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Recycling compatibility of EVOH barrier polymers in polyethylene-based packaging compositions

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Abstract

The background of this work is the mechanical recycling of PE-based food packaging films in post-consumer waste. This is a lab-scale simulation of the recycling process, where the films are extrusion compounded and regranulated. Recyclates made of PE-based packaging films can be used for injection moulding or blown film applications. The blown film application was not tested in this study. Recyclate compounds of PE, EVOH and a tie layer resin (PE-g-MA) were processed by twin-screw extrusion. The impact of EVOH rate, type, and extrusion temperature on the compatibility of the recyclates were determined.
The content of PE-g-MA in the recyclate improves the interfacial adhesion between the EVOH and PE-LD layers, and leads to a phase compatibility. The elastic properties and the tensile strength of injection moulded articles made of the recyclate are improved by increasing the EVOH rate. The extrusion temperature has a significant impact on the compatibility of the injection moulded compounds: An increased compounding temperature leads to higher tensile strengths in this recycling application. The addition of EVOH and tie layer resin to the PE recyclate increases the MFR and therefore reduces the melt viscosity of the recyclates. By increasing the extrusion temperature, the MFR of the compounds also increases. Higher EVOH and tie layer resin amounts causes a decrease in the crystallinity of the polyethylene in the recyclate.
The conclusion of this work is that PE-based packaging materials with coextruded EVOH as a barrier layer are recycling compatible for injection moulding applications. The degree of recyclability and thus the compatibility of the recyclates for injection moulding applications depends on the composition and the recycling process temperature. A particularly important factor here is the ratio of tie layer resin and EVOH content. Results of earlier published studies could be disproved, according to which an EVOH content in PE-based packaging films of more than 5% would lead to incompatibilities in mechanical recycling.

Keywords: low-density polyethylene (PE-LD); ethylene vinyl alcohol copolymer (EVOH); maleic anhydride-grafted linear low-density polyethylene (LLD-g-MAH), compatibility, recycling.

INTRODUCTION:

Polyolefins are the main material of plastic packaging and containers, which have a very short lifetime compared to other polymeric products. Polymer recycling is one of the most important actions currently available and is receiving increasing attention to reduce negative impacts. Therefore, polymer recycling can be classified into three broad categories, namely mechanical, chemical and energetic recycling. Recycling allows the use of recycled polymer waste to replace virgin materials in certain applications, such as non-food packaging and automotive components. One challenge is the fact, that mostly no pure materials are provided for recycling processes. In packaging e.g., one polymeric material cannot alone offer all the properties required. Therefore, a combination of polymers is required. Polymer-based multilayer packaging materials are used to combine the properties of different polymers. The packaging features are configured to adequately protect vital food products, thus achieving a longer shelf life through this strategy. The most common materials are EVOH, different types of PA, copolyesters and others. These polymers are mainly not recyclable or only to a limited extent. Some barrier polymers are known to be a contamination for the recyclability of polyolefins due to incompatibilities. A study on the compatibility of EVOH with PE showed that at 5% EVOH the mechanical properties are degraded.

Most recyclates made from packaging films are essentially compounds or blends, these polymer blends are incompatible in most cases and need to be compatibilized. This "compatibilization" is carried out by the addition of a compatibilizer or by a reaction process. The selection of the compatibilizer is aided by the application of organic interactions.

Task

To evaluate the impact of commonly used EVOH barrier layers in packaging films on the recyclability of PE, various recyclate blends based on polyethylene (PE-LD/PE-LLD), ethylene vinyl alcohol (EVOH) copolymer and maleic anhydride-grafted linear low-density polyethylene (PE-g-MAH) are prepared. These materials are directly used as compounds to simulate the recycling of comparable packaging films with the same compositions. The process includes extrusion compounding at different temperature levels of 220 to 250°C with a twin-screw lab extruder. PE-g-MAH in various concentrations, typically used as tie layer resin in the packaging films, was used as a tie layer resin for the recyclate blends.

EXPERIMENTAL

Materials:

Recyclate compounds obtained from mixtures of PE, EVOH and a tie layer resin processed by twin-screw extrusion, the addition of PE-g-MA leads to a phase compatibility between the EVOH and PE-LD phases.

The following table shows the polymer grades used in this study:

Table 1: The materials used during the experiments

Type	Grade
PE-LLD	LL6910AA by INEOS
PE-LD	22H594 by INEOS
EVOH-44 (44% ethylene)	SoarnoL® AT4403B by Mitsubishi EVAL® E171B by Kuraray
EVOH-29 (29% ethylene)	SoarnoL® DT2904RB by Mitsubishi
Tie layer resin PE-LLD-based	Admer® NF518E by Mitsui Chemicals Yparex® 9603 by Yparex

Table 2: The variables and their range of variation

Variables	The range of variation
EVOH content	0% - 20%
Tie layer resin content	0% -15%
Extrusion temperature	220°C and 250°C

Blend Preparation:

In the first test series, the effect of EVOH-29 content on the compatibility of blends was investigated, with a focus on up to 20% weight proportion of EVOH.

Table 3: The composition of the compounds

Compounds	EVOH	TLR	PE
Compound 1	-	-	100% PE (50% PE-LLD + 50% PE-LD)
Compound 2	10%	-	90%
Compound 3	20%	-	80%
Compound 4	-	15%	85%
Compound 5	10%	15%	75%
Compound 6	20%	15%	65%

In the second series the rate of EVOH and the type (EVOH-44 and EVOH-29) have been varied in order to determine the impact of EVOH on the compatibility of the compounds.

Table 4: The composition of the compounds

Compounds	EVOH	TLR	PE
Compound 44-1*	5%	3.75%	91.25%
Compound 44-2	10%	7.50%	82.50%
Compound 44-3	20%	15.00%	65.00%
Compound 29-1*	5%	3.75%	91.25%
Compound 29-2	10%	7.50%	82.50%
Compound 29-3	20%	15.00%	65.00%

*Compound 44-1: EVOH ethylene content (mol %) =44
*Compound 29-1: EVOH ethylene content (mol %) =29

In the third part the influence of the processing temperature on the compatibility of the compounds with EVOH-29 was investigated.

Extrusion:

Extrusion was carried out using a twin-screw extruder (Haake PolyLab OS, Rheomex OS PTW16/25:1, Thermo Scientific) to determine the impact of temparature on the compatibility of the compounds, the extrusion temperature was varied, the extrusion melt temperature was set at 220°C and 250°C.

All compounds were premixed in a twin-screw extruder, the temperature profile of the six heating sections of the extruder for the 250°C setting was set as follows: 180, 200, 220, 230, 230 and 230°C, and the screw speed was set to 10 rpm.

In Order to obtain an extrusion temperature of 220°C the following parameters were used: the temperature profiles for the six heating sections of the extruder were set at 175, 175, 200, 205, 205 and 205°C, and the screw speed was 10 rpm. EVOH was dried in a vacuum oven for 4 h at 110°C before blending, because of its hygroscopic behaviour.

Injection moulding:

Specimen for mechanical analyses (tensile stress-strain and impact strength) were prepared using a Minijet (Haake MiniJet II, Thermo Scientific).
The experiments were performed with a mould temperature of 50°C, a holding pressure of 400 bar was adopted with a holding time of 10 s.

Mechanical Properties: Tensile and impact strengths and E-modulus.

The tensile properties of the compounds were measured with a tensile tester (Z030 (modernized by manufacturer), Zwick Roell) at room temperature, following the procedure described in DIN EN ISO 527-1. During the measurement, a stress-strain diagram was created from which the various mechanical parameters can be determined.

The impact test is a method for evaluation the toughness of Materials. The test samples were placed in a horizontal position. 3 Samples from each compound were tested, the height and width of the notch were measured three times.

Viscosity measurements:

The melt flow index test was carried out with melt flow meter (Q-0402 Davenport-Grader 3) to determine the flow behaviour of the compounds. The MFR was determined for the compounds at 190°C / 5 kg with a reference to ISO 1133.

Thermal measurements:

DSC (Differential Scanning Calorimetry) (DSC 200 PC, Netzsch) is an analytical technique used to detect the physical transformation of the sample such as the crystallinity, T_m, and T_g. The principle of the DSC is based on the differences in heat flux between the sample and the reference sample. In this study DSC was used to study the effects of EVOH rate on the melting, and crystallinity of PE. The sample was maintained to about 10 mg and placed in aluminium pans. Measurement program:

1) Heating up to 240°C with 20°C/min
2) Cooling down to 20°C with 10°C/min

RESULTS AND DISCUSSION

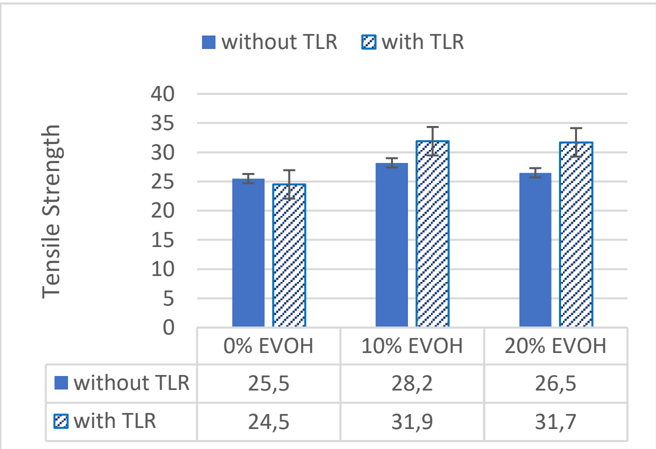
Effect of the compatibilization:

Effect of tie layer resin and EVOH-content on the tensile strength and E-modulus of injection moulded recyclate blends.

The effect of the tie layer resin on the mechanical properties of PE (50% PE-LLD + 50% PE-LD) recyclate with EVOH was investigated. Maleic anhydride-grafted linear low-density polyethylene (PE-LLD-g-MA) was used as a tie layer resin in the blends.

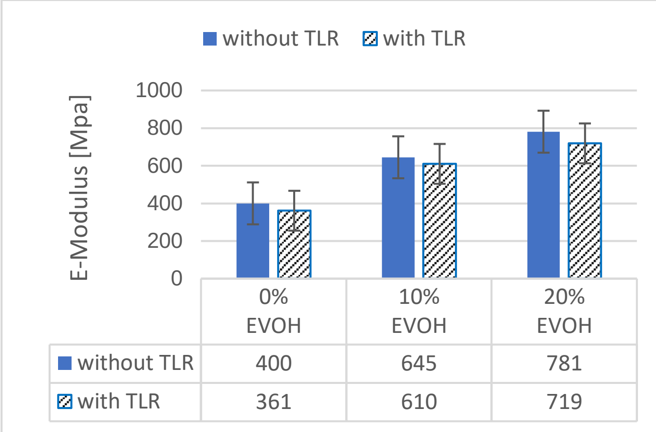
The composition of the compounds is summarized in table 3.

Diagram 1: The effect of compatibilization on the tensile properties of the blends [EVOH-29]



The diagram shows that the tensile strength of compatible compounds is significantly improved compared to non-compatible mixtures, which indicates that PE-g-MAH acts as an effective tie layer resin to improve the compatibilization between the dispersed EVOH and PE-LD matrix.

Diagram 2: E-modulus of the compounds [EVOH-29]



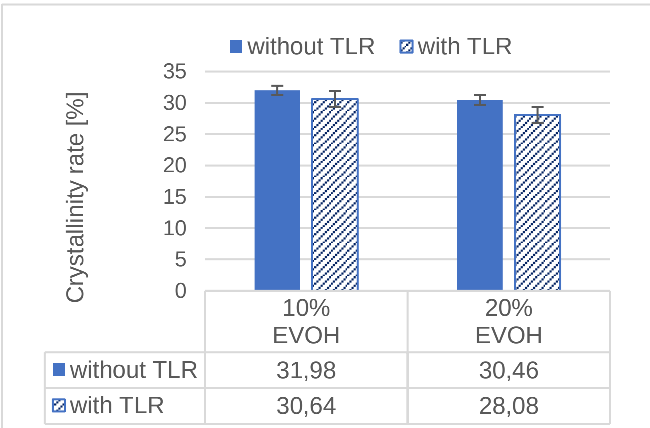
From the diagram it can be observed that the compound with 20% EVOH + 15% TLR + 65% PE has a higher E-modulus than the compound with 10% EVOH + 15% TLR + 75% PE, this might be due to the large number of bridges between the EVOH and the compatibilizer. The E-modulus increased as expected with increasing EVOH content in the samples. The addition of the brittle polymer EVOH with high modulus to PE-LD matrices improves the elastic properties of the final product, the E-modulus of the blend is improved.

Effect of the EVOH content on the crystallinity of PE in the blends:

Differential scanning calorimetry (DSC) was employed to characterize the thermal properties of the composites, melting point Tm, crystallization temperature Tc, and the crystallization rate.

The composition of the compounds is summarized in table 2.

Diagram 3: The effect of compatibilization on the crystallinity of PE in the blend. [EVOH-29]



The addition of tie layer resin to the compounds causes a decrease in the crystallinity of the polyethylene in the blend. By increasing the EVOH content, a decrease in the crystallinity of PE is clearly observed. A high content of unbound MAH in the tie layer resin leads to a plasticizing effect.

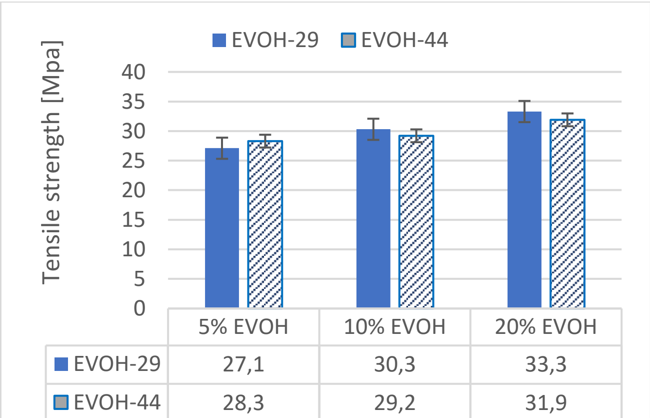
Increases in chain mobility in amorphous regions due to the plasticizing effect probably affect the whole structure, resulting in a slight stretching of the spacing between the crystal sections.

Effect of EVOH types:

Effect of the EVOH types on the tensile strength and E-modulus of injection moulded recyclates:

To determine the impact of EVOH type on the mechanical properties of the compounds, compounds were prepared with EVOH with 44%- and 29%-ethylene, the TLR/EVOH ratio is 0.75. The results of the tensile test are presented in diagram 4. The composition of the compounds is summarized in table 3.

Diagram 4: The effect of EVOH-types on the tensile properties of the blends.

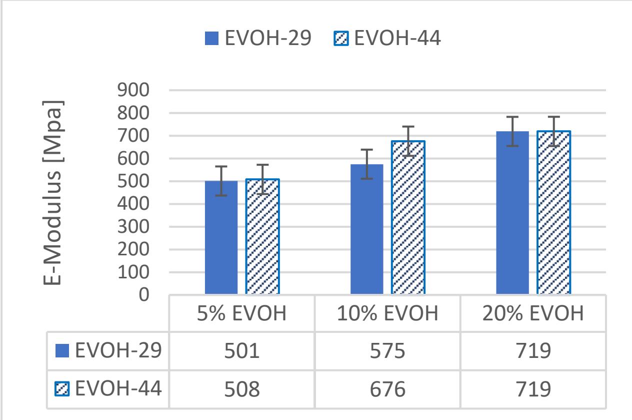


	5% EVOH	10% EVOH	20% EVOH
EVOH-29	27,1	30,3	33,3
EVOH-44	28,3	29,2	31,9

The two EVOH types with a high or low ethylene content showed no significant effect on tensile strength because the differences of the values lie within the standard deviation of the measurements.

In the diagram 5 are the results for the elasticity modulus of the compounds, the composition of the compounds is summarized in table 3.

Diagram 5: The effect of EVOH types on E-Modulus of the blends.



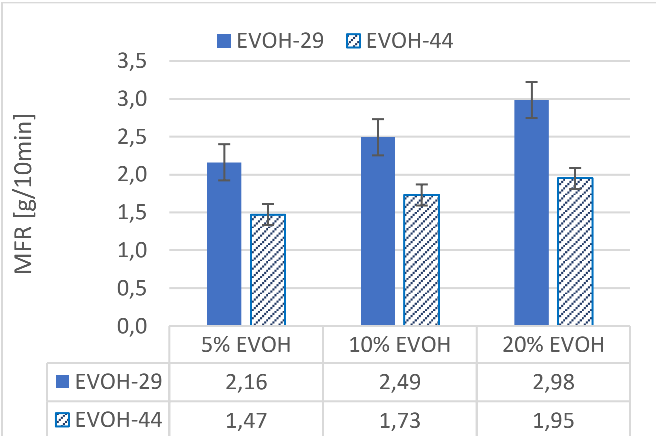
	5% EVOH	10% EVOH	20% EVOH
EVOH-29	501	575	719
EVOH-44	508	676	719

The diagram illustrates the tensile modulus of the blends. The compound 10% EVOH with EVOH-44% showed a higher E-Modul than the compound with EVOH-29, while the ethylene content makes no difference in the compounds with 20% EVOH or 5% EVOH.

Effect of the EVOH types on the flow rate of the blends:

To study the impact of EVOH type on the rheological properties of blends, blends were prepared with EVOH-44% and others with EVOH-29%, the MFR test results are presented in the diagram 6.

Diagram 6: Melt flow rate of the compatibilized blends



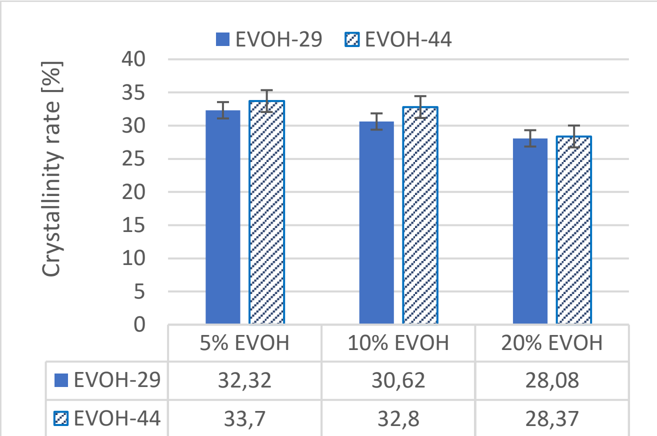
	5% EVOH	10% EVOH	20% EVOH
EVOH-29	2,16	2,49	2,98
EVOH-44	1,47	1,73	1,95

Since the melt flow rate is inversely proportional to viscosity of the melt, the PE-LLD/PE-LD blend has higher viscosity than EVOH. The addition of the higher MFR EVOH to lower PE-LLD/PE-LD blend increases the MFR of the blends. All compounds with either EVOH-44% (MFR 3.5) or EVOH-29% (MFR 3.8) show an increase in MFR with increasing EVOH content.

Effect of EVOH-Types on the crystallinity of PE in the Blends:

To determine the impact of EVOH type on the crystallinity of PE in blends, compounds with EVOH-29 and others with EVOH-44 were tested, the results of the DSC tests are presented in the following diagram. The composition of the compounds is summarized in table 2.

Diagram 7: Effect of EVOH-type on the crystallization rate of PE in the blends.



	5% EVOH	10% EVOH	20% EVOH
EVOH-29	32,32	30,62	28,08
EVOH-44	33,7	32,8	28,37

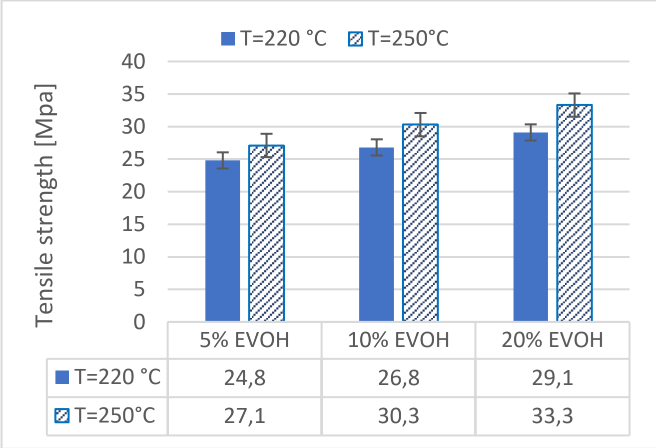
The increase in the amount of EVOH concentrations decreases the enthalpy and the crystallinity rate of PE. Increasing the content of EVOH into the blend system decreases the heat of fusion of PE. There was no big change in the position of the peaks for the melting and crystallization temperatures of the compounds, but there was a definite change in the enthalpies. EVOH is a random copolymer that can crystallize due to the strong hydrogen bonding of relatively small hydroxyl groups. With a relatively high vinyl alcohol content, EVOH copolymers crystallize like polyvinyl alcohol, independently of ethylene sequences.

Effect of extrusion temperature

Effect of extrusion temperature on the tensile strength and E-modulus of injection moulded recyclates:

To study the effect of the recycling temperature on the mechanical properties of the compounds, two temperatures were chosen: T1 = 220°C and T2 = 250°C. The test results are presented in the following diagram.

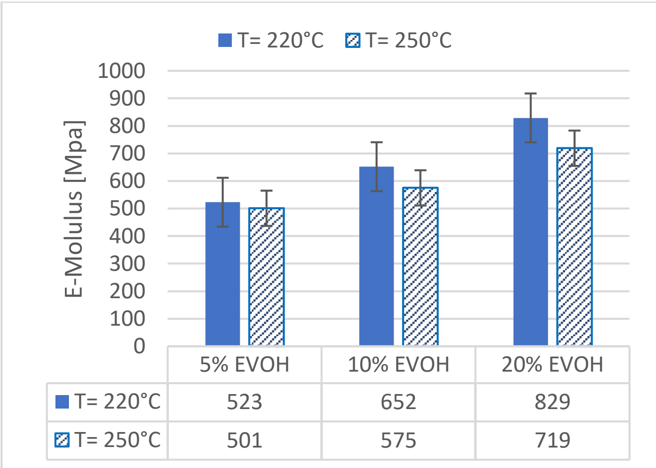
Diagram 8: Effect of extrusion temperature on the tensile strength of the blends [EVOH-29].



	5% EVOH	10% EVOH	20% EVOH
T=220 °C	24,8	26,8	29,1
T=250°C	27,1	30,3	33,3

The injection moulded specimens from extruded compounds at high temperature show a higher tensile strength than those extruded at low temperature. The results show that the extrusion temperature is a very important parameter: using higher processing temperature enhance the tensile strength. This behaviour can be attributed to interfacial adhesion between the phases in the blend. Higher processing temperature is preferred for enabling the diffusion of polymer chains, and this increases the compatibility between the phases. The chemical reaction between the MAH groups of the tie layer resin and the hydroxyl groups of EVOH is intensified by the higher extrusion temperature giving longer block copolymers. Creating such copolymers, could be responsible for the higher tensile strength.

Diagram 9: Effect of extrusion temperature on the E-Modulus of the blends. [EVOH-29].



	5% EVOH	10% EVOH	20% EVOH
T= 220°C	523	652	829
T= 250°C	501	575	719

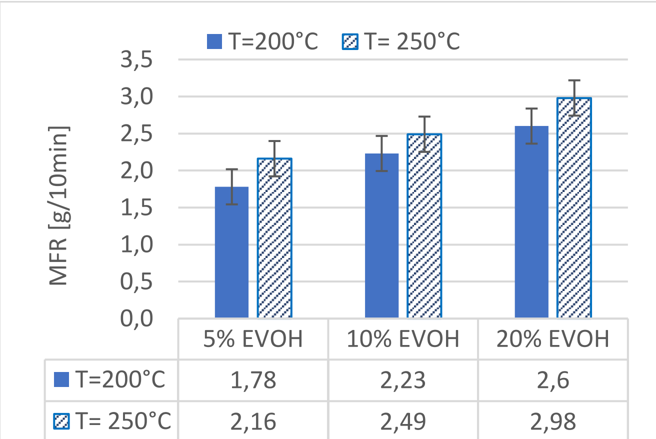
The E-modulus of compounds that have been processed at a temperature of 220°C is higher than the

E-modulus of compounds extruded at high temperatures of 250°C. This can be attributed to the decomposition of EVOH molecules due to thermal instability. When the temperature of the extruder exceeds the recommended upper limit, the polymer may decompose resulting in gels, voids, in the extrudate. During extrusion, the material is highly oriented in the axial direction of the rod. As the extrusion temperature increases, the degree of orientation and crystal perfection initially increases. The effect of extrusion on the mechanical properties can be explained in terms of the changes occurring in the material at the molecular levels.

Effect of extrusion temperature on the flow rate of the blends:

Processing parameters have an impact on the rheology of the compounds. To study the effect of extrusion temperature on the MFR of the compounds, compounds were tested that have been extruded at different temperatures (T1 = 220°C and T2 = 250°C) with varied EVOH-29 content.

Diagram 10: Melt flow rate of blends extruded at different temperature. [EVOH-29]



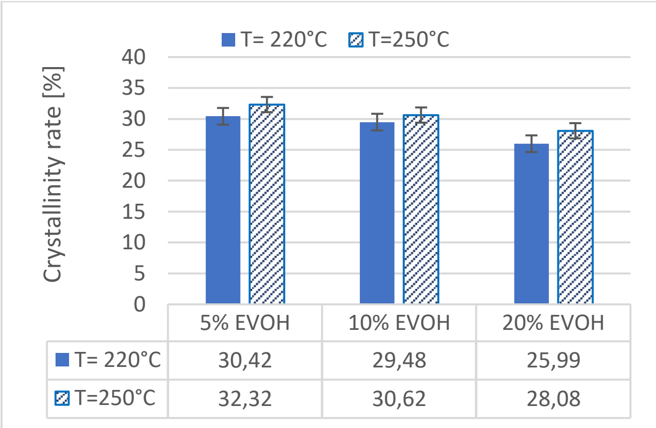
By increasing the extrusion temperature, the MFR of the compounds increases:

If the processing temperature is increased, the influence of molar mass degradation due to chain shortening becomes predominant and a viscosity reduction occurs. If the materials were to be further damaged by the processing, a further reduction in viscosity would occur. A higher extrusion temperature during the recycling process showed a favorable aspect, but it should not reach the recommended upper temperature limit, as the polymer might decompose.

Effect of extrusion temperature on the crystallinity of PE in the blend

The processing temperature is one of the parameters that impact the crystallinity of the compounds, to study the effect of extrusion temperature on the crystallinity of PE in blends, we tested compounds extruded at different temperatures T=220°C and T=250°C.

Diagram 11: Crystallinity rate of extruded blends at 220°C and 250°C



The compounds extruded at high temperature have a higher crystallinity than compounds extruded at low temperature. The increase of EVOH content in the mixture also leads to a decrease of PE crystallinity.

Extrusion causes the material to be significantly oriented in the axial direction. Initially, both orientation and crystalline perfection increase with increasing extrusion temperature. Since at higher temperatures, molecular adjustments are easier due to the increased mobility of the molecules, the material extruded at high temperatures has a higher orientation

CONCLUSIONS:

EVOH has a primarily positive effect on recycling and the properties of PE-LD-based recyclates, with some limitations.

A content of up to 10% EVOH in the initial product improves the E-modulus and the tensile strength of the final recycling product which is favourable for injection moulding applications.

The content of maleic anhydride-grafted PE as tie layer resin in the recyclate improves the phase compatibility between the EVOH and PE-LD phases caused by the chemical reaction of maleic anhydride (MAH) and hydroxyl groups of EVOH. As expected, the tensile strength is improved by increasing the tie layer resin contents in the recyclate compounds.

Blending with tie layer resin and up to 10% EVOH showed good mechanical, thermal and rheological properties, which is beneficial for both injection moulding and blown films. It should be taken into consideration that the viscosity of the recyclates decreased with a higher EVOH content which is unfavourable for blown film applications. As no blown film tests have been carried out, this is a theoretical statement based on experience.

A higher extrusion temperature during the recycling process showed a favourable aspect regarding the tensile strength. A comparable effect is expected by increased process temperatures in further recyclate applications.

Other studies have shown that a rate of more than 5% of EVOH causes a decrease in the properties of the materials, but we must not neglect the impact of other parameters on the properties such as the amount of tie layer in the mixture, the temperature of extrusion and other parameters.

When all the results and findings of this work are taken into account, it can be summarised that PE-based packaging materials with EVOH as a barrier layer are recyc*ling compatible*. The degree of recyclability and thus the compatibility of the recyclates for common applications - especially injection moulding - depends on the composition and the recycling process temperature. A particularly important factor here is the PE-g-MAH content in relation to the EVOH content. Based on these results and taking into account the usual components in coextruded packaging films (especially tie layer resins), results from earlier studies could be disproved, according to which an EVOH content in films of more than 5% would lead to incompatibilities in mechanical recycling. These findings would have to be verified in further studies for blown film applications.

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