

## DEVELOPMENT OF NANOCLAY REINFORCED HDPE/PA6 NANOCOMPOSITES

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### Abstract

*In our experiments HDPE/PA6 blends (75/25 wt%) were produced and maleic anhydride grafted polyethylene (PEgMA) was used as chemical coupling agent. To enhance the mechanical properties the blends were compounded with the layered structure montmorillonite (MMT) in different concentrations. The effect of PEgMA, MMT and their combination on the mechanical and melting properties were examined in this study.*

### 1 Introduction

Due to their several advantages, PA6 and HDPE polymeric materials are widely used in the package and automobile industries. They can be easily processed, have low gas permeability and good mechanical properties. By mixing two or more polymers their properties can be alloyed, and by changing the components and their composition the properties of the system can be varied in a wide range [1,2].

There is a chemical incompatibility in the most polymer combinations, which means that after the melt mixing process of two or more thermoplasts, a phase separation occurs at room temperature. The immiscibility of the polymers results in globular morphologies, where spheroidal droplets of the minor phase are suspended in a matrix constituted by the major constituent [3,4]. The micron-scale arrangement of the phases and the properties of the single constituents have also a strong effect on the blend properties. However, in determining the final properties of the polymer blends the strength of the chemical interaction on the interfaces and the process parameters play the major role [5]. Because of the phase separation and the weak adhesion of the components the impact toughness can be dramatically decreased [4].

In the last few years beside the traditionally used chemical coupling agents, the effect of nano sized particles as compatibilizers are more and more widely studied in polymer blends [6]. Nanoparticles have a strong effect on the microstructure of the immiscible polymer blends; they resulted in the decrease of the minor phase and thus finer microstructure [7-9].

The positive effect of using nanostructured materials in polymer matrix have been reported in many papers. By using clay minerals like montmorillonite the gas permeability and the heat resistance of the composite can be decreased due to the Barrier-effect and the mechanical properties can be increased.

In our experiments, PA6/HDPE blends were produced. Maleic anhydride grafted polyethylene was used as coupling agent and the blends were reinforced by nanostructured clay material.

Layered structure montmorillonite was applied in different concentrations and its effect on the mechanical and melting properties of the blend were investigated.

## 2 Experiments

### 1.1 Materials

High-density polyethylene (HDPE, TIPELIN 6000B (TVK, Hungary), MFR: 1.30 g/10 min (5 kg 190°C)), and polyamide6 (PA6, HVF (A. Schulman)) were blended in our experiments as matrix materials.

Chemical coupling agent (Polybond 3009 (Chemtura Corp.) – PEGMA (M<sub>w</sub>=186000)) was added in different concentrations – 0.5 wt%, 1 wt% and 3wt% (related to the matrix weight) – to the polymer blends.

As nano reinforcement layered structure montmorillonite (MMT, Cloisite 20 A, Southern Clay Products) was applied in 1wt% and 3wt%.

### 1.2 Production of blends and specimen preparation

Polymers were compounded by melt mixing in a laboratory twin-screw extruder (LAb-Tech Scientific) in ratios of 25wt% PA6 and 75wt% HDPE. Blends and nanocomposite blends were produced by adding PEGMA (0.5-1-3 wt%) or MMT (1-3wt%) alone and by applying both (1wt%PEGMA and 1-3wt% MMT). Their amounts are related to the common weight of HDPE and PA6 polymers. The zone temperatures of the extrusion varied in the 180 -240°C range. The test specimens were produced by injection molding from the nanocomposite blend granules made by extrusion according to MSZ EN ISO 527-2. The raw materials were dried before the extrusion and the injection molding at least 16 hours on 80 °C.

### 1.3 Testing methods

The specimens used for three point bending and the impact tests were made by cutting the ends of the dump-bell shaped samples. All specimens were conditioned (50% RH, 23°C) at least 24 hours before testing.

Tensile tests were carried out at room temperature on a standard tensile Instron machine, model 3344 equipped with a 2 kN load cell (cross-head speed of 1 mm/min and then 50 mm/min).

Three point bending tests were performed by Instron 5582 equipment (support span of 6.4 mm, loading speed of 2 mm/min).

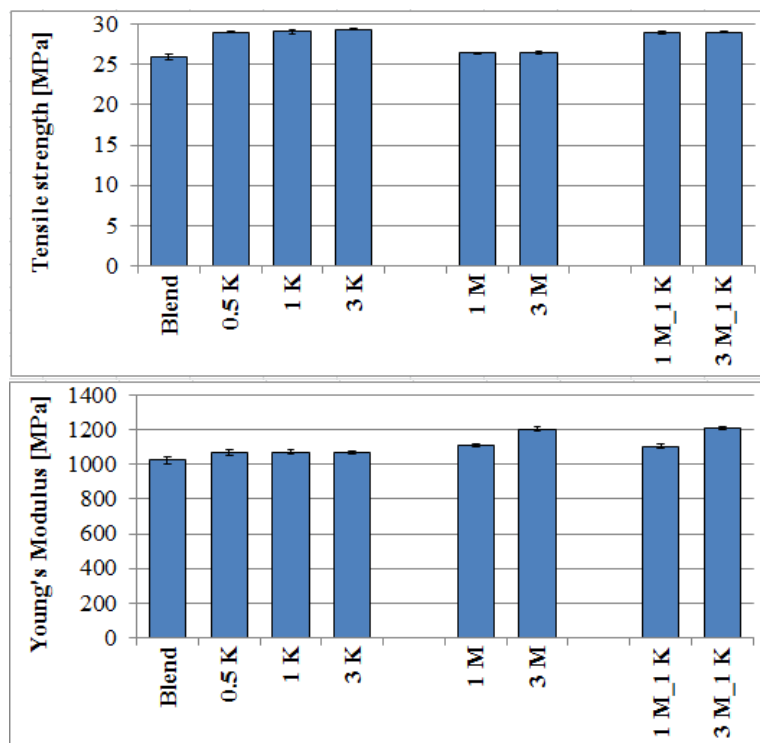
Notched Charpy impact tests were carried out as per ISO 179-1 standard by using a 15 J pendulum impact machine (Model 8545/000, CEAST) at room temperature on single-notched specimens.

The melt volume rates (MVR) of all formulations were measured by a CEAST 7026 Modular Melt Flow Index tester at 240°C and by 10 kg load.

Differential scanning calorimetry (DSC) was performed using a SETARAM DSC131 equipment. In order to erase any thermal history effect, the samples were heated from 30 °C to 270 °C, cooled to 30 °C, and then they were heated again up to 270 °C. The data presented refer to the second heating scans. The heating and cooling cycles were all carried out at 20 °C min<sup>-1</sup>.

### 3 Results and discussion

Tensile strength and Young's modulus values for each nanocomposite blends are summarized in Figure 1. Positive effect of PEgMA compatibilizer on the tensile strength can be clearly seen on the diagrams. Nearly the same results were measured for blends containing both PEgMA and montmorillonite. By using 3wt% of coupling agent 13% higher tensile strength could be achieved.



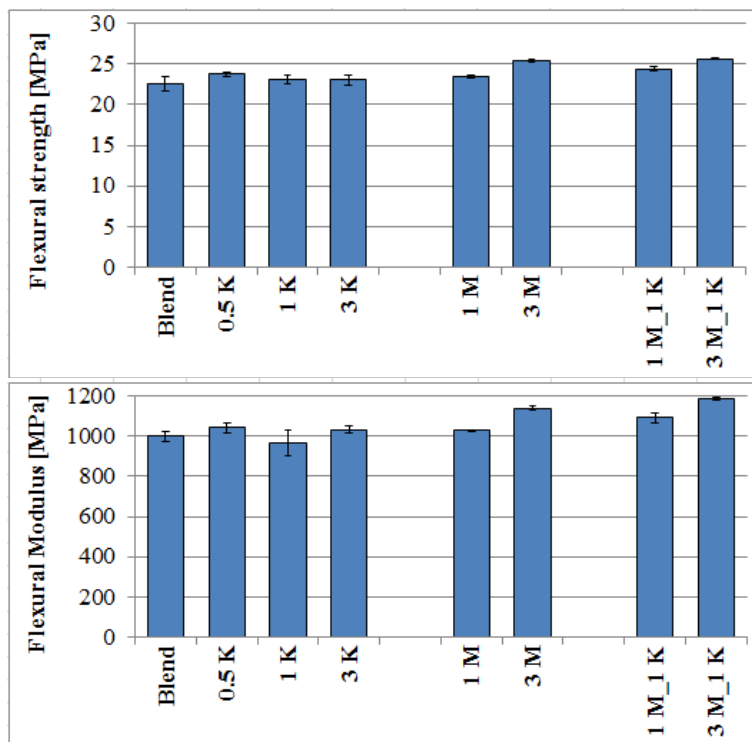
**Figure 1.** Results of tensile tests on neat and modified/nanocomposite 75HDPE/25PA6 based polymer blends (K: PEgMA, M: montmorillonite)

Compounding of blends resulted the improvement of Young's modulus in all combinations. PEgMA had no significant effect, while modulus increased by adding nanoclay. 8% improvement could be achieved by adding 1wt% of MMT and about 20% when the higher amount of montmorillonite was incorporated.

From the load-deflection curves of three point bending tests flexural strength (limit bending strength) and modulus were determined. Results for the different blend combinations can be seen on Figure 2.

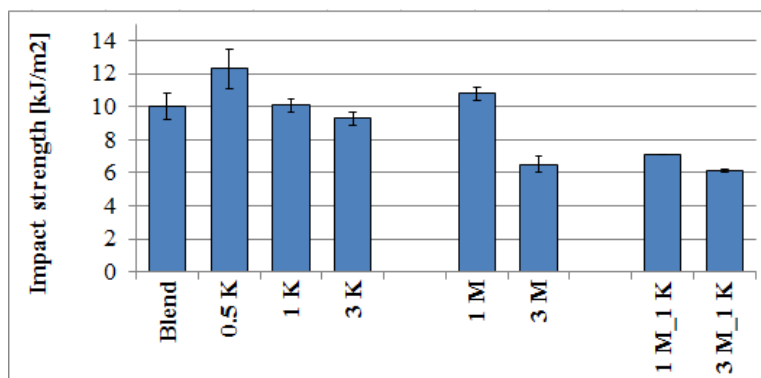
Application of PEgMA or the montmorillonite in low concentration had only slight effect on the flexural strength. Similar to the tensile properties the highest values could be found at 3wt% MMT content.

For the flexural modulus of the different blends far the best results, a ~20% improvement was measured by applying 3wt% MMT and 1wt% PEgMA in the same time.



**Figure 2.** Results of three point bending tests on neat and modified/nanocomposite 75HDPE/25PA6 based polymer blends (K: PEgMA, M: montmorillonite)

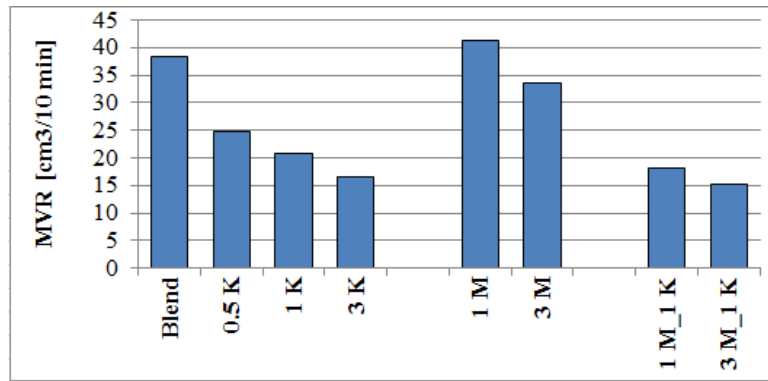
There is a well-known relationship between the stiffness and the toughness: the highest is the modulus the lowest is the stiffness. The results of the Charpy impact tests are in accordance with this tendency (Figure 3).



**Figure 3.** Results of Charpy impact tests on neat and modified/nanocomposite 75HDPE/25PA6 based polymer blends (K: PEgMA, M: montmorillonite)

The impact strengths of most blend compositions decreased, while the maximum improvement (23%) was found by adding of 0.5 wt% PEgMA.

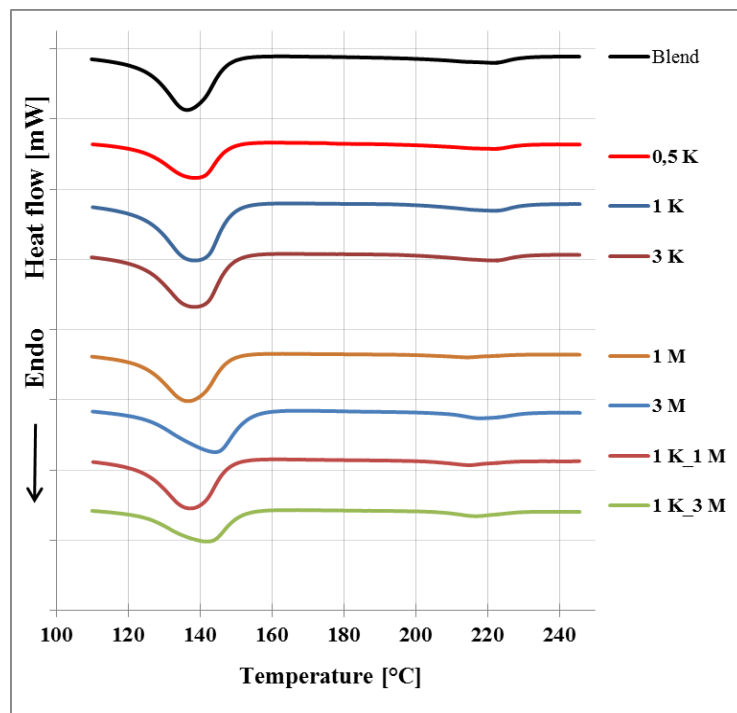
To characterize the processability of the blends melt flow test was carried out and the melt volume rates (MVR) [cm<sup>3</sup>/10min] were determined. The MVR values of the different blends are presented in Figure 4.



**Figure 4.** Results of melt flow tests on neat and modified/nanocomposite 75HDPE/25PA6 based polymer blends (K: PEgMA, M: montmorillonite)

The tendency of the MVR results is very interesting. When PEgMA is incorporated into the blends the MVR decreases dramatically, while the addition of montmorillonite improved the processability in a low amount.

The DSC traces of the second heating scans for the different samples are shown in Figure 5, and the temperatures,  $T_m$ , and the enthalpies,  $\Delta H_m$ , of the melting peaks are summarized in Table 1.



**Figure 5.** DSC traces of the second heating scans for different samples (K: PEgMA, M: montmorillonite)

The chemical coupling agent affects the melting temperature of the polyethylene, but stronger effect could be found by adding 3wt% MMT. That results in the better thermal resistance of the polymer blend.

Sample	HDPE melting peak		PA6 melting peak	
	T <sub>m</sub> (°C)	ΔH <sub>m</sub> (J/g)	T <sub>m</sub> (°C)	ΔH <sub>m</sub> (J/g)
HDPE/PA6	136.5	94.3	221.7	13.8
0.5K*	138.9	96.6	221.6	18.9
1K	139.0	108.9	222.3	13.6
3K	138.8	108.8	222.1	12.7
1M**	136.7	123.5	214.4	5.9
3M	144.2	102.0	218.0	11.3
1K_1M	137.4	116.2	214.8	7.3
1K_3M	142.0	103.0	216.9	8.5

\*: 0.5 wt% PEgMA in HDPE/PA6 (75/25wt%) blend

\*\* : 1 wt% MMT in HDPE/PA6 (75/25wt%) blend

**Table 1.** Temperatures, T<sub>m</sub>, and enthalpies, ΔH<sub>m</sub>, of the melting peaks of the second DSC heating scans for various samples

#### 4 Conclusions

Blends of PA6 and HDPE (25/75 wt%) was produced by melt mixing in twin screw extruder. The effect of using PEgMA as chemical coupling agent and montmorillonite in different ratios were examined on the processability, thermal and the mechanical properties of the blends.

Based on the test results the followings can be concluded:

- Static mechanical properties are increased by using 3wt%MMT alone or combined with 1 wt% PEgMA (by ~20%), while their impact strengths are decreased.
- Using of 0.5 wt% PEgMA has only a slight effect on the tensile and bending properties, but the impact strength increased by 23%.
- 1 wt% montmorillonite increased the melt flow properties while use of PEgMA decreased dramatically.
- The higher amount of MMT has positive effect on the melting temperature of the HDPE phase, thus better thermal resistance can be achieved.

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