 1993; 28, 5560-5568.

[9] The, J.W. Structure and Properties of Polyethylene-Polypropylene Blend. J. Appl. Polym. Sci. 1983;28, 605-618.

[10] Bonnet, M.; Loos, J.; Petermann J. On the crystallization of syndiotactic polypropylene (sPP)/high density polyethylene (HDPE) blends. Colloid. Polym. Sci. 1998; 276, 524-528.

[11] Martuscelli, E.; Pracelle, M.; Volpe, D.G.; Greco, P. Morphology, Crystallization and Thermal Behaviour of Isotactic Polypropylene/Low Denstiy Polyethylene Blends, Macromol. Chem. Phys. 1984; 185(5), 1041-1061.

[12] Blackadder, A.D.; Richarson, M. J.; Savill, G.N. Characterization of Blends of High Density Polyethylene with Isotactic Polypropylene, Macromol. Chem., 1981;182, 1271-1282.

[13] Liang, J.Z.; Ness, J.N. Investigation on the Melt Flow Properties of Polyethylene and Polypropylene Blends. Polym. Test. 1997;16, 379-389.

[14] Schürman B.L.; Niebergall, U.; Severin, N.; Burger, Ch.; Stocker, W.; Rabe, J.P. Polyethylene/Polypropylene Blends: Mechanical Properties, Structure and Morphology. Polymer. 1998 ;39, 5283-5291.

[15] Liang, J.Z.; Tang, C.Y.; Man, H.C. Flow and Mechanical Properties of Polypropylene/Low Density Polyethylene Blends. J. Mater. Process. Tech. 1997; 66,158-164.

[16] Loos, J.; Bonnet, M.; Peterman, J. Morphologies and Mechanical Properties of Syndiotactic Polypropylene/Polyethylene. Polymer. 2000; 41, 351-356.

[17] Brandrup, J.; Immergut, E.H.; Grulke, E.A; Abe, A.; Bloch, D.R. Polymer Handbook Fourth Edition, John Wiley and Sons, USA, 2005.

[18] Souza, A.M.C.; Demarquette, N.R.; Influence of Composition on The Linear Viscoelastic Behavior and Morphology of PP/HDPE Blends., Polymer., 2002; 43, 1313-1321.

[19] Utracki, L. A. Polymer Blends Handbook (vol. 1). Kluwer Academic Publishers, London, 2002.