Modification of Recycled Polymer Blends with Activated Natural Zeolite

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Summary: The growing interest in the natural zeolite is based on some specific peculiarities of its structure, which after dehydration enables adsorption processes of some polymer molecules and/or segments to take place on the zeolite surface. The main goal of the study is to investigate the effect of dehydrated zeolite on the flow behavior, mechanical properties and morphology of immiscible blends from unsorted polymer wastes. A tetra-component blend consisting of 40 wt.% polypropylene (PP), 40 wt.% high-density polyethylene (HDPE), 15 wt.% low-density polyethylene (LDPE) and 5 wt.% polystyrene (PS), was studied as a model system of commingled plastic wastes. Compositions from recycled blend and dehydrated zeolite in a wide concentration range (from 0 to 20 wt.%) were prepared using a twin-screw extruder Brabender DSE 35/17D in the temperature range from 140 to 190 °C. The compositions were characterized by capillary rheometry, differential scanning calorimetry (DSC), site-resolved wide-angle X-ray scattering (WAXS) and mechanical tests. The results show a compatibilizing effect of dehydrated zeolite at low concentration levels (1-2 wt.%) and open wide possibilities for utilization of dehydrated zeolite in the recycling of unsorted polymer wastes.

Keywords: blends from unsorted polymer wastes; dehydrated zeolite; flow behavior; mechanical properties; morphology

Introduction

Polymer materials have been filled with several inorganic fillers in order to improve some properties like tensile strength, impact resistance, conductivity, heat resistance, flame retardance, etc. One of the fillers, which attracted much attention recently, is the natural zeolite. The natural zeolite has some specific peculiarities of its structure which is characterized by a tree system of channels and interconnected voids occupied by cations and water molecules. The treatment used to modify the zeolite surface can be divided into two steps: the first is the direct heating (dehydration) and the second the adsorption. After dehydration about 30 % of the whole volume of the zeolite particle is freed. This enables adsorption processes of different molecules or their parts (gases, liquids and polymers) to take place on the zeolite surface.[1,2] In dependence on the

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adsorbed substance, the activated zeolite can be used as a filler for polymers, as a compatibilizer for immiscible polymers as well as a modifier of blowing agent systems.[3-5] As filler zeolite exerts a strengthening effect on the polyolefins. The addition of zeolite (20 wt.%) to HDPE and PP improves significantly the tensile strength of the composition, its elastic modulus, as well as the processability because the linear polyethylene molecules and polypropylene segments are commensurable with dimensions of zeolite channels and can go into the channels.[3,4] The typical immiscible blend HDPE/PS shows an increase of impact strength by addition of 1 wt.% dehydrated zeolite.[4] These findings led us to the idea to investigate the effect of zeolite on the flow behavior, morphology and mechanical properties of recycled polymer blends.

Experimental

Materials

A tetra-component blend consisting of commingled plastic wastes from 40 wt.% polypropylene (PP), 40 wt.% high-density polyethylene (HDPE), 15 wt.% low-density polyethylene (LDPE) and 5 wt.% polystyrene (PS) was studied as a basic blend. The physical characteristics of the polymers are given in Table 1. Natural zeolite, clinoptilolite - $(K_2,Na_2,Ca)Al_6Si_{30}O_{72}x23H_2O$, micro milled with particle size < 40 μm, was supplied by Zeo products Ltd. The activation of natural zeolite was carried out by dehydration at 350 °C for 3 hours.

Table 1. Characteristics of recycled polymers

Materials	Density (g/cm^3)	MFI [a] (g/10 min)	T_m (°C)	T_{cr} (°C)
LDPE	0.912	1.15	116.1	91.9
HDPE	0.932	0.70	139.6	110.8
PP	0.904	7.18	164.9	106.3
PS	1.039	4.31	102.9 [b]	-

[a] PE(190/2.16); PP(230/2.16); PS(200/5)
[b] glass transition temperature

Mixing

Compositions from the basic polymer blend (K) and activated zeolite in a wide concentration range from 0 to 20 wt.% (denoted as K, K1Z, K2Z, K3Z, K5Z and K20Z, respectively) were prepared in the molten state using a twin-screw extruder Brabender DSE 35/17D in the temperature range from 140 to 190 °C at a screw speed of 20 rpm.

Injection molding

Specimens for mechanical testing (dumb-bell shaped samples and bars) were prepared on an in-line injection molding machine TOSS 140/36 at the following injection conditions: melt temperature 240 °C, mold temperature 20 °C, injection pressure 16 MPa, packing time 3 s, cooling time 7 s.

Characterization of blends

The rheological properties (apparent flow curves and viscosity) were measured using a Brabender extrusiograph 30/25D with a cylindrical die of 1.5 mm diameter and length-to-diameter ratio L/D = 16. Bagley and Rabinowitch corrections were not applied. The experiments were carried out at a melt temperature of 200 °C and shear rates γ in the range from 100 to 5000 s^{-1}.

Calorimetric measurements (DSC) were made by means of a Perkin Elmer DSC–7 equipment. DSC thermograms were obtained from 6 - 10 mg samples, cut from the middle of the bars. The samples were first heated at a rate of 10 °C/min to 300 °C, held at that temperature for 5 min and then cooled at 10 °C/min. The values of melting temperature T_m and enthalpy ΔH_m for PE and PP in the respective compositions and the crystallization temperature T_{cr} and enthalpy ΔH_{cr} were determined.

Appropriate specimens (cross-sections) cut from the middle of the bars were investigated by site-resolved wide-angle X-ray scattering (WAXS) in "parallel transmission" geometry using a specially adapted Kratky camera and a two-circle goniometer.[6-9] The data presented in 2D-intensity maps showing the scattering curves (intensity vs. scattering angle 2θ) either as function of position in the cross-section (Kratky camera) or as function of azimuthal angle ϕ (two-circle goniometer) were interpreted in terms of orientation parameters of α-PP (R_{110PP}, R_{040PP}) and PE (R_{110PE}, R_{200PE}) crystallites (Eqs. 1and 2), concentration parameter B of β-PP crystallites (Eq. 3), orientation of zeolite particles, and apparent crystallinity X_C.

$$R_{110PP} = \frac{I_{110PP}}{I_{110PP} + I_{040PP} + I_{130PP} + I_{\beta-110PP}}, \quad R_{040PP} = \frac{I_{040PP}}{I_{110PP} + I_{040PP} + I_{130PP} + I_{\beta-110PP}} \tag{1}$$

$$R_{110PE} = \frac{I_{110PE}}{I_{110PE} + I_{200PE}}, \quad R_{200PE} = \frac{I_{200PE}}{I_{110PE} + I_{200PE}} \tag{2}$$

$$B = R_{\beta\text{-}110PP} = \frac{I_{\beta\text{-}110PP}}{I_{\beta\text{-}110PP} + I_{110PP} + I_{040PP} + I_{130PP}} \qquad (3)$$

The apparent crystallinity X_C was determined from the scattering curves by means of Hermans' method[9], after an appropriate randomization (i.e. elimination of the effect of orientation).

Mechanical properties (tensile strength σ_t, elongation at break ε, impact strength σ_i) of the investigated specimens were tested according to ISO methods by means of a dynamometer INSTRON Model 1185 and Charpy impact tester with environmental chamber at –30 °C. Ten samples were tested in each case.

Results and discussion

Rheology

In general, our first observation on flow behaviour of recycled polymer blends showed that the addition of a small amount of activated zeolite (1 – 2 wt.%) enhanced the flowability of the compositions and the extrudate quality. At the same time, the melt fracture occurs at a higher level of shear stresses. Additional information can be extracted from the flow curves if one compares the viscosity of the investigated compositions at fixed shear rate. Figure 1 presents the concentration dependence of viscosity of zeolite-filled compositions at different shear rates. It can be seen that this dependence exhibits a minimum at low zeolite content, much more expressed at low values of shear rate.

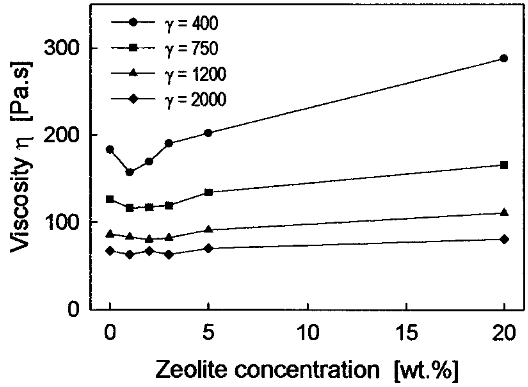

Figure 1. Concentration dependence of viscosity at different shear rates.

DSC measurements were conducted to evaluate the influence of zeolite particles on the melting and crystallization behavior of the basic composition. The melting of this composition is characterized by two melting peaks: a high melting peak at 153.5 °C for PP and a joint low melting peak at 129.7 °C for PE. It is evident, that the presence of different species of PE strongly reduces the melting temperature of PP in the basic composition. When the composition was cooled rapidly from the melt, PP and PE crystallize simultaneously. The activated zeolite changes the parameters of non-isothermal phase transition of the basic composition (Table 2), but it has a different influence on PP and PE due to their different nucleation ability. No clear differences in the melting temperature of PE are observed in the compositions at low zeolite concentration, but an addition of 20 wt.% of zeolite increases the melting temperature of PE by about 10 °C. The melting temperature of PP strongly increases yet at low zeolite concentration (1-2 wt.%), after that it decreases slightly. The activated zeolite acts as a nucleating agent during the crystallization of zeolite-filled compositions, since the melting enthalpies increase with increasing zeolite content.

Table 2. Parameters of non-isothermal phase transition

Compositions	T_m / PE (°C)	T_m / PP (°C)	T_{cr} (°C)	ΔH_m / PE (J/g)	ΔH_m / PP (J/g)	X_C
K	129.7	153.5	110.4	59.8	43.1	0.412
K1Z	130.7	164.2	111.3	59.6	43.7	0.414
K2Z	130.8	165.3	111.0	60.4	44.2	0.418
K3Z	129.9	163.9	110.1	58.8	42.8	0.407
K5Z	128.1	162.2	111.2	63.2	45.9	0.436
K20Z	139.1	163.8	110.2	60.2	43.8	0.416

WAXS

The intensity maps in Figure 2a,b are characterized by variation in intensity of most reflections with the distance from the surface and the zeolite content, in particular of the dominating reflections of α-PP (110, 040), β-PP (110) and orthorhombic PE (110, 200). The surface layers exhibit high 040 and low 110 intensities of α-PP, indicating a preferential orientation of (040) planes parallel to the surface. The intensity of the 040 reflection shows a broad minimum in the core regions, accompanied by a maximum of the 110 reflection of α-PP, which tends to decrease with increasing zeolite concentration. In comparison to α-PP, the intensity of the 110 reflection of PE is much higher and shows three maxima in the surface layers and intermediate zone. The intensity maps of injection-molded bars from K5Z, obtained from measurements in the two-circle goniometer (Fig. 2c,d) confirm and complete this picture. Measured near the surface (depth 0.2 mm), the intensity of the 040 reflection of α-PP has an intense maximum around the equator (ϕ ≈ 90°), indicating a preferential orientation of the 040 planes of PP parallel to the flow direction; this maximum is more expressed at low zeolite concentration. In the core, the azimuthal intensity distributions are characterized by almost constant intensities of most reflections over the entire range of azimuth angles. It has to be mentioned that at low zeolite concentration the reflections of zeolite are not detected in the maps.

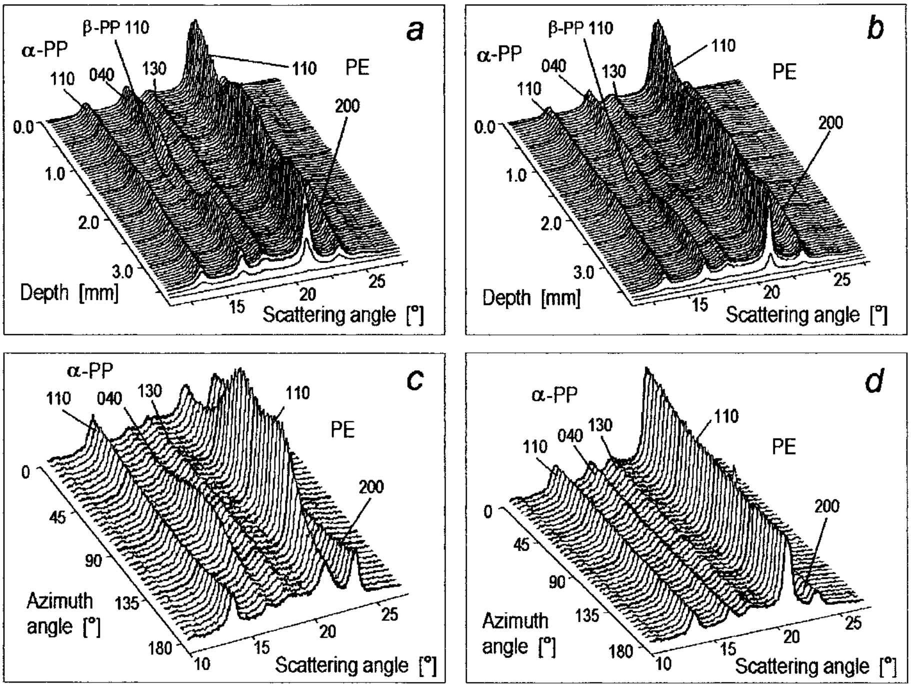

Figure 2. Intensity maps of injection-molded samples from zeolite-filled compositions. (a,b) Maps showing scattering curves vs. distance from the surface, derived from measurements with the adapted Kratky camera: a – K; b – K2Z. (c,d) Maps showing scattering curves vs. azimuth angle ϕ for K5Z, derived from measurements in the two-circle goniometer: c – 0.2 mm from the surface; d – core region.

It was found from the scattering curves of the composition K20Z, that the reflections 020, 200, 131 and 151 of zeolite correspond to scattering angles of 9.65, 11.16, 22.46 and 30.21°, respectively. The azimuthal intensity distributions of most zeolite reflections are characterized by nearly constant intensities over the entire range of azimuth angles everywhere in the cross-section. Only the intensity of the zeolite 020 reflection (Fig. 3) exhibits a maximum around the equator (i.e., at $\phi \approx 90°$) in the surface layers, indicating a weak preferential orientation of the (020) planes parallel to the flow direction, whereas the orientation is random in the core regions.

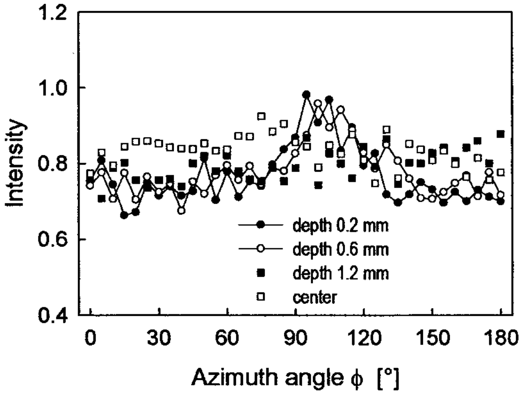

Figure 3. Azimuthal intensity distribution of the 020 reflection of zeolite in K20Z, derived from measurements with the two-circle goniometer.

The analysis of depth profiles of the intensities resulted in depth profiles of the orientation parameters of PP and PE crystallites and the concentration parameter for β-PP (Figs. 4 and 5). In general, the orientation parameter R_{110PP} for α-PP has low values in the surface layers, reaching maximal values in the core region (not shown). The profiles of the orientation parameter R_{110PE} of PE crystallites reveal that the PE crystallite orientation also varies with the depth, showing three clearly distinguished maxima in the surface layers and core region, most pronounced in the absence of zeolite. The influence of zeolite concentration on the depth profiles of the orientation parameter R_{040PP} (a measure for epitaxial double-orientation of α-PP crystallites) is complex, indicating an increase of this parameter with increasing zeolite content. A comparison of the β-PP concentration parameter B reveals that β-PP is located in the core regions and its concentration decreases with increasing zeolite content.

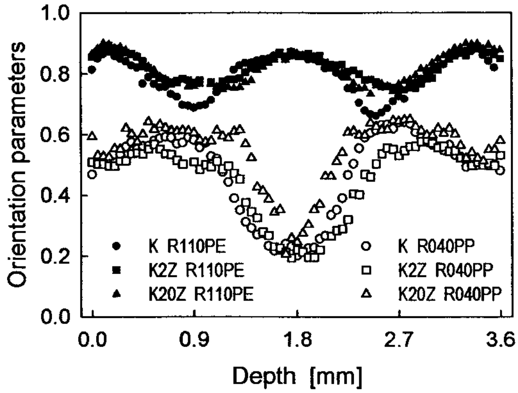

Figure 4. Profiles of the orientation parameters R_{110PE} and R_{040PP} in dependence on the zeolite concentration, derived from measurements with the adapted Kratky camera.

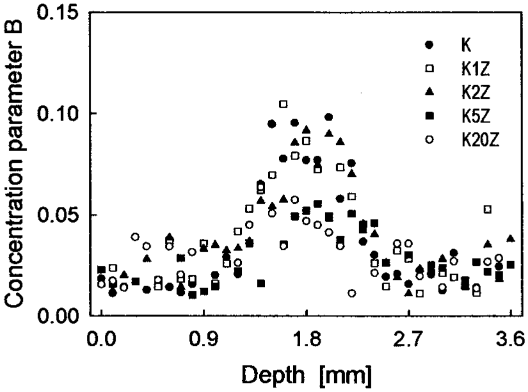

Figure 5. Profiles of the concentration parameter B for β-PP in dependence on the zeolite concentration, derived from measurements with the adapted Kratky camera.

The apparent crystallinity, derived from scattering curves by means of Hermans' method exhibits a slightly expressed maximum at low zeolite concentrations (Fig. 6). These findings are in accordance with the results for crystallinity from DSC measurements.

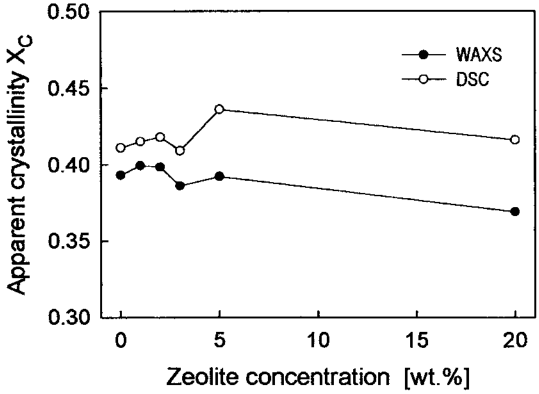

Figure 6. Apparent crystallinity X_C vs. zeolite concentration, derived from WAXS and DSC measurements.

Mechanical properties

Table 3 summarizes the mechanical properties of the investigated compositions. It can be clearly seen, that there is no significant variation in the tensile strength of the compositions, whereas the elongation at break decreases with increasing zeolite content. An improvement of impact strength was observed at low zeolite concentration. The addition of 2 wt.% zeolite leads to an improvement of this parameter by about 25 % in comparison to the reference sample; this is an indirect measure of the compatibilizing effect of activated zeolite. Further enhancement of zeolite content up to 20 wt.% reduces the impact strength by about 50 %.

Table 3. Variation of mechanical properties of recycled compositions modified with activated zeolite

Compositions	Young's modulus E (MPa)	Tensile strength σ_t (MPa)	Elongation at break ε (%)	Impact strength σ_i (kJ/m^2)
K	212	22.5	10.6	12.6
K1Z	221	22.1	10.0	11.9
K2Z	214	21.1	10.2	16.7
K3Z	218	21.4	9.8	9.8
K5Z	243	21.5	8.4	8.2
K20Z	290	21.8	7.5	5.7

Conclusions

The activated zeolite at low concentrations (1 – 2 wt.%) enhanced the flowability of the compositions and the extrudate quality. The activated zeolite acts as a nucleating agent during the crystallization, increasing the apparent crystallinity. Detailed information about the orientation of the PP and PE crystallites and filler particles was obtained for injection-moldings in dependence on the zeolite content. On the whole, zeolite particles are preferentially oriented parallel to the flow direction only in the surface layers in the high-filled composition (20 wt.%). With addition of zeolite the tensile strength and elongation at break of the system decrease slightly, whereas the impact strength at low concentrations (2 wt.%) increases. The activated zeolite changes strongly the morphology of the basic composition and arranges between the PP and PE crystallites. Therefore zeolite makes easier the dispersion and improves the interaction at surfaces. The results show that the activated zeolite can be used as a physical compatibilizer at low concentrations and open wide possibilities in the recycling of unsorted polymer wastes.

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