Foamed Crosslinked LDPE/PP Blends Made by Hot Mold Injection Molding

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Summary: Foamed and crosslinked blends of LDPE and i-PP were investigated. The specimens were made by hot mold injection molding process at the temperature of the mold of 210°C. Azodicarbonamide as foaming agent and 2,5-dimethyl-2,5-di(tert.-butylperoxy)hexane as crosslinked agent were used. The chemical changes as a result of the crosslinking were determined by gel content. Thermal behavior of the blends was studied by DSC. The difference of influence of crosslinking agent on chemical changes of both polymers was established. An improvement of the mechanical properties due to crosslinking between PE and PP on their interface was observed. The interaction on the PE/PP interface was confirmed by phase transition parameters determined on the basis of DSC-curves.

Introduction

Preparation of PE/PP blends is a way of modification of their properties. The main reason that hinders to achieve good ultimate properties is the low compatibility of this polymer pair.[1,2] A possibility to improve the compatibility between PP and PE is peroxide-induced crosslinking.[3] However, crosslinking efficiency in PE differs from that in PP since an intensive destruction accompanies crosslinking. PP degradation can be avoided by addition of coagents such as phenols, polyfunctional monomers or quinones.[4] When the crosslinked PP/PE blends are used for the production of foamed samples by injection molding the problem to be solved is to prevent crosslinking in the plasticizing cylinder of the machine. A possibility to overcome this limitation is an injection molding process in a heated mold with a temperature appropriate for crosslinking and foaming.[5] In this work, we studied the mechanical properties and the behavior during melting/crystallization of the foamed and crosslinked LDPE/PP blends made by hot mold injection molding process.

Materials and methods

The materials used were i-PP “Buplen”6631, Lukoil Neftochim, [MFI(230/2,16) = 2.28 g/10 min] and LDPE “Ropoten”OV-03-110, Lukoil Neftochim [MFI(190/2,16) = 0.25 g/10 min]. 2,5-Dimethyl-2,5-di(tert.-butylperoxy)hexane (Trigonox 101, Akzo Nobel Chemicals) was used as the initiator of crosslinking and Hydroquinone (Fluka AG) was used as the coagent of crosslinking. Azodicarbonamide (“Genitron” AC-4, Fisons Ltd) with interval of decomposition

CCC 1022-1360/00/$ 17.50+.50/0

in the range of 200-230⁰C was used as chemical blowing agent.

The components were blended using a twin screw extruder (DSE Brabender 35/17D) at temperatures of the extruder barrel in the range from 135 to 190⁰C. The blends prepared are given in Table 1. These blends were mixed with 0.5 wt. % azodicarbonamide and then test specimens were produced by a hot mold injection molding process at process conditions shown in Table 2.

Table 1. Blends prepared on a twin screw extruder.

Nr	LDPE/PP	Initiator, wt. %	Coagent, wt. %
1	0/100	0.7	0.175
2	15/85	0.7	0.175
3	30/70	0.7	0.175
4	50/50	0.7	0.175
5	70/30	0.7	0.175
6	85/15	0.7	0.175
7	100/0	0.7	0.175
8	50/50	0	0
9	50/50	0.5	0.125
10	50/50	1.0	0.25

Table 2. Injection molding process conditions.

Temperature of the cylinder, ⁰C	130-200
Mold temperature, ⁰C	210
Mold heating time, min	15
Time for foaming and crosslinking, min	15
Rate of screw rotation, rev/min	35.5
Rate of injection shot, ccm/sec	200

The hot mold injection molding process is a variation of the reaction injection molding one: the short shot of the polymer melt containing foaming and crosslinking agents was injected into a heated mold where foaming and crosslinking occurred. Two types of specimens were made: paddle type test specimens with the size of the working sector 80x20x12.5 mm and prismatic test specimens, 160x24.5x12.5 mm.

The following was defined for the blends: The gel content was determined by weight analysis after a 14 h extraction in boiling xylene. The tensile strength of the paddle type samples was determined at a deformation rate of 50 mm/min. The Sharpy impact strength of the prismatic test samples was determined at a distance between supports of 40 mm. The phase transition parameters were measured by means of Differential Scanning Calorimetry. The scans were made at heating and cooling rates of 10 °C/min.

Results

The gel content data (Figure 1) shows that when pure PP is used for preparing of the test specimens by hot mold injection molding process the PP macromolecules undergo destruction rather than crosslinking. Shown in Figure 1 is that the unsoluble portion is proportional to the

LDPE concentration. Hence, it can be assumed that crosslinkig occurrs mainly in the polyethylene phase. However, mechanical properties of the foamed crosslinked LDPE/PP blends led to a different assumption. The tensile strength decreases and the impact strength increases with the increase of LDPE concentration (Figure 2). Both strengths have higher values for crosslinked polymer blends and these values increase with the increase of the degree of crosslinking (Figure 3). Therefore, crosslinking is probably occurred not only in LDPE phase but between LDPE and PP chains on the interface.

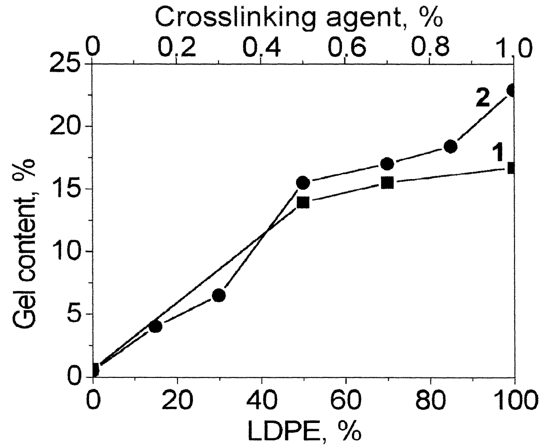

Figure 1. Gel content in dependence on: 1 – LDPE/PP ratio (crosslinking system contains 0.700 wt. % initiator and 0.175 wt. % coagent); 2 – initiator concentration (LDPE/PP = 50/50).

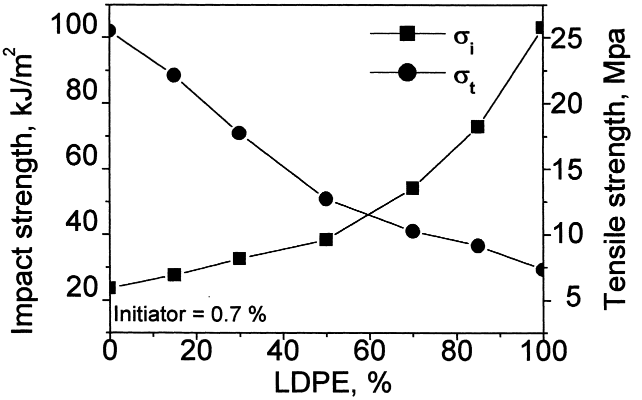

Figure 2. Impact strength σ_i and tensile strengt σ_t vs. LDPE concentration.

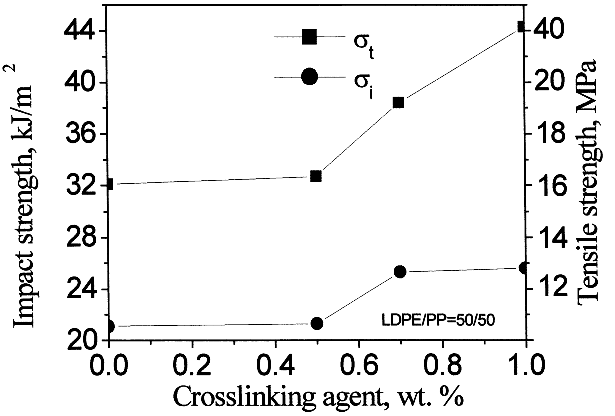

Figure 3. Impact strength σ_i and tensile strength σ_t vs. concentration of the crosslinked agent

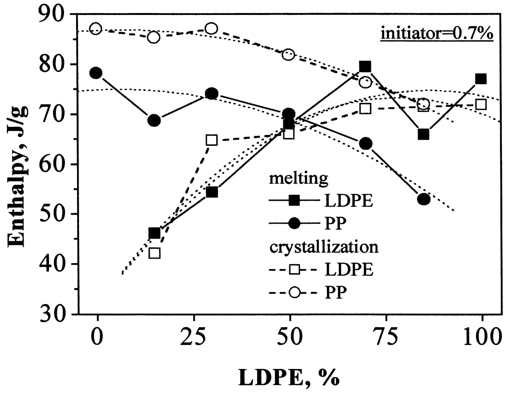

Figure 4. Enthalpy of melting and crystallization in dependence of the LDPE concentration.

Enthalpies of the phase transition of both polymers decrease with decreasing its amount in the blends (Figure 4). There is a positive deviation from linearity which shows comparatively good compatibilization. It is probably due to the crosslinking on the PE/PP interface.[6] Melting peaks of PE and PP in the blends come closer to each other (Figure 5), which means that there is an interaction between them on the phase boundary.[7] It confirms the assumption about crosslinking between PE and PP.

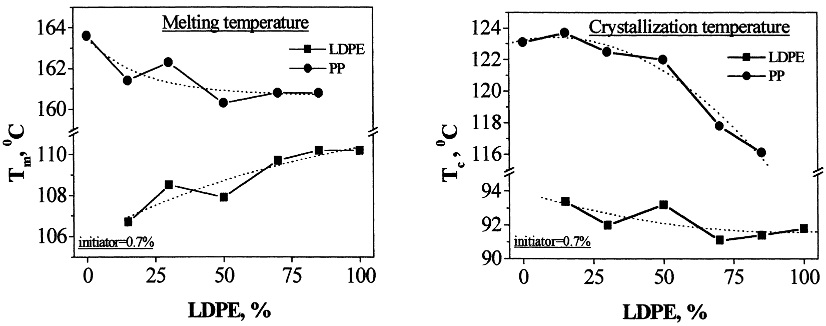

Figure 5. Melting and crystallization peek temperatures of LDPE and PP in dependence on the LDPE concentration.

Conclusion

The hot mold injection molding process is appropriate for the production of the foamed crosslinked LDPE/PP blends since foaming and crosslinking occur at a single step. An improvement of the mechanical properties due to crosslinking between PE and PP on their interface is observed. The interaction on the interface is confirmed also by phase transition parameters determined on the basis of DSC-curves. That leads to the increase of the compatibility in the LDPE/PP blends.

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