Thermal properties of polypropylene and polyethylene blends (PP/LDPE)

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Abstract. The paper investigates the thermal properties of polymer blends of polypropylene and low-density polyethylene.

1. Introduction
Investigations of polypropylene thermal properties are important from a scientific point of view as they explain the polymer performance at elevated temperatures and define the choice of a suitable material according to the application, as well as predict the structure and methods of creating new materials with required properties [1, 2].

2. Body text
The properties of polypropylene (PP)- and polyethylene (PE)-based blends are known to differ from the properties of primary polymers, but the system data are not compatible. PE crystallizes into more stable orthorhombic lattice and PP – into monocline form, but each component also has a significant influence on the structure and properties of final polymer blends [1, 3-7].

One of the underlying issues regarding blends of mutually soluble polymers is the definition of strength of intermolecular interactions between polymer components. Analysis of melting-point depression is widely used for mutually soluble blends containing partially crystalline polymers. The method includes the comparison between the equilibrium melting points of unblended partially crystalline polymer and the same polymer in different polymer blends [2].

Differential scanning calorimetry (DSC) was used to define the experimental melting points. DSC analysis was recorded with Netzsch differential scanning calorimeter DSC 204 F1 Phoenix. The investigation was performed in dynamic heating/cooling conditions at a rate of 10 °C/min under argon purge with a rate of 50 cm³/min.

Table 1 shows the DSC data derived from PP and PE melting endotherms and crystallization exotherms. As a result of calculation of crystallinity the heat of fusion for completely crystalline PP is 198 J/g [8, 10-11].

Table 1. Thermophysical properties of PP and PE blends

| No of PE/PP sample | T_{maxmelt} (PE), °C | T_{cr} (PE), °C | T_{maxmelt} (PP), °C | ΔH_{fus} (PP), J/g | T_{cr} (PP), °C | Crystallinity (PP), % |
|-------------------|-----------------|--------------|-----------------|----------------|----------------|---------------------|
| 0/100             | -               | -            | 161.8           | 72.0           | 108.1          | 36.3                |
| 10/90             | 107.3           | 91.4         | 162.9           | 43.5           | 107.3          | 22.0                |
The analysis of table 1 shows that the value of PE melting point (Tmelt) in polymer blends with PP varies within a range of 107.1 ±0.2 °C, and PP melting point (Tmelt) – within a range of 160.3-162.9 °C. The compound PE/PP-10/90 is observed to have higher PP melting point (162.9 °C) in comparison with the melting point of primary PP (161.8 °C). The crystallinity of PP blended with PE decreases as the PE content increases from 36.3 % to 17.9 %: maximum value for the compound PE/PP-20/80 (24.2 %) and minimum value for PE/PP-50/50 (17.9 %). It has to be noted that these polymers in blends have two PP melting peaks, the first peak is small and shifted from the main peak towards the low temperatures by 18.5 °C. It can be assumed that such behavior during melting of PP blend samples with 10 %, 20 % and 40 % is related to recrystallization.

The compound PE/PP-10/90 has the most perfect crystalline structure with higher melting point, which features the lowest number of defects as they have been forced into the amorphous phase during the crystallization.

Therefore, based on the DSC data it can be concluded that the introduction of polyethylene into PP leads to a small shift of PP melting point to the lower-temperature region. It indicates that the structure is changed and low-melting crystals are formed. In addition, as the content of polyethylene increases the propylene enthalpy of fusion as well as its crystallinity decrease, suggesting the partial amorphicity of polypropylene. Of the investigated blends the compound PE/PP-50/50 has the lowest crystallinity.

Degradation processes play a key role for the correct usage of blended PP polymers in the various fields. During the thermal degradation of polymers in the inert atmosphere the molecular mass decreases and highly volatile components are formed [1].

The thermal stability and degradation of PP and PE blends were investigated with Netzsch thermogravimetric analyzer TG 209 F1 Iris. The samples were heated up to 550 °C with a rate of 10 K/min under continuous argon purge.

Table 2 shows the processing results of thermogravimetric analysis. Addition of up to 30 % of PE increases the temperature of loss of 5, 10 и 20 % of PP, and with the PE content of 40 % and 50 % the temperature of maximum degradation rate (Tmax) and final weight loss (Tfinal) increase significantly. These findings indicate the thermostabilizing effect of polyethylene.

Table 2. Processing results of thermogravimetric analysis

| PE/PP composition | Tmax | T5  | T10 | T20 | Tfinal |
|-------------------|------|-----|-----|-----|-------|
| 10/90             | 452  | 394 | 419 | 436 | 493   |
| 20/80             | 456  | 414 | 428 | 439 | 493   |
| 30/70             | 449  | 405 | 423 | 438 | 494   |
| 40/60             | 453  | 419 | 431 | 442 | 504   |
| 50/50             | 466  | 374 | 407 | 431 | 504   |

Therefore, the thermal degradation runs slower in PP and PE blends than in unblended PP due to the influence of the thermally stable PE.

PP is known to be more susceptible to degradation than PE. It is due to the fact that one half of PP carbons is linked to methyl groups which activate a hydrogen atom with a tertiary carbon. As a result, it turns to be more reactive than hydrogen of methylene or methyl group. A higher PE content in the blend leads to higher degradation temperature.

One of the main PP disadvantages is its low resistance to thermo-oxidative degradation, resulting in poor processability, lower stress-strain and electric properties of polymers in products, as well as color
change. In view of this, the product resistance to thermo-oxidative degradation is the critical property for a material during the operation.

Thermal-oxidative resistance was evaluated by oxidative induction time [8]. It is the time when the oxidation reaction starts, which manifests itself by exothermic effect in the DSC curve (table 3).

Table 3. Oxidative induction time for PP, and PP and PE polymer blends

| PE/PP composition | Oxidative induction time, min |
|-------------------|-----------------------------|
| 0/100             | 1.00                        |
| 20/80             | 1.17                        |
| 40/60             | 1.31                        |
| 50/50             | 1.63                        |

The analysis of table 3 shows that introduction of PE into PP leads to increase in the oxidative induction time in comparison with PP. Higher PE content (up to 50 %) increases the oxidative induction time from 1 to 1.63 minute.

These findings indicate the thermostabilizing effect of polyethylene, which can result from hindered oxygen diffusion for PP chains due to formation of the interfacial layer.

Thus, thermo-oxidative degradation can be improved by adding 20 %, 40 % of PE.

3. Conclusions

Therefore, the addition of polyethylene to polypropylene gives an insignificant shift of polypropylene melting point to the lower-temperature regions, suggesting the change in structure and the formation of low-melting crystals. In this case, the thermal degradation is slower than in unblended polypropylene due to the influence of more stable polyethylene. Based on the thermal-oxidative resistance polyethylene is found to have thermostabilizing effect which results from hindered oxygen diffusion for polypropylene chains due to formation of the interfacial layer.

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