Structure-property relations of heterophasic ethylene-propylene copolymers based on a single-site catalyst

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Received 9 August 2016; accepted in revised form 10 October 2016

Abstract. The target of the present study was to investigate the structure-property relationships of heterophasic ethylene-propylene (EP) copolymers based on a single-site (metallocene) catalyst (SSC) supported with an emulsion technology developed by Borealis. The structure of these copolymers, their morphology evolution, as well as resulting mechanical properties were studied by varying the composition of the dispersed phase, i.e. the amorphous ethylene-propylene copolymer or rubber (EPR), in a systematic series of bench-scale products. Next to composition effects, an attempt was made to understand the key differences between products based on Ziegler-Natta catalysts (ZNC) and single-site catalysts (SSC) in terms of polymer structure and property profile. A remarkably different phase morphology with very good phase coupling to the matrix PP and the absence of crystallizable polyethylene in the ethylene-rich copolymers (EPR) was observed for the SSC-based grades, resulting in a high level of impact strength over a wide composition range.

Keywords: polymer synthesis, polypropylene, morphology, single-site catalyst, mechanics

1. Introduction

Among the wide range of polypropylene (PP) grades, the class of heterophasic ethylene-propylene (EP) copolymers has conquered a wide range of applications from seemingly trivial packaging uses to technically complex parts, for example in the automotive area. Initially produced by melt mixing PP homopolymers with different amounts of externally produced elastomers like ethylene-propylene rubbers (EPR) or ethylene-propylene-diene elastomers (EPDM), products commonly referred to as ‘block copolymers’ (correctly ‘heterophasic copolymers’, HECOs) were later developed in multi-reactor gas phase plants (e.g. Novolen process) or in bulk/gas phase combinations (Spheripol or Borstar PP process). These combine a crystalline PP matrix (produced in the first 1–2 reactors) with embedded particles of EPR and PE (produced in 1 or more following reactors) [1]. Structural

and compositional aspects of such heterophasic EP copolymers (EP-HECOs) have been studied extensively in the past and are reported e.g. in papers of Doshev and coworkers [2, 3] and Grein and coworkers [4, 5]. The key influence factors on performance can be summarized as amount [6], composition and molecular weight of the disperse (EPR) phase as well as the properties of the matrix phase like crystallinity and ductility.

Aspects of their synthesis have been studied e.g. by Cecchin *et al.* [7], highlighting process and catalyst effects on the possible composition and property range, but also by McKenna *et al.* [8] and others. Mostly conventional Ziegler-Natta type catalysts (ZNC) are used for EP-HECO production, but these have some limitations in terms of composition range and especially regarding the way of comonomer incorporation. In practice these limitations define the practically

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achievable product range, an expansion of which is often desirable. An alternative are single-site catalysts (SSC), especially metallocenes which have been tested in PP production since the mid-1990s [9, 10]. While early SSC generations were too limited in terms of catalyst lifetime and molecular weight, more recent developments as studied for example by Tynys and coworkers [11, 12] have also enabled the production of SSC-based EP-HECOs. In the present paper an asymmetric zirconocene similar to the ones in [12] was used to polymerize such copolymers in a wide composition range to study structure-property relations. It should be mentioned that also hybrid catalyst systems with a combination of ZNC and SSC have been tested by a number of authors [13, 14], with the main advantage seen in the possibility to use higher α -olefins like 1-octene [14] for polymer design.

In order to investigate the structure-property relationships of heterophasic ethylene-propylene copolymers based on this class of catalysts, a series of EP-HECO compositions with identical PP homopolymer matrix and different composition of EPR phase were produced in bench scale polymerization. The amount of EPR phase was attempted to be kept constant, but some variations resulted from activity changes here as well. An extensive characterization of these materials allowed establishing some essential structure-property relations as done for ZNC-based products before [2–6, 15, 16]. Special attention was paid to the consequence of different comonomer incorporation at high ethylene (C2) content in the EPR phase where ZNC-based products normally comprise a significant amount of crystalline polyethylene (PE).

2. Experimental

2.1. Materials

All investigated polymers were produced in the laboratories of Borealis and polymerized with same

type of metallocene (MC) catalyst, an emulsion-type catalyst [17] with the complex dimethylsilyl [(2-methyl-(4'-tert.butyl)-4-phenyl-indenyl)(2-isopropyl-(4'-tert.butyl)-4-phenyl-indenyl)]zirconium dichloride [18]. The polymerizations were carried out in a batch reactor in two stage mode under industrially relevant conditions. First, the matrix part of the composition was polymerized in liquid bulk phase at 70 °C, followed by a second step where EP copolymer (rubber) was produced in gas phase at 85 °C. While the bulk step was kept constant, reaction time of the gas phase step was adapted to the change in reactivity in order to control the EPR amount mostly in the range of 15–20 wt%. This approach resembles typical bulk/gas phase combinations like the Spheripol or the Borstar PP process in terms of pressure, temperature and residence time.

Compounding was done in a laboratory-scale twin-screw extruder with the addition of a standard antioxidant package. Basic properties of polymers are presented in Table 1, in which the material code (which will be used throughout the paper) is taken from the ethylene content in the EPR phase. The matrix PP homopolymer had always an MFR (230 °C/2.16 kg) of ~30 g/10 min, corresponding to an intrinsic viscosity (IV) of about 1.3 dL/g (this is identical to IV_{XCI} for the copolymers) and a weight average molecular weight M_w of about 290 kg/mol. For the homopolymer and the PP/EP33 this was checked by SEC, finding a polydispersity M_w/M_n of 2.5 in both cases.

2.2. Characterization

Melt flow rate (MFR) was determined according to standard ISO 1133 at 230 °C and 2.16 kg load with a Zwick Grader 4 (Zwick-Roell, Germany). Xylene cold soluble (XCS) fraction was determined at 25 °C according to ISO 16152 using standard laboratory equipment. This is used as a measure of the EPR

Table 1. Summary of investigated materials; the matrix PP homopolymer has always an MFR (230 °C/2.16 kg) of ~30 g/10 min and IV ~ 1,3 dL/g (this is identical to IV_{XCI}). Ethylene contents for XCS, XCI and total polymer were measured by FT-IR spectroscopy

Material	MFR [g/10 min]	XCS [wt%]	IV_{XCS} [dL/g]	$M_{w,XCS}$ [kg/mol]	$M_w/M_{n,XCS}$	$C2_{XCS}$ [wt%]	$C2_{XCS}$ [wt%]	$C2_{total}$ [wt%]
PP/EP9	15	3.2	2.1	n.d.	n.d.	9	1.5	1.6
PP/EP10	11	14.3	2.2	355	2.9	10	1.9	3.0
PP/EP22	8	32.9	1.7	n.d.	n.d.	22	1.9	8.8
PP/EP32	17	19.2	2.0	n.d.	n.d.	32	1.1	6.0
PP/EP33	11	18.5	1.7	288	3.0	33	1.3	6.7
PP/EP51	15	15.1	2.4	386	3.1	51	1.5	7.5
PP/EP68	19	16.6	3.4	n.d.	n.d.	68	3.3	9.9

content, even considering that with high ethylene or propylene contents the EPR is partly crystalline and this fraction may remain in the xylene insoluble part (XCI) which otherwise mostly represents the matrix phase.

For both XCS fraction and matrix PP (XCI), intrinsic viscosities (IV) were measured in decalin at 135 °C according to standard DIN EN ISO 1628-1 and 3 in order to check the molecular weight effects. A Lauda PVS automated capillary viscometer with Ubbelohde capillaries (Lauda, Germany) was used for this purpose. For some materials the molecular weight distribution was in addition determined by size exclusion chromatography (SEC) according to standard ISO 16014-1,2 and 4. The measurements were done with a Waters Alliance GPC(V) 2000 (Waters Corp., USA) equipped with a refractive index (RI) detector and a visco-detector. As solvent 1,2,4-trichlorobenzene at 145 °C was used.

Ethylene content in the XCS and XCI fractions was measured with Fourier Transform Infrared (FT-IR) spectroscopy. The equipment was a Perkin Elmer Infrared Spectrometer FT-IR System 2000 (Perkin Elmer, USA), and the spectrum was recorded from compression-molded films between 400 and 4000 cm⁻¹. To quantify the composition the absorption spectra is detected and compared with to library spectra calibrated with ¹³C nuclear magnetic resonance (NMR) spectroscopy in solution.

For analyzing the detailed composition of the XCS and XCI fractions, monomer triad distributions were determined. The respective ¹³C NMR measurements were performed with a Varian Gemini 2000 300 MHz spectrometer operating at 125 °C [19] (Varian Inc., USA). The materials were dissolved into a mixture of 1,2,4-trichlorobenzene (TCB) and benzene (C₆H₆) in a weight ratio of 80/20. The acquisition time was 2 s, acquisition delay was 8 s. Assignment of the peaks was performed according to Randall [20]. The comonomer fraction was quantified using the method of Wang and Zhu [21] through integration of multiple signals across the whole spectral region in the ¹³C{¹H} spectra. This method was chosen for its robust nature and ability to account for the presence of regio-defects when needed. From the spectra triad distributions were calculated allowing an analysis of the statistics of comonomer incorporation using the analysis method of Kakugo *et al.* [22] which was chosen for its robust nature.

From the NMR investigation, next to C2(XCS) the normalized isolated C2-units have been calculated as a measure for the ‘randomness’ of C2 distribution. This parameter, abbreviated as ‘PEP normalized’ or ‘*I(E)*’, is defined by Equation (1):

$$I(E) = \frac{f_{\text{PEP}}}{f_{\text{EEE}} + f_{\text{PEE}} + f_{\text{PEP}}} \cdot 100 \quad (1)$$

In analogy to *I(E)*, also a parameter for the blocky PE fraction based on EEE-triads can be calculated and termed ‘EEE normalized’ or ‘*B(E)*’, as defined by Equation (2):

$$B(E) = \frac{f_{\text{EEE}}}{f_{\text{EEE}} + f_{\text{PEE}} + f_{\text{PEP}}} \cdot 100 \quad (2)$$

Differential scanning calorimetry (DSC) was done on samples of 5–10 mg according to standard ISO 11357 using a TA-Instruments 2920 Dual-Cell with RSC refrigeration apparatus and data station (TA Instruments, USA). Melting and crystallization temperatures (*T_m* and *T_c*), and corresponding enthalpies (ΔH_m and ΔH_c) were measured using a TA-Instruments 2920 Dual-Cell with RSC refrigeration apparatus and data station. The measurements were done for the whole material, calculating the degree of crystallinity (*X_c*) using a melting enthalpy for fully crystalline PP equal to 209 J/g [23].

In order to determine mobility transitions, dynamic mechanical analysis (DMA) was done according to standard ISO 6721-7 in torsion mode on specimens cut from compression molded plates (40×10×1 mm³) in a TA Instruments ARES rheometer at a heating rate 2 °C/min and at 1 Hz frequency (TA Instruments, USA).

For phase morphology analysis, transmission electron microscopy (TEM) images were taken for selected samples using a combination of contrasting with RuO₄ [24] with cryo-ultramicrotomy. Samples were taken from the core of an injection molded Charpy bar, capturing images with a TEM Tecnai 12 (FEI, The Netherlands) equipped with a Gatan Bioscan CCD camera (Gatan Inc., USA).

The Charpy notched impact strength test was performed with an Automated Pendulum Co. HKE for injection moulded samples (80×10×4 mm³) according to standard ISO 179-1/1eA at varying temperatures and with impact velocity 1.5 m/s. Flexural tests were done on a ZWICK Universal Test Apparatus according to standard ISO 178 for the same specimen geometry (both instruments Zwick/Roell, Germany).

As a reference series based on ZN-catalyst some of the materials from the paper by Grein *et al.* [5] were selected. These have a PP homopolymer with an MFR (230 °C/2.16 kg) of 10 g/10 min as matrix and comprise an EPR phase equivalent to 18 wt% XCS with an IV(XCS) of 2.1 dl/g. The C2 content of said EPR phase is varied between 25 and 62 wt%.

3. Results and discussion

3.1. Composition and morphology

In general it should be noted that while numerous reports deal with the effect of viscosity ratio of PP/EPR blend systems as well as their ternary counterparts, PP/EPR/PE blends, on morphology [4, 15, 16, 25–27], the effect of EPR composition on the same has been studied significantly less [2, 3, 5, 28–30]. In both cases a decisive parameter of polymer blend theory is modified, and both for the viscosity ratio as for the compatibility the change can be effected for the matrix component as well as for the disperse one. The present study follows the work of Grein *et al.* [5] by keeping the PP homopolymer matrix as well as the content and viscosity of the disperse EPR phase rather constant while primarily varying the EPR composition.

The composition analysis based on the XCS/XCI fractionation and the following ^{13}C NMR analysis results in the triad distribution presented in Table 2 and consequently in the normalized $I(E)$ and $B(E)$ parameters in Figure 1. These materials switch from PPP rich material (PP/EP10XS) to EEE rich material (PP/EP68XS), meaning that the relative amount of randomly distributed ethylene (PEP) goes down as the randomly distributed propylene (EPE) goes up. The increasing ‘blocky’ structure of the elastomer phase in the investigated material series with increasing ethylene content is obvious from Figure 1. A look at the corresponding DSC results in Table 3 however shows the absence of crystalline PE even at higher C2(XCS), quite in contrast to results normally found

Figure 1. Effect of the C2-content of XS fraction on its composition. Normalized $I(E)$ and $B(E)$ parameters calculated from NMR triad distribution (see Table 2).

Table 3. DSC data and crystallinity for analysed EP-HECO materials and PP matrix

Material	T_m [°C]	ΔH_m [J/g]	T_c [°C]	ΔH_c [J/g]	X_c [%]
PP/EP9	156	90	117	86	43
PP/EP10	155	76	116	72	36
PP/EP22	157	68	116	63	33
PP/EP32	157	82	117	75	39
PP/EP33	157	86	117	81	41
PP/EP51	157	89	118	80	43
PP/EP68	157	83	118	77	40
Matrix PP	158	107	120	102	51

for ZNC-based EP-HECOs. Doshev *et al.* [3] reports clear melting points for the PE phase of ZNC-grades from 70 wt% C2(XS) upwards, i.e. very close to the composition of PP/EP68. The structural difference of SSC-based EP-HECO materials in this respect is therefore quite obvious.

A complete list of all characteristic temperatures and enthalpies from DSC is listed in Table 3. The respective DMTA data in Figure 2 show that $T_g(\text{EPR})$ coincides with the glass transition of the matrix-PP for the lowest two values of C2(XS), meaning that no phase separation can be expected here. Otherwise the fact that there is a minimum in the glass transition of the elastomer phase at ~50 wt% C2(XCS) is

Table 2. ^{13}C NMR triad analysis results for selected XCI and XCS samples including triad-based C2 content

Material	C2 [wt%]	PPP [mol%]	PPE [mol%]	PEP [mol%]	PEE [mol%]	EPE [mol%]	EEE [mol%]
PP/EP33 _{XCI}	3.0	92.1	3.0	1.9	1.6	0.5	1.0
PP/EP68 _{XCI}	3.3	93.1	1.3	0.2	1.6	0.7	3.0
PP/EP10 _{XCS}	11.0	61.9	20.4	9.4	5.3	2.0	1.0
PP/EP22 _{XCS}	22.9	35.1	27.8	12.0	13.8	6.2	5.0
PP/EP33 _{XCS}	34.0	21.0	26.7	11.5	20.0	8.8	12.1
PP/EP51 _{XCS}	49.9	9.5	22.4	7.8	24.1	10.9	25.3
PP/EP68 _{XCS}	66.5	2.6	11.5	3.4	23.2	11.1	48.3

Figure 2. Measured T_g (PP/matrix) and T_g (EPR) from DMTA as a function of the ethylene content in the elastomer phase. ZNC references from [5].

similar to the findings of the respective C2(EPR)-series of [3] and [5], even if the position is not identical. For the latter ZNC-based series the T_g -values from [5] have been added to Figure 2 to highlight the differences.

The effect of increasing the ethylene content in the EPR fraction on the phase structure of the EP-HECOs is not only reflected by the DMA results presented in Figure 2, but also by the phase morphology results from TEM. Ethylene content in the copolymer fraction indeed has a massive influence on the compatibility of phases as also shown by other authors [2, 5, 29, 30]. The material PP/EP10 shows a single broad glass transition temperature, shifted to -8°C . This single glass transition peak does not necessarily reflect miscibility of blends but may also indicate a very

fine state of dispersion [2]. The respective TEM picture shows no visible EPR particles in PP/EP10 but rather reminds of a homogeneous crystalline polypropylene structure (see Figure 3). Thus, co-crystallization of PP and long propylene sequences of EPR is suggested. The non-crystallizable sequences seem to be distributed between the lamellae. Still, they do slow down the crystallization process of the PP, as indicated by the reduced crystallinity X_c for this material (see Table 3) which is typical for random copolymers [2, 31].

Otherwise, with increasing ethylene content the glass transition temperatures are shifted more and more apart, moving T_g (EPR) towards the glass transition temperature of polyethylene (PE). This indicates poorer compatibility between the phase and the maximum is reached with material PP/EP51.

The morphology images from transmission electron microscopy (TEM) in Figures 3 and 4 illustrate this trend of phase coarsening and increase of EPR particle size starting at the still homogeneous structure of PP/EP10 through a system of ‘fuzzy’ interfaces in PP/EP22 to clear particle structures in the materials PP/EP33 and PP/EP51. The effect of increasing interfacial tension is, however, increased for the last material in this series by an increasing viscosity ratio between dispersed phase and matrix on morphology. This is caused by the differences in the molecular weight of the EPR with growing ethylene amount in the fraction as a result of a changing hydrogen response of the catalyst. The particle size of PP/EP33 is

Figure 3. TEM images of two of the investigated SSC-HECOs: (a) PP/EP10, (b) PPP/EP22; scale bar 0.2 μm

Figure 4. TEM images of two of the investigated SSC-HECOs: (a) PP/EP33, (b) PP/EP51; scale bar 0.2 μm

roughly 100–400 nm and the particle size grows with materials PP/EP51. At the same time the amount of large coalesced particles of up to 2 μm increases. With this, the inter-particle distance becomes higher as the average dispersed particle size goes up.

An essential question is now, why the phase morphology in the dispersed particles is so different for C2-rich materials, like in PP/EP51 (Figure 4), compared to similar Ziegler-Natta (ZNC) materials. With high ethylene contents, ZNC-based materials generally

represent so called ‘core-shell’ or ‘salami’ structure [3, 5, 6] consisting of semi-crystalline PE (actually a linear low density PE with C3 as comonomer) in the core surrounded by an amorphous EPR layer. In contrast to that, PP/EP51 and PP/EP68 still show rather homogeneous rubber particles. As discussed above, a melting peak for crystalline PE at DSC was not found (Table 3) which is in agreement with this homogeneity. A look at comparable ZNC cases at 70 wt% C2(XCS) in [3], and 62 wt% in [5] not only

Figure 5. TEM images of one of the investigated SSC-HECOs (a) PP/EP68 and a comparable ZNC-HECO PP-C4.4 from ref. [5] (b); scale bar 0.5 μm

demonstrates the different comonomer incorporation of SSC, but also highlights the architectural differences of ZNC-based EP-HECO systems.

Figure 5 highlights this difference in a direct comparison between the TEM-based morphologies of PP/EP68) and a comparable ZNC-HECO PP-C4.4 from ref. [5] (note the difference in scale to Figures 3 and 4 dictated by the limited image availability from the earlier study). The two polymers have a comparable ethylene content in the XCS fraction (68 wt% C2(XCS) in PP/EP68 vs. 62 wt% C2(XCS) in PP-C4.4), but the structural difference is obvious in terms of the clearly visible crystalline PE lamellae in the EPR particles of the ZNC-based product.

3.2. Mechanical properties

Table 4 summarizes the Charpy impact strength data at 23 and at -20°C , and the flexural test results for all investigated materials. Polypropylene homopolymer shows a brittle behaviour in the whole temperature range, and the stiffness of the SSC-based material is lower as a result of the chain defects from this type of catalyst, reflected as well in the lower melting point (158 vs. 165°C for a ZNC-PP) [10, 32]. With low C2 content in EPR phase the material is still rather brittle; PP/EP10 shows a twice as high impact strength at room temperature compared to pure matrix, but at sub-zero temperatures that effect is lost due to the lack of stress concentrators and reduced total crystallinity of PP (Table 3). Especially this reduced crystallinity further affects flexural properties [2, 23], as can also be seen for materials PP/EP10 and PP/EP22 with remarkably lower crystallinity. On the other hand, PP/EP22, which have the highest EPC content (XCS ~ 33 wt%) shows superior impact properties at both room and sub-zero temperatures. HECOs with C3-rich EPR generally show fine dispersion of rubber due to high compatibility, but a loss of impact at $<-10^{\circ}\text{C}$ [2]. The special impact behaviour

of PP/EP22 however cannot be explained only by the high XCS reducing interparticle distance, and the corresponding results from the DMA analysis (Figure 2). The interesting phase compatibility is visualized by TEM (Figure 3) showing a less clear surface, with PP crystals mixing with the EPR surface. Increased co-crystallization effects at the interface, as also observed in case of annealing of ZNC-based EP-HECOs [33], may play a role. Both because of higher EPR content as well as better phase coupling, it is expected that the brittle-to-ductile transition (BDT) of material PP/EP22 shifts to even lower temperatures. Unfortunately this could not be tested in detail due to a too small material amount.

In the brittle-to-ductile transition curves Figure 6 it can be seen that materials PP/EP32, PP/EP33 and PP/EP68 show brittle-to-ductile transition (BDT) between -10 and -5°C , for which comparable results could not be found in the literature. Quite in contrast, PP/EP51 shows BDT at 4°C but also lower impact through whole temperature range. At this point it is important to notice that the EPR content is slightly lower for PP/EP51 (~ 15 wt%). The increasing copolymer content is positively correlated both to an increase

Figure 6. Brittle-to-ductile transition curves (Charpy NIS) of matrix PP and heterophasic SSC-copolymers with varying EPR composition (arrows indicate the BDT)

Table 4. Charpy impact strength at $+23$ and -20°C , and flexural properties for the investigated materials. Note the effect of higher EPR content (32,9 wt%) in PP/EP22 on mechanical properties.

Material	Charpy $+23^{\circ}\text{C}$ [kJ/m ²]	Charpy -20°C [kJ/m ²]	Flexural modulus [MPa]	Flexural strength [MPa]	Strain at flexural strength [%]
PP/EP10	8.5	1.6	754	25.4	7.8
PP/EP22	74.9	14.0	449	13.5	7.2
PP/EP32	47.2	10.0	857	24.3	6.9
PP/EP33	50.3	8.4	819	23.2	6.7
PP/EP51	31.4	7.6	984	27.4	6.4
PP/EP68	50.1	11.2	849	25.2	7.3
Matrix PP	3.9	2.7	1568	44.6	6.9

of the impact strength and to a reduction of the BDT temperature [5], but it should be noted here that the studied region of molecular weight of the EPR phase (as expressed by IV(XCS) has also been found to be sensitive to variations in terms of BDT shifts. In another paper by Grein *et al.* [4] a variation by more than 30 °C in BDT temperature has been shown for an IV variation from 1.7 to 3.0 dL/g.

Doshev *et al.* [2] reported for ZNC heterophasic copolymers that increased ethylene content in EPR had a positive effect on sub-zero temperature impact, but a negative effect on room temperature impact as well as increasing the BDT temperature. For our case an interesting aspect is that the copolymer composition has such a small effect on impact properties. It seems that materials with C2(XCS) between 32 and 68 wt% show rather similar impact behavior, indicating the change in the average sequence length of propylene between two ethylene units is less significant. The relatively more even distribution of comonomer of EPR produced by SSC (as expressed by the NMR data as well as the absence of crystalline PE formation) compared to ZNC plays a vital role in determining impact properties. It seems that the interfacial coupling is very different compared to ZNC, also indicated by the shift of BDT temperature to such low values.

Finally, the property balance relevant from a product design aspect should be presented: Figure 7 shows the Charpy impact data at +23 °C and Figure 8 the flexural modulus. Data are represented as a function of C2(XCS) for our data set as well as for ZNC reference grades from [5]. Differences in the MFR resp. M_w and polydispersity (M_w/M_n) and chain structure (in detail, the stereoregularity and the presence of

Figure 7. Charpy NIS at 23 °C presented as a function of C2/XS for SSC and the reference ZNC [5] data series with similar EPR content

Figure 8. Flexural modulus presented as a function of C2/XS for SSC and the reference ZNC [5] data series with similar EPR content

regiodefects [34–36]) of the matrix PP homopolymer should be kept in mind when comparing stiffness values, and some variation in the impact strength must be attributed to the differences in EPR content (see Table 4 for details). Nevertheless, one can conclude that the stiffness-toughness-balance for the SSC-based material is very different compared to the ZNC-based system, providing new opportunities for material design. The crystalline PE in EPR does have positive effect on the overall stiffness of the material, but it also may influence the impact behavior at low temperatures in a negative way [37], making the structural difference visible in Figure 5 even more relevant.

4. Conclusions

Combined results of ^{13}C NMR, DMA and TEM analysis of a series of SSC-based heterophasic EP copolymer showed, for varying EPR composition, a systematic shift from propylene rich EPR with randomly distributed ethylene units to ethylene rich EPR with isolated propylene units. This enables a remarkably different phase morphology compared to ZNC-products with very good phase coupling with matrix PP and the absence of crystallizable polyethylene in the C2-rich copolymers. While similarities exist, the difference in EPR composition and, consequently, phase morphology increases with increasing comonomer content in the EPR phase.

The materials show an interesting mechanical performance, especially stiffness – toughness balance being very different to conventional ZNC PP HECO. Some interesting aspects were the similar impact behaviour in a broad range of EPR composition (C2 content 32–68 wt%), the very low brittle-to-ductile transition (BDT) temperature, and the fact that even

a small increase/decrease of copolymer amount shifted the mechanical properties significantly. A definitely interesting area for further study are propylene rich EPRs, such as PP/EP22, showing heterophasic structure with very good phase coupling resulting in very good impact performance.

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