

Article

Interplay Between Octene Content and Grafting-Induced Molecular Weight Deviations and Their Effect on the Impact Toughness of Ethylene/1-Octene-Modified Polyamide 6

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Abstract

The impact modification of polyamide 6 (PA6) using maleic anhydride-grafted ethylene/1-octene copolymers (EOR-g-MAH) involves a trade-off between improved compatibilization, grafting-induced changes in modifier molecular weight MW, and melt processability. In this study, EOR modifiers with comparable initial MW but different octene contents ($c_{\text{oct}} = 13, 15$, and $16 \text{ mol\%}$) were grafted to two MAH levels ($c_{\text{MAH}} = 0.5$ and $1.0 \text{ wt\%}$) and incorporated into PA6 at a fixed composition. The system was designed to maintain a comparable microstructure, enabling the isolation of grafting-induced changes in modifier properties from microstructural effects. MW distributions were analyzed by gel permeation chromatography, and the impact behavior was evaluated over a wide temperature range, using an instrumented Charpy impact test. The results reveal a strong, interrelated, c_{oct} - and c_{MAH} -dependent competition between β -scission and cross-linking during grafting, which governs the modifier's MW distribution and particle strength. Higher c_{oct} (15 and $16 \text{ mol\%}$) enhances the impact performance up to $\approx 0 \text{ }^{\circ}\text{C}$, well above the brittle–ductile transition temperature (BDTT), through increased elastic and plastic deformation capability of the modifiers. At elevated temperatures, however, successive melting of the modifiers leads to a loss of particle strength. At high c_{oct} and $c_{\text{MAH}} = 1.0 \text{ wt\%}$, susceptibility to β -scission increases, leading to MW reduction that, for $c_{\text{oct}} = 16 \text{ mol\%}$, is detrimental to impact performance, particularly above the BDTT. This effect is further amplified by reduced ductility due to stronger polar intermolecular interactions at high grafting levels. A moderate $c_{\text{MAH}} = 0.5 \text{ wt\%}$ and $c_{\text{oct}} = 15 \text{ mol\%}$ provides an optimal compromise between strength and ductility, delivering high impact strength across a broad temperature range. At this c_{MAH} level, the number of PA6 chains covalently anchored to the modifier particles is moderate, resulting in lower compound viscosity and supporting favorable melt processability.

Keywords: impact toughness; ethylene/1-octene copolymers; octene content; maleic anhydride grafting; molecular weight degradation

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1. Introduction

Melt blending of polyamide (PA) with soft (co)polymers exhibiting low stiffness and a low glass transition temperature T_g , such as styrene-ethylene-butylene-styrene (SEBS) [1–4], acrylonitrile-butadiene-styrene (ABS) [5,6], ethylene-propylene rubber (EPR) [1–4,7–10], ethylene/1-octene rubber (EOR) [1,11–15], or ethylene-propylene-diene rubber (EPDM) [7,8,10,16], in amounts of 15–30 wt% is a well established approach to reduce the notch sensitivity of PA. This modification enables PA to achieve high notched impact strength NIS , particularly at low temperatures T [1–5,7–9,11–13]. The present study focuses on EOR modifiers due to their cost competitiveness and broad commercial availability in multiple grades offering a range of intrinsic parameters, including molecular weight MW , comonomer content c_{oct} , and crystallinity [17,18]. Their favorable cost arises from large-scale production for applications such as packaging and the use of simple olefin monomers, reducing the processing complexity. In addition, EOR modifiers exhibit UV stability, a favorable volatile organic compound (VOC) emission profile, and good resistance to automotive-relevant chemicals (e.g., cleaning agents), making them well suited for automotive components. These factors render EOR a technically and economically attractive alternative to styrene-based modifiers such as SEBS and ABS [19–22].

Due to the immiscibility arising from the different polarities of PA and copolymers, typically, a highly reactive unsaturated monomer, such as maleic anhydride (MAH), is grafted onto the copolymer backbone using an initiator, most commonly peroxide [19,23–26]. Peroxide-induced hydrogen abstraction from the copolymer chain enables covalent bonds with MAH [19,23–25]. Achieving higher MAH grafting degrees c_{MAH} requires increased amounts of both MAH and peroxide [24,26]. Typical grafting levels range from 0.5 to 2.0 wt% [19].

During grafting, side reactions such as cross-linking, recombination, and β -scission influence the molecular weight distribution (MWD) of the modifiers [19,23–26]. Cross-linking or recombination of two chains via radical sites located on the polymer backbone leads to the formation of high- MW macromolecules. β -scission, which occurs predominantly at tertiary carbon atoms and increases proportionally with the c_{oct} , reduces the MW [19,25,27,28]. The addition of excess MAH can mitigate degradation [29], as it competes with the polymer backbone for reactive radicals, thereby suppressing β -scission. However, it may lead to an undesired release of unbound MAH during subsequent processing, which can be harmful due to outgassing, as well as its irritant and sensitizing effects.

During subsequent melt blending, a two-phase system forms, in which the modifier is dispersed as spherical particles within the PA matrix. The PA chains react with MAH on the particle surfaces, establishing connectivity through entanglements with the surrounding matrix. This ensures efficient stress transfer between the matrix and the modifier particles [30–33]. Below T_g of the modifier, both phases deform predominantly elastically, and the compound fails in a brittle manner. Above the modifier's T_g , the modifier particles are capable of plastic deformation; however, a transition to ductile fracture occurs only at the brittle–ductile transition temperature (BDTT). At the BDTT, the particles elongate under deformation and undergo cavitation, thereby converting a triaxial stress state into a predominantly uniaxial one. This stress redistribution promotes shear yielding of the surrounding matrix and results in ductile fracture, which is accompanied by a significant increase in NIS [2,7,10,30,32,34,35].

A homogeneous particle size distribution with controlled size and spacing is essential for achieving high NIS and low BDTT [4,10,36,37]. Particles below a critical size do not cavitate, whereas excessively large particles increase the interparticle distance ID , thereby reducing the stress-transfer efficiency and restricting the plastic deformation of the matrix. Within an optimal particle size window, however, the NIS has been reported

to be largely insensitive to particle size [1,4]. For PA6.6- and PA6-based systems, an ID below a critical value of $ID_c \approx 300$ nm is required, which is largely independent of the modifier chemistry and modifier content [36,37], because ID_c represents a matrix-controlled geometric criterion for overlapping stress fields and the onset of collective plastic deformation. Moreover, for EOR-modified PA6 compounds, an optimal weight-average particle diameter $d_{w,opt}$ has been identified, with particle sizes of approximately 90–250 nm associated with a low BDTT and 150–800 nm associated with high NIS values [1], with identical modifier content to this study. In contrast to ID , $d_{w,opt}$ depends on modifier content, which controls the particle number density and thus the particle size required to provide a sufficient stress-affected volume to trigger cavitation.

In addition to an optimized microstructure, a low elastic modulus E (i.e., low stiffness) of the modifiers, facilitating cavitation, and a low T_g , which increases deformability at low T , are required to achieve lower BDTT and high NIS at low T [2,8,10,38–41].

Previous studies have focused on adjusting the c_{MAH} to attain high NIS and low BDTT through an optimal microstructure [2,4,7,8,10,36,42,43]. As c_{MAH} increases, the particle size decreases due to reduced interfacial tension [1,2,4,11–13,39]. Consequently, higher c_{MAH} values have been considered advantageous for achieving low BDTT and high NIS [1,2,4,8,11,13,16,39,44].

However, achieving higher c_{MAH} requires larger amounts of MAH and peroxide, which intensify the side reactions, in particular β -scission, and thereby reduce the modifier's MW [24,26]. In our previous study [41], we showed that low- MW modifiers exhibit reduced particle strength, promote less pronounced matrix shear yielding, and consequently lead to consistently lower NIS and a higher BDTT than high- MW modifiers. Therefore, it is crucial to understand how c_{MAH} affects MW , since c_{MAH} not only improves compatibilization and reduces particle size but can simultaneously decrease the modifier's MW , thereby diminishing particle strength and NIS . Despite the strong interest in understanding the influence of c_{MAH} on compound properties, earlier studies did not account for the effect of grafting on the modifier's MW , even though variations in MW significantly affect the compound's NIS and BDTT, as demonstrated in our previous study [41]. Although numerous scientific publications exist, to the best of our knowledge, no study examined how deviations in the MWD—in particular, how different levels of c_{MAH} and c_{oct} lead to distinct changes in this distribution—affect the NIS .

Furthermore, the compound viscosity is higher than that of pure PA and rises further with increasing c_{MAH} . Thus, while c_{MAH} must be sufficiently high to obtain an optimal microstructure, excessively high levels should be avoided because they undesirably increase viscosity and may negatively impact subsequent forming processes [3,19,44,45].

The present study focuses on how c_{MAH} and c_{oct} , individually and in combination, affect the MWD of the modifiers and, in turn, the NIS of the compounds. The system was designed to keep the microstructure comparable, thereby isolating the effects of c_{MAH} and c_{oct} .

To this end, EOR modifiers with comparable initial MW in the range of 34,000–42,000 g/mol were selected, as variations outside this range would significantly alter the viscosity ratio between the modifier and matrix, which governs droplet breakup and dispersion during melt mixing.

Modifiers were grafted with $c_{MAH} = 0.5$ and 1.0 wt%, values that are both industrially relevant and widely reported in the literature [1,2,4,8,11,16,39,44]. Although MAH grafting may induce MW degradation, compensating for this effect by using substantially higher- MW base polymers is not a viable option in practice. EOR modifiers are predominantly produced for packaging applications, where low to moderate MW are required to ensure low melt viscosity, high processing stability at elevated throughputs, and cost-

efficient large-scale manufacturing. As a result, high-*MW* EOR grades are rarely available at an industrial scale.

EORs with relatively high octene content ($c_{\text{oct}} = 13, 15, \text{ and } 16 \text{ mol\%}$) were chosen to ensure low T_g and high deformability. Our preceding study [41] demonstrated that lower c_{oct} (8 mol%) results in a higher BDTT and reduced toughening efficiency. Higher c_{oct} grades beyond this range were not investigated, as excessive comonomer incorporation leads to pronounced material softening and tackiness, which can cause feeding and extrusion instabilities, such as pellet agglomeration, feeder blockage, or adhesion to the extruder screw. Moreover, such grades are associated with increased synthesis complexity, higher production costs, and limited availability at an industrial scale.

An instrumented Charpy impact test was employed to record force-displacement curves, enabling a more detailed analysis of fracture mechanisms than is possible with standard impact testing. Experiments were conducted over a broad T range, and the interpretation of the impact behavior was supported by thermal and mechanical characterization of the modifiers. This approach allows for the evaluation of grafting-induced *MW* changes and their influence on *NIS* in an industrially scalable PA6/EOR-g-MAH system with a controlled microstructure. The results indicate that MAH grafting influences strength and plastic deformability and, consequently, *NIS*, with effects that depend on T and c_{oct} .

Overall, an optimized combination of c_{MAH} and c_{oct} in the modifiers not only enhances the impact resistance of the compound across a wide T range but also improves processability by reducing its viscosity. While core-shell structures and more complex polymer alloys can offer superior performance in certain cases [46], they generally demand more intricate material design and processing compared to the approach presented here.

2. Materials and Methods

2.1. Materials

Three metallocene-catalyzed ethylene/1-octene copolymers (EORs) with different octene contents of $c_{\text{oct}} = 13, 15, \text{ and } 16 \text{ mol\%}$ and nearly identical initial molecular weights *MW* (prior to grafting) were grafted with maleic anhydride (MAH), resulting in MAH-functionalized EORs (EOR-g-MAH) with MAH contents c_{MAH} of approximately 0.5 and 1.0 wt%. The chemical structures of EOR and EOR-g-MAH are shown in refs. [19,27,28]. These EOR-g-MAH were added at 20 wt% to a medium-viscosity, heat-stabilized polyamide 6 (PA6, AKROMID® B3 1 natural) supplied by AKRO-PLASTIC GmbH (Niederzissen, Germany) to achieve impact toughening.

The nomenclature for the modifier follows the scheme EOR-“ c_{oct} [mol%]”-“ c_{MAH} [wt%]”, while the corresponding PA6 compounds are designated as PA-EOR-“ c_{oct} [mol%]”-“ c_{MAH} [wt%]”.

2.2. Modifier Characterization

The various characterization methods applied to the modifiers have been described in detail in a previous publication [41]. In this study, only the supplementary information that is required for interpreting the results is provided. The properties of the modifiers used in this work are summarized in Table 1.

Table 1. Properties of the ungrafted and grafted EOR copolymers used in this study: ρ = density, c_{oct} = octene content, c_{MAH} = MAH content, T_g = glass transition temperature, T_m = melting temperature, $X_c^{(a)}$ = uncorrected crystallinity, $X_c^{(b)}$ = crystallinity corrected for the process additive contribution, M_n = number-average molecular weight, and M_w = weight-average molecular weight. Values are reported as mean values with standard deviations where applicable. Data for EOR-13-1 and EOR-15-1 are taken from ref. [41].

Designation	Gravimetry		FTIR	DMTA		DSC		GPC	
	c_{oct} [mol%]	ρ [g/cm ³]	c_{MAH} [wt%]	T_g [°C]	T_m	$X_c^{(a)}$ [%]	$X_c^{(b)}$	M_n [kg/mol]	M_w
EOR-13-0		0.8705 ± 0.0004	-	−51	58.9 ± 0.1	16.0 ± 0.1	-	59	130
EOR-13-0.5	13.0 ± 0.2		0.47 ± 0.02	−49	53.8 ± 0.3	14.6 ± 0.1	13.9 ± 0.2	45	126
EOR-13-1		-	0.95 ± 0.04	−50	54.5 ± 0.1	14.7 ± 0.1	14.0 ± 0.1	39	146
EOR-15-0		0.8647 ± 0.0004	-	−52	52.1 ± 0.5	12.5 ± 0.4	-	58	132
EOR-15-0.5	14.9 ± 0.2	-	0.52 ± 0.01	−51	47.5 ± 0.9	12.7 ± 0.3	11.9 ± 0.3	45	125
EOR-15-1		-	0.95 ± 0.02	−51	48.5 ± 0.4	11.5 ± 0.1	11.1 ± 0.1	42	138
EOR-16-0		0.8609 ± 0.0004	-	−55	40.9 ± 0.5	8.1 ± 0.4	-	58	126
EOR-16-0.5	16.2 ± 0.2	-	0.71 ± 0.04	−55	36.1 ± 3.1	7.2 ± 0.1	6.7 ± 0.2	44	116
EOR-16-1		-	1.09 ± 0.04	−54	34.0 ± 0.1	7.3 ± 0.1	6.9 ± 0.1	37	99

The densities ρ of the ungrafted EOR modifiers were measured by the buoyancy (Archimedes) method, and c_{oct} was subsequently determined from these values, according to the methods described in ref. [47]. The degree of MAH grafting c_{MAH} was quantified on vacuum-dried, pressed films using Fourier transform infrared spectroscopy (FTIR), following the procedures described in refs. [19,44,48]. Exemplary infrared (IR) spectra of the ungrafted (EOR-13-0) and MAH-grafted samples (EOR-13-0.5 and EOR-13-1) are shown in Figure S1 (Supporting Information), and procedures are further discussed in both the Supporting Information and ref. [41]. The number-average and weight-average molecular weight (M_n and M_w) were determined from the molecular weight distribution (MWD) obtained by high-temperature gel permeation chromatography (GPC). The glass transition temperature T_g was measured by dynamic mechanical thermal analysis (DMTA). The melting temperature T_m and the crystallinity X_c of the modifiers were extracted from differential scanning calorimetry (DSC) thermograms. Both the overall X_c and the X_c corrected for the contribution of the process additive are reported in Table 1 (see also FTIR results in the Supporting Information, Section S1). The contribution of the additive appears as a shoulder in the DSC thermograms around 80 °C, quantified by fitting a Lorentzian, and subsequently subtracted from the overall X_c . The corrected X_c values allow us to unambiguously isolate the effect of the grafting process on X_c . In contrast, in refs. [41,49], no correction was applied, as the effective uncorrected X_c was considered decisive for the performance of the modifiers in the compound.

When interpreting the impact test results, it should be noted that the difference in strain rates between DMTA and impact testing leads to an upward shift in the apparent T_g by approximately 9 °C. Even considering this shift, the effective $T_{g,\text{shifted}} < -41$ °C of the modifiers remains well below the brittle–ductile transition temperatures (BDTT) (≈ -20 °C) observed in the impact tests (see also Section 3.2.3). For further details, the reader is referred to ref. [41].

Finally, Table 2 summarizes the tensile properties of the modifiers, including the elastic modulus E , working capacity W , stress at yield σ_y , strain at yield ε_y , stress at break σ_b , and strain at break ε_b , obtained from uniaxial tensile testing.

2.3. Preparation and Characterization of the Compound

2.3.1. Compounding

The compounds were melt-blended in a co-rotating twin-screw extruder (FED 26 MTS, FEDDEM GmbH & Co. KG, Sinzig, Germany) at a set temperature of 250 °C, a screw rotational speed of 660 min^{−1}, and a feed rate of 50 kg/h. A screw with an outer-to-inner screw diameter ratio $D_o/D_i = 1.55$ and a configuration incorporating both distributive and dispersive mixing elements was used to ensure a reproducible microstructure and fine dispersion. All raw materials were simultaneously fed into the extruder at a constant PA6/EOR-g-MAH ratio of 80/20 wt%. The moisture content of the PA6 used during compounding was maintained below 0.1 wt%.

2.3.2. Impact Test

The specimens for the impact tests on the PA6/EOR-g-MAH compounds were processed using an injection molding machine (ARBURG 420 C 1000-250, ARBURG GmbH & Co. KG, Loßburg, Germany) at barrel and nozzle temperatures between 240 and 255 °C and a mold temperature of 80 °C. Prior to processing, compound granules were dried in a vacuum oven at 80 °C to a residual moisture content of (0.05 ± 0.01) wt%. The moisture content was determined by Karl Fischer titration (C30 Coulometric KF Titrator, Mettler-Toledo GmbH, Greifensee, Switzerland).

The impact test specimens were prepared by injection molding Type A1 tensile bars according to the geometry specified in DIN EN ISO 527-2 [50]. The shoulders were subsequently removed, and a 45° V-notch with a notch radius of (0.25 ± 0.05) mm was introduced, in accordance with DIN EN ISO 179-1/1eA [51]. Prior to impact testing, the notched specimens were conditioned under standard climate conditions at 23 °C and 50% relative humidity for 16–24 h, in accordance with DIN EN ISO 179-1 [51]. For impact tests conducted at different temperatures T , the specimens were conditioned at the respective test temperature prior to each measurement to ensure a uniform T throughout the specimens. Conditioning was performed in a climate chamber for more than 3 h. The specimens were removed using tweezers and tested within 5 s, following the procedure described for metals in DIN EN ISO 148-1 [52].

The impact response of the compounds was measured using an instrumented 25 J hammer mounted on an impact testing device (HIT25P, ZwickRoell GmbH & Co. KG, Ulm, Germany). Tests were performed following DIN EN ISO 179-2 [53]. The instrumented striker recorded the force F experienced by the specimen during impact. The area under the resulting force-deflection curves $F(s)$ was separated into the energy dissipated up to crack initiation, E_{init} , and the energy associated with crack propagation, E_{prop} . To determine the force maximum, a Lorentzian was fitted to the peak region of $F(s)$. For each material and T , at least five specimens were tested. The reported NIS values represent mean values, and the error bars correspond to the standard deviations.

2.3.3. Viscosity Measurement

The compound viscosities, η , were measured at 240 °C, using a high-pressure capillary viscometer (Göttfert RG50, Göttfert GmbH, Buchen, Germany) over a shear-rate range $\dot{\gamma} = 3.5 \times 10^2$ – 3.7×10^4 s^{−1}. Capillaries with a length-to-diameter ratio L/D of 20/1 and 40/1 were employed. Measurements were initiated 10 min after the target temperature had been reached. All reported η data were corrected according to the Bagley and Weissenberg–Rabinowitsch procedures. To ensure a constant moisture content of (0.05 ± 0.01) wt%, the compounds were dried in a vacuum oven at 80 °C prior to testing. The moisture content was confirmed by Karl Fischer titration (C30 Coulometric KF Titrator, Mettler-Toledo GmbH, Greifensee, Switzerland).

2.3.4. Scanning Electron Microscopy

The compounds' microstructure was examined by scanning electron microscopy (SEM, Jeol JSM-7200F, JEOL Ltd., Tokyo, Japan) operated at an acceleration voltage of 15 kV. Cryo-fractured specimens were immersed in boiling xylene overnight to dissolve the modifier phase. Subsequently, a 6 nm thick iridium layer was sputtered onto the specimens, using a sputtering device (Safematic CCU-010, Safematic GmbH, Zizers, Switzerland).

Image analysis was performed using Image-Pro Premier Ver. 9.2 (Media Cybernetics Inc., Rockville, MD, USA) to determine the dimensions of the voids remaining after dissolution of the modifier, which were associated with the particle diameter. For each compound, at least 400 particles were evaluated. From the void-diameter distribution, the number-average particle diameters $\bar{d}_n$, the weight-average particle diameters $\bar{d}_w$, the volume-average particle diameters $\bar{d}_v$, and the interparticle distances ID were determined. The corresponding formulas are provided in our previous study [41]. The polydispersity index PDI was calculated as the ratio $\bar{d}_v/\bar{d}_n$. The different average particle diameters, PDI , and ID values, together with their standard deviations derived from the analysis of at least two SEM microphotographs, are summarized in Section 3.2.1.

3. Results and Discussion

3.1. Modifier Properties

3.1.1. Thermal and Temperature-Dependent Dynamic–Mechanical Properties

The thermal properties of the EOR-g-MAH modifiers with varying c_{MAH} and c_{oct} were analyzed using DSC and DMTA. Figure 1a presents the DSC thermograms (heat flow from the second heating runs) for the ungrafted and grafted EOR copolymers ($c_{MAH} = 0.5$ and 1.0 wt%) with $c_{oct} = 13, 15$, and 16 mol%. The corresponding values for T_m and X_c are listed in Table 1. To provide a more complete picture of how thermal properties evolve with c_{oct} , the Supporting Information (Section S2) also includes DSC and DMTA results for EOR-8 (see also [41]).

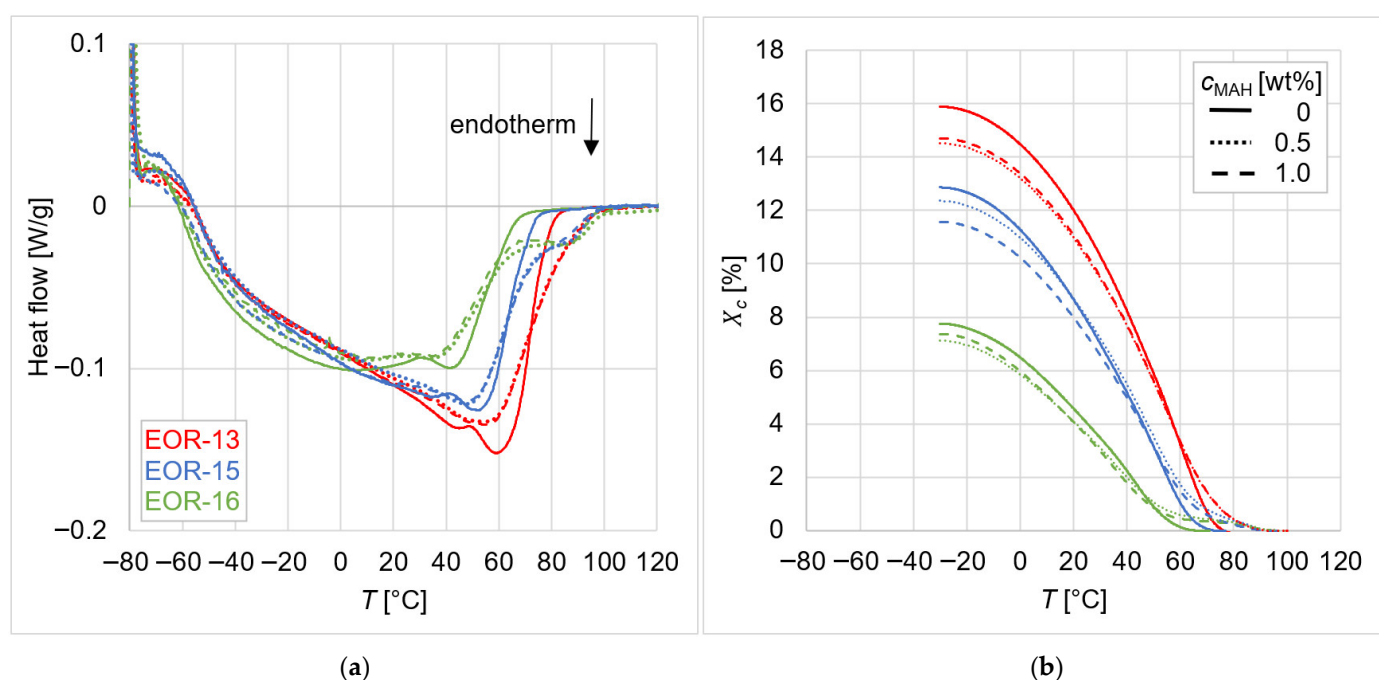


Figure 1. Exemplary DSC endotherms (heat flow from the 2nd heating runs) as a function of temperature T for all investigated modifiers (a) together with the corresponding cumulative residual crystallinities X_c (b). Data for EOR-13-1 and EOR-15-1 are taken from ref. [41].

All materials exhibit a broad melting region that begins immediately above the glass transitions. The T_g values, determined from the peak of the loss modulus from DMTA measurements (see Figure 2 and Table 1), are equal to $(-55 \pm 1)^\circ\text{C}$ (EOR-16), $(-51 \pm 1)^\circ\text{C}$ (EOR-15), and $(-50 \pm 1)^\circ\text{C}$ (EOR-13) and are independent of c_{MAH} within the experimental error. The hexyl side chains of the octene comonomer increase the free volume relative to polyethylene and simultaneously hinder crystallization. Consequently, increasing c_{oct} leads to lower T_g , T_m , and X_c , shifting the entire melting region to lower T , as also discussed in our previous study [41] and ref. [17]. Grafting slightly affects the melting behavior of the modifiers, as the MAH units interfere with polymer chain packing during crystallization [54–57]. This reduced packing efficiency results in smaller and imperfect crystallites, leading to lower melting peak heights, a shift of T_m to lower T , and a tendency toward reduced X_c compared to the ungrafted materials (see Table 1 and refs. [54–57]). Increasing c_{MAH} beyond 0.5 wt% does not further hinder crystallization.

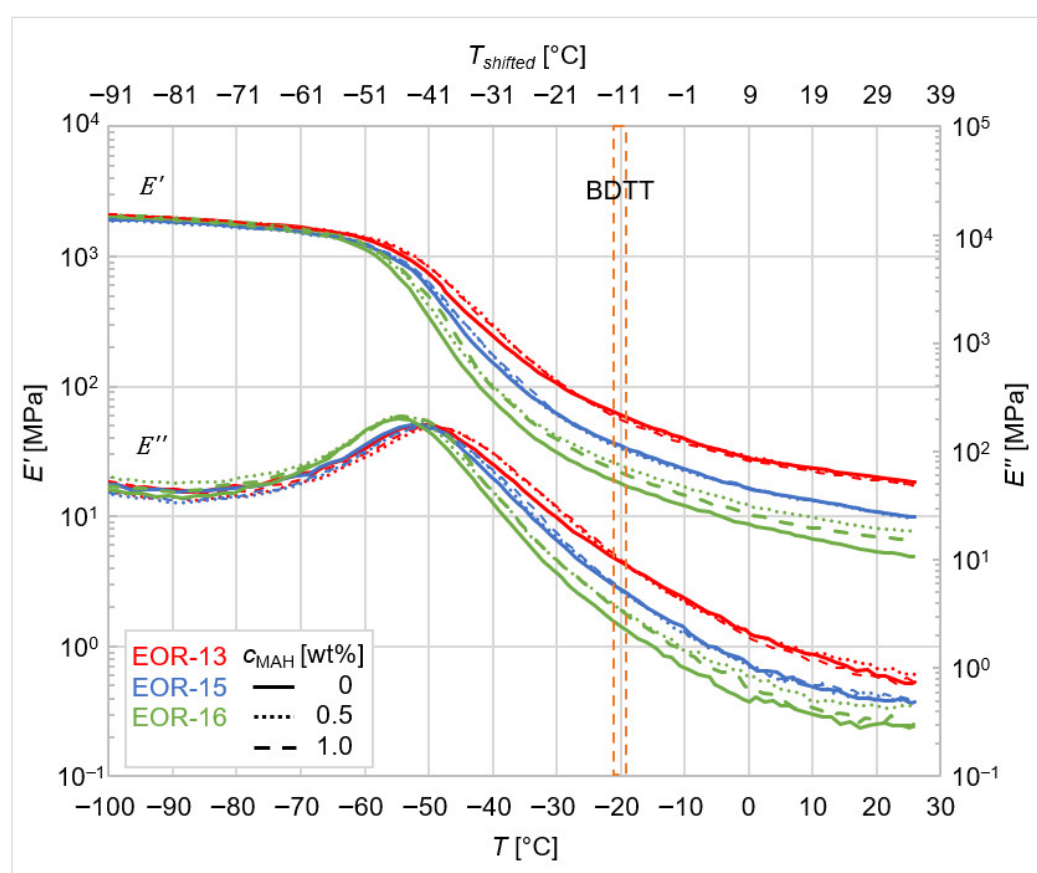


Figure 2. Loss modulus E'' and storage modulus E' (log-scale) versus temperature T , measured by DMTA for all investigated modifiers. The brittle–ductile transition temperature (BDTT) range obtained from impact tests is shown as orange dashed lines. The shifted temperature T_{shifted} accounts for the high strain rates experienced during impact testing [8]. Data for EOR-13-1 and EOR-15-1 are taken from ref. [41].

In the DSC thermograms, a shoulder appears at approximately 80°C , which is attributed to a process additive present in the peroxide- and MAH-containing masterbatch used for grafting, which was also observed in the IR spectrum (see Section S1, Supporting Information). X_c were corrected for the contribution of the additive; however, the correction reduces X_c by a maximum of only 0.8% and is therefore considered negligible for further discussion.

For interpreting the NIS behavior of the compounds, the X_c of the modifiers at the testing temperature is more relevant than the original X_c , determined from the area under

the entire melting peak. Figure 1b shows the uncorrected residual X_c of the modifiers as a function of T . Due to the early onset of melting, X_c decreases continuously above T_g , and at room temperature ($RT = 23\text{ }^\circ\text{C}$), it is substantially reduced. For EOR-16, EOR-15 and EOR-13, independent of c_{MAH} , the reduction amounts to approximately $(47 \pm 1)\%$, $(35 \pm 1)\%$, and $(28 \pm 1)\%$, with residual X_c of about $(4 \pm 1)\%$, $(8 \pm 1)\%$, and $(11 \pm 1)\%$, respectively. The melting of the modifiers, accompanied by a significant loss of crystalline material, affects their strength at elevated T . Modifier strength is critical for the toughness of the compounds, as it governs the induction of shear yielding in the PA6 matrix (see discussion below).

Figure 2 shows the storage modulus E' and loss modulus E'' as a function of T , measured by DMTA, for the ungrafted and grafted modifiers investigated in this study: EOR-13, EOR-15, and EOR-16. The measurements cover the T range that is relevant for interpreting the impact tests. According to ref. [8], the higher strain rates in an impact test compared to the low strain rates in a DMTA experiment can be accounted for by a T shift T_{shifted} of approximately $9\text{ }^\circ\text{C}$ toward higher T . Even after applying this shift, the glass transitions of all modifiers $T_{g,\text{shifted}} \approx -41\text{ }^\circ\text{C}$ (EOR-13), $-42\text{ }^\circ\text{C}$ (EOR-15), and $-46\text{ }^\circ\text{C}$ (EOR-16) remain well below the BDTT observed in the impact tests (see Section 3.2.3).

Consistent with the DSC results, the gradual softening of the materials above T_g , as indicated by the decrease in E' , is attributed not only to the increased mobility of the amorphous phase but also to the onset of melting of the crystalline phase just above T_g [17,58]. Above T_g , E' is systematically lower and decreases more rapidly with increasing T for EOR-16 compared to EOR-15 and EOR-13, reflecting the higher chain mobility (due to a larger free volume) and lower X_c associated with higher c_{oct} , as also discussed in refs. [17,28]. For EOR-13 and EOR-15, no significant effect of c_{MAH} on the DMTA results is observed. In contrast, for EOR-16, both moduli above T_g are systematically higher for the grafted samples compared to the respective ungrafted ones. With increasing c_{oct} , the crystalline network weakens and contributes less to E' . At lower c_{oct} levels, the modulus is dominated by the crystalline phase, masking polar interactions induced by (MAH) and maleic acid (MA) moieties, whereas at $c_{\text{oct}} = 16\text{ mol}\%$, the amorphous phase dominates and MA(H)-induced dynamic physical cross-links become mechanically significant, increasing both E' and E'' . MA is formed via hydrolysis of MAH [59] during processing. The effect of the polar interactions on the mechanical properties of the modifiers is discussed in more detail in Section 3.1.3.

3.1.2. Gel Permeation Chromatography

In Figure 3, the MWD of the copolymers EOR-13, EOR-15, and EOR-16 are presented for different c_{MAH} (ungrafted, 0.5 wt%, and 1.0 wt% MAH). Figure S4 in the Supporting Information shows the same data but compares the effect of varying c_{oct} at fixed c_{MAH} . Values for M_n and M_w are summarized in Table 1.

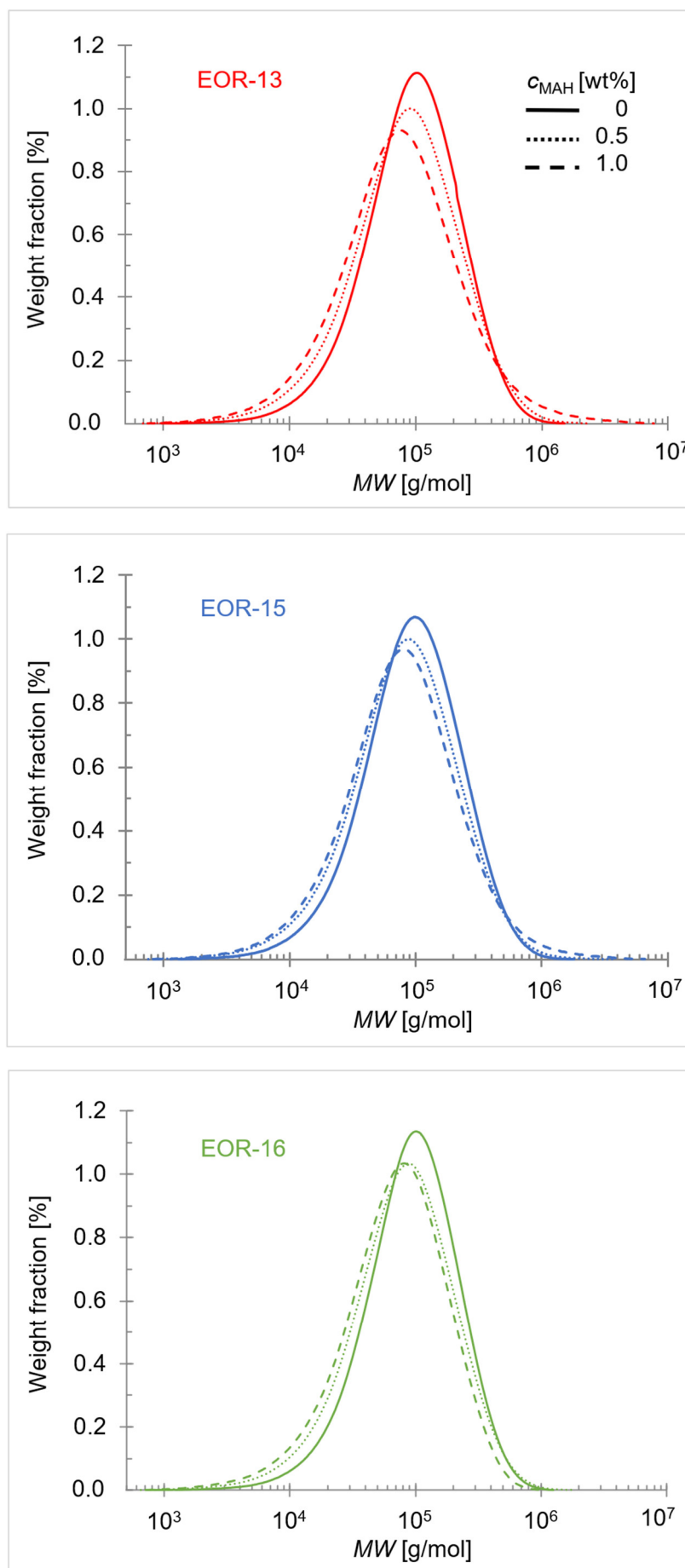


Figure 3. Molecular weight distributions (MWD) of all investigated modifiers.

The changes observed in the MWD are attributed to side reactions, including β -scission and cross-linking, that occur during the grafting process [19,21,24,56,60,61]. During grafting, the polymer is mixed with MAH and peroxide. The elevated T associated with the mixing process induces thermal decomposition of the peroxide, leading to the formation of free radicals [19,56,60,61]. These radicals can abstract hydrogen atoms from the copolymer chains, generating macroradicals (EOR•) that are capable of undergoing a wide variety of subsequent reactions [19,28,56,60,61]. For the purpose of the present discussion, we focus on the most relevant reactions.

The reaction is initiated by the thermal decomposition of the peroxide, generating primary radicals that abstract hydrogen atoms from the polymer backbone and form EOR• macroradicals. In the desired reaction, EOR• reacts with MAH, forming an EOR-g-MAH• macroradical, which can then abstract a hydrogen atom from the same or another polymer chain, terminating the radical at that position while simultaneously generating a new macroradical at the site of abstraction [56,60,61]. In addition to this intended propagation, both EOR• and EOR-g-MAH• can react with each other, resulting in chain coupling (e.g., EOR-EOR or EOR-g-MAH-EOR) or cross-linked structures, in which large macromolecules are formed.

Hydrogen abstraction can also initiate β -scission, which may occur either directly at tertiary carbon atoms or initially at secondary carbon atoms, followed by radical migration along the polymer chain and eventual stabilization at a tertiary carbon site [19,24,28,56,61]. Consequently, β -scission predominantly occurs at tertiary carbons, due to the lower energy required for hydrogen abstraction and the higher stability of the resulting tertiary radicals compared to the secondary radicals [28,62].

To illustrate the extent of the respective side reactions as a function of c_{oct} and c_{MAH} , Figure 4 presents the relative MW changes $\Delta M_i/M_i = (M_{i,\text{EOR-g-MAH}} - M_{i,\text{EOR}})/M_{i,\text{EOR}}$ ($i = n, w$), comparing M_n and M_w of the grafted copolymers ($M_{i,\text{EOR-g-MAH}}$) with those of the corresponding ungrafted EOR materials ($M_{i,\text{EOR}}$) for all modifiers.

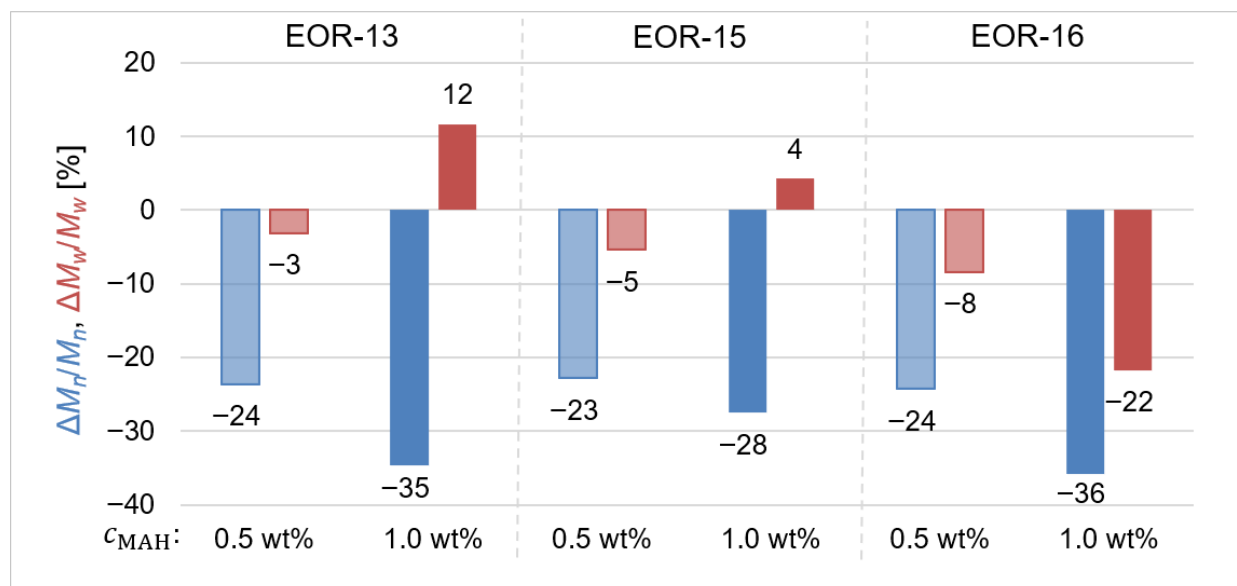


Figure 4. Relative changes in molecular weight of all investigated grafted modifiers compared with their ungrafted counterparts: $\Delta M_n/M_n$ (blue) and $\Delta M_w/M_w$ (red).

Upon grafting, M_n decreases for all modifiers, with the reduction becoming more pronounced at higher c_{MAH} . Elevated peroxide concentrations are required to achieve higher grafting densities. Under these conditions, the increased radical concentration enhances the probability of β -scission relative to graft formation, even though the MAH

concentration is increased to a greater extent than the peroxide concentration. β -scission is a unimolecular, intramolecular reaction that proceeds more rapidly than the bimolecular propagation involving MAH addition. Furthermore, the formation of relatively stable tertiary radicals during grafting kinetically favors chain cleavage over propagation. The dependency of M_w on the c_{oct} and c_{MAH} requires a more detailed discussion. At $c_{\text{MAH}} = 0.5$ wt%, M_w is lower than that of the ungrafted modifiers and decreases further with increasing c_{oct} . At this grafting level, the amounts of peroxide and MAH are insufficient to induce significant cross-linking, and β -scission predominates. With increasing c_{oct} , the number of tertiary carbons rises, further enhancing the probability of β -scission.

At $c_{\text{MAH}} = 1.0$ wt%, the increased amounts of peroxide and MAH not only enhance β -scission but also promote cross-linking. M_w is increased for EOR-13-1 and EOR-15-1 compared to the corresponding ungrafted modifiers, which is likely due to the higher macroradical concentrations, which reduce the average distances between radicals and thereby increase the probability of recombination of large and bulky macroradicals, as discussed in refs. [29,63]. As c_{oct} increases from 13 to 16 mol%, β -scission becomes increasingly dominant over cross-linking due to the higher proportion of tertiary carbons, which is consistent with refs. [28,57]. For EOR-16-1, a significant relative decrease in M_w is observed, indicating that cross-linking is no longer significant. This is most likely a consequence of steric hindrance between macroradicals arising from the increased number of side chains, as noted in ref. [27], combined with a high probability of β -scission.

3.1.3. Tensile Properties

Figure 5 shows one representative stress σ –strain ε curve for EOR-13, EOR-15 or EOR-16, either ungrafted or grafted with $c_{\text{MAH}} = 0.5$ or 1.0 wt%, respectively. The corresponding values of the elastic modulus E , stress at yield σ_y , strain at yield ε_y , stress at break σ_b and strain at break ε_b of the pure modifiers are listed in Table 2.

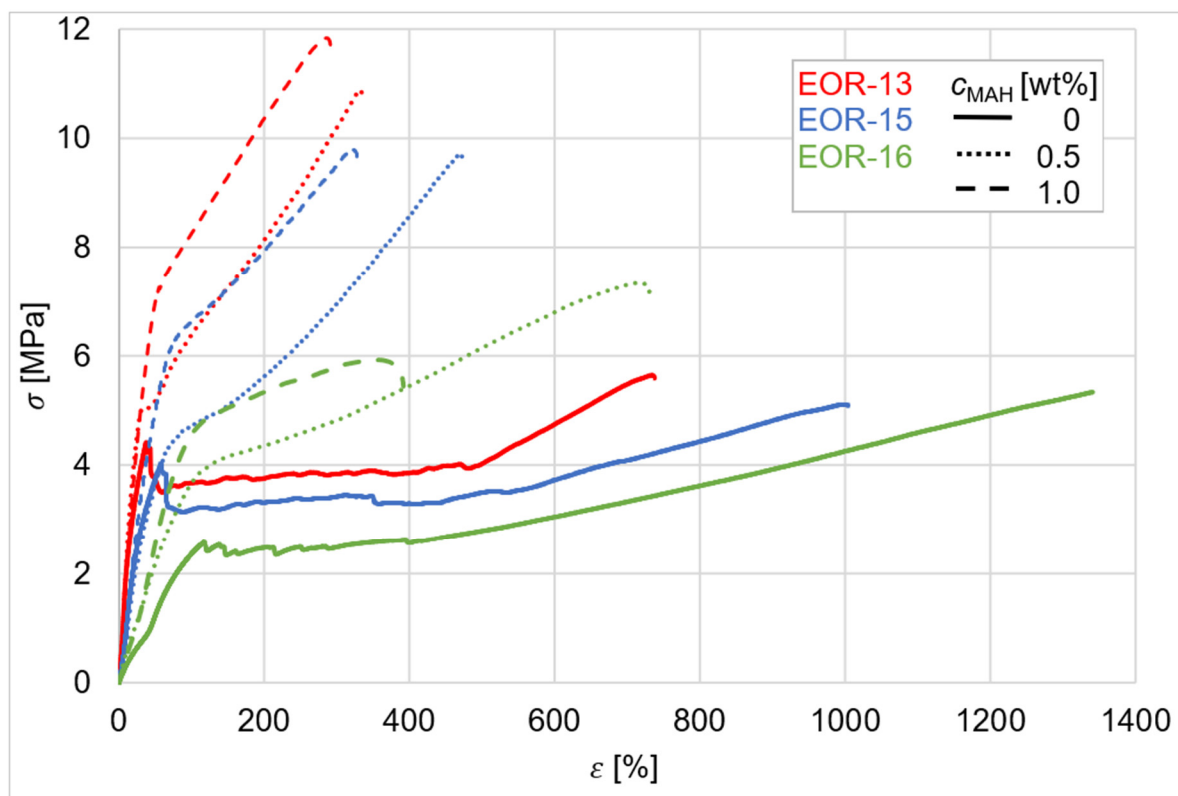


Figure 5. Representative stress σ –strain ε curves obtained from tensile tests at 23 °C of all investigated modifiers. Data for EOR-13-1 and EOR-15-1 are taken from ref. [41].

Table 2. Summary of the tensile test results of the modifiers: elastic modulus E , working capacity W , stress at yield σ_y , strain at yield ε_y , stress at break σ_b , and strain at break ε_b . Values are listed as mean values with standard deviations. Data for EOR-13-1 and EOR-15-1 are taken from ref. [41].

Designation	E [MPa]	W [J]	σ_y [MPa]	ε_y [%]	σ_b [MPa]	ε_b [%]
EOR-13-0	12.7 ± 0.7	4.9 ± 0.9	4.5 ± 0.1	41 ± 2	5.6 ± 0.4	695 ± 120
EOR-13-0.5	12.9 ± 0.2	4.3 ± 0.3	5.1 ± 0.1	34 ± 1	10.9 ± 0.3	327 ± 11
EOR-13-1	13.2 ± 0.2	4.3 ± 0.1	7.4 ± 0.1	63 ± 1	11.5 ± 0.2	291 ± 5
EOR-15-0	6.3 ± 0.2	6.2 ± 1.6	4.1 ± 0.1	54 ± 3	4.9 ± 0.2	942 ± 235
EOR-15-0.5	8.8 ± 0.4	5.8 ± 0.5	4.9 ± 0.1	82 ± 1	9.5 ± 0.4	496 ± 29
EOR-15-1	8.0 ± 0.4	4.3 ± 0.1	6.2 ± 0.1	84 ± 2	9.4 ± 0.2	348 ± 6
EOR-16-0	4.5 ± 0.2	12.0 ± 0.9	2.6 ± 0.1	114 ± 5	5.3 ± 0.1	1452 ± 67
EOR-16-0.5	6.0 ± 0.3	7.9 ± 0.4	4.0 ± 0.1	139 ± 3	7.3 ± 0.2	720 ± 25
EOR-16-1	4.2 ± 0.1	3.6 ± 0.2	4.8 ± 0.1	111 ± 3	5.4 ± 0.2	374 ± 13

To determine ε_y , the minimum of the first derivative of the stress–strain curve was used, and the stress at this strain was taken as σ_y . However, for EOR-13-1, EOR-15-1, and EOR-16-1, no minimum in the first derivative could be identified. In these cases, ε_y was identified as the intersection point of the slopes of the first derivative in the two approximately linear regions immediately before and after the pronounced change in slope. The corresponding stress at this intersection point on the stress–strain curve was taken as σ_y .

In the following, the influence of c_{oct} on the tensile properties of the ungrafted modifiers is discussed first, before the effect of c_{MAH} is addressed.

The deformability in the low-strain region, i.e., the elastic regime, systematically increases with increasing c_{oct} from EOR-13-0 to EOR-15-0 and EOR-16-0. As reported in refs. [17,18], this behavior is predominantly governed by X_c , which decreases from EOR-13 over EOR-15 to EOR-16, as confirmed by the DSC measurements (see Section 3.1.1 and Table 1). Lower X_c increases the amorphous fraction, leading to enhanced deformability. These results also align with the trend in E' obtained from DMTA above T_g (see Section 3.1.1).

As the strain increases, the ungrafted modifiers exhibit a distinct stress maximum followed by a pronounced stress drop, indicating the onset of necking. Specimens of EOR-13-0 and EOR-15-0 show strongly localized necking, whereas EOR-16-0, with higher c_{oct} , exhibits broader, less localized necking, reflected in a wider stress maximum [17,64,65].

Increasing c_{oct} , corresponding to a higher number of hexyl side chains, affects the deformation behavior through several mechanisms: (i) it reduces X_c by disturbing the regular packing of the polymer backbone [17,64], and (ii) it introduces strong steric hindrance [65]. As a direct consequence of steric hindrance, the free volume in the amorphous regions increases (iii) [17,64], which reduces the probability of topological interchain entanglements, lowering the effective entanglement density (iv) [66]. Although reduced entanglement density (iv) tends to promote localized necking, steric hindrance from bulky side chains (ii), together with increased free volume (iii), limits the molecular orientation under tensile load and distributes deformation, suppressing localized volume contraction perpendicular to the stretching direction and thereby reducing necking [17,18,65]. Reduced X_c also contributes by enlarging the amorphous phase, allowing deformation to be spread over a broader region [17]. Correspondingly, as c_{oct} increases, σ_y decreases, while ε_y increases, reflecting the delayed onset of necking and the more distributed stress over a larger effective cross-section.

In the subsequent cold-drawing regime, the neck propagates along the specimen and develops an oriented fibrillar morphology, stabilizing once it reaches the specimen shoulders, as previously described in ref. [17]. Following this, strain hardening occurs, where

stress increases until failure as chains align and stretch, constrained by entanglements and tie molecules connecting crystalline domains [17,67]. Increasing c_{oct} reduces these constraints, weakening strain hardening. Higher ε_b is consistent with the larger amorphous fraction and the presence of fewer, smaller, less interconnected fringed micelles [17,18]. Despite the weakened strain hardening, the overall strength remains roughly constant because the reduced effect of necking (larger effective cross-section) offsets the expected weakening. Consequently, the working capacity W , defined by the area under the stress–strain curve, is comparable for EOR-13-0 and EOR-15-0 within the error bars, but is significantly higher for EOR-16-0 due to its greater ductility, reflected in the higher ε_b at a similar apparent strength.

For the grafted modifiers, tensile properties differ significantly from those of the ungrafted ones. In the elastic region, grafting has only a minor influence on stiffness, as the slight reduction in X_c is largely compensated, or even outweighed, by stronger polar interactions between the grafted chains in the amorphous phase, particularly for the high- c_{oct} modifiers (see Table 1, Section 3.1.1, and discussion below). For EOR-16-1, however, the pronounced reduction in MW and the associated loss of entanglements counteract this stiffening effect, resulting in a lower E compared to EOR-16-0.5.

At higher strains, clear distinctions between the various c_{MAH} levels emerge. Whereas ungrafted modifiers exhibited pronounced necking, necking formation is strongly suppressed at $c_{\text{MAH}} = 0.5$ wt% and absent at $c_{\text{MAH}} = 1.0$ wt%. Grafted modifiers display reduced ε_b and generally higher ε_y , σ_b and σ_y compared to their ungrafted counterparts, with the increase in σ_y and the reduction in ε_b becoming more pronounced at higher c_{MAH} , consistent with refs. [55,68].

These effects can be primarily attributed to attractive, polar interactions between maleic anhydride (MAH) and maleic acid (MA) moieties along the grafted polymer chains [54,55,57,68]. MA units form via hydrolysis in the presence of ambient moisture during processing at elevated T [59]. The resulting dipole–dipole interactions between MAH groups [69] and hydrogen bonding between MA groups [70] act as additional physical cross-links within the amorphous phase, increasing the resistance to plastic deformation and suppressing necking.

Compared to the ungrafted materials, grafting introduces additional physical constraints in the amorphous phase, which serve as load-transferring bridges between crystalline clusters and represent the primary site of plastic deformation. Attractive polar interactions between MAH and MA groups act as reversible physical cross-links, effectively increasing the density of intermolecular junctions [55]. Bulky grafted moieties impose steric constraints that reduce segmental mobility and increase resistance to chain sliding and disentanglement. Both effects are expected to intensify with increasing c_{MAH} .

As a consequence, once the amorphous phase has stretched and the crystalline domains become aligned in the loading direction, stronger intermolecular interactions and steric hindrance prevent local rearrangement of the crystalline domains and limit chain disengagement from them [55,67]. This stabilizes the oriented network structure, increases resistance to plastic flow, and enhances the strain-hardening modulus, albeit at the expense of reduced ε_b . These two constraint mechanisms reduce the ability of both amorphous chain segments and crystalline domains to undergo further reorganization and alignment under continued deformation. As a result, strain localization is suppressed and necking is reduced or even absent, maintaining a larger cross-sectional area during deformation and thereby influencing the measured strength. Compared to the ungrafted counterparts, the combination of reduced necking and stronger intermolecular interactions increases both σ_y and σ_b , while ε_b decreases upon grafting. In contrast, ε_y tends to increase, relative to the ungrafted materials, because necking is hindered, causing σ_y to be reached at higher strains.

Increasing c_{MAH} from 0.5 to 1.0 wt% does not significantly change the values of σ_b and ε_b for EOR-13. Similarly, σ_b remains comparable between EOR-15-0.5 and EOR-15-1; however, ε_b decreases as c_{MAH} increases from 0.5 to 1.0 wt% MAH. Increasing the MAH grafting level beyond 0.5 wt% does not lead to further enhancement in modifier strength. Although β -scission reduces M_n , this effect is at least partially offset by an increase in M_w , i.e., by the presence of additional high- MW chains formed by cross-linking, thereby preserving the density of tie-molecule-based junctions between crystalline domains. The observed reduction in ε_b arises because enhanced intermolecular interactions induced by MAH and MA hinder chain sliding in the amorphous regions and thus limit plastic deformation, causing σ_b to be reached at lower strains, as discussed in refs. [55,68], with steric constraints possibly further limiting chain sliding and disentanglement.

According to ref. [57], the impact of cross-linking and β -scission on the stress-strain behavior is smaller than the effects discussed above. For EOR-16-1, however, both σ_b and ε_b are significantly reduced compared to EOR-16-0.5. This behavior is primarily a consequence of the substantial decrease in MW caused by grafting and the dominance of β -scission over cross-linking (Section 3.1.2), which outweighs the positive contributions of enhanced intermolecular interactions through MAH and MA and diminishes the effective bridging between crystalline domains. This response is consistent with the premature failure of the low- MW modifier compared to the high- MW counterpart ($c_{\text{oct}} = 15 \text{ mol\%}$, $c_{\text{MAH}} = 1.0 \text{ wt\%}$) discussed in the previous study [41]. Furthermore, the effect of increased polar interactions and steric hindrance on ε_b is expected to become more pronounced at higher c_{oct} , due to the larger fractions of amorphous regions. This also explains why increasing c_{MAH} has little effect on ε_b in EOR-13, as stronger polar interactions contribute less due to the relatively small amorphous fraction, while the highly crystalline domains act as the main load-bearing network during deformation.

Finally, W is mainly determined by the trend in ε_b . W is comparable for the ungrafted and grafted EOR-13 modifiers, indicating that the increased strength upon grafting compensates for the reduction in ε_b . For EOR-15, W is comparable for EOR-15-0 and EOR-15-0.5, but is significantly lower at EOR-15-1, due to the noticeably reduced ε_b at higher c_{MAH} . For EOR-16, W decreases from EOR-16-0 to EOR-16-0.5 and, in particular, shows a strong drop for EOR-16-1, resulting from the reductions in both σ_b and ε_b caused by the substantial decrease in MW .

3.2. Compound Properties

3.2.1. Microstructure

Given the strong influence of microstructure on NIS , particle diameters were measured and the corresponding ID calculated. Particles below a critical size cannot cavitate, whereas excessively large particles, depending on the modifier volume fraction, lead to ID s that are too large, preventing the initiation of shear yielding in the surrounding matrix [1,36,37]. Within this optimal size range, NIS shows little dependence on the particle diameter [1]. For PA6- and PA6.6-based systems, effective toughening requires an ID below a critical value of $ID_c \approx 300 \text{ nm}$, largely independent of modifier chemistry and content [36,37]. For EOR-modified PA6, the optimal weight-average particle diameter $d_{w,opt}$ lies between approximately 90–250 nm for low BDTT and 150–800 nm for high NIS , at modifier contents that are identical to those in this study [1].

Table 3 summarizes the number-average $\bar{d}_n$, weight-average $\bar{d}_w$, and volume-average diameters $\bar{d}_v$, the corresponding polydispersity indices PDI , and the calculated interparticle distance ID for all compounds investigated in this study. Figure 6 shows representative surfaces of cryo-fractured and xylene-etched specimens for the compounds PA-EOR-13-0.5 and PA-EOR-13-1. SEM micrographs for all remaining compounds used

in this study are provided in the Supporting Information (Section S4). In all cases, the modifier is dispersed as spherical particles within the matrix.

Table 3. Microstructural properties of all compounds investigated in this study: number-average particle diameter $\bar{d}_n$, weight-average particle diameter $\bar{d}_w$, volume-average particle diameter $\bar{d}_v$, polydispersity index PDI , and interparticle distance ID . Values are given as mean values with standard deviations. Data for PA-EOR-13-1 and PA-EOR-15-1 are taken from ref. [41].

Designation PA-EOR-*	c_{MAH} [wt%]	Particle Size [nm]			PDI	ID [nm]
		$\bar{d}_n$	$\bar{d}_w$	$\bar{d}_v$		
13-0.5	0.5	184 ± 4	240 ± 10	356 ± 17	1.93 ± 0.05	53 ± 2
13-1	1.0	154 ± 4	184 ± 6	263 ± 6	1.70 ± 0.03	47 ± 2
15-0.5	0.5	175 ± 2	228 ± 6	346 ± 31	1.98 ± 0.09	50 ± 1
15-1	1.0	156 ± 5	188 ± 6	261 ± 6	1.67 ± 0.04	45 ± 2
16-0.5	0.5	174 ± 7	210 ± 16	294 ± 43	1.68 ± 0.15	50 ± 2
16-1	1.0	149 ± 2	180 ± 2	265 ± 5	1.78 ± 0.02	42 ± 1

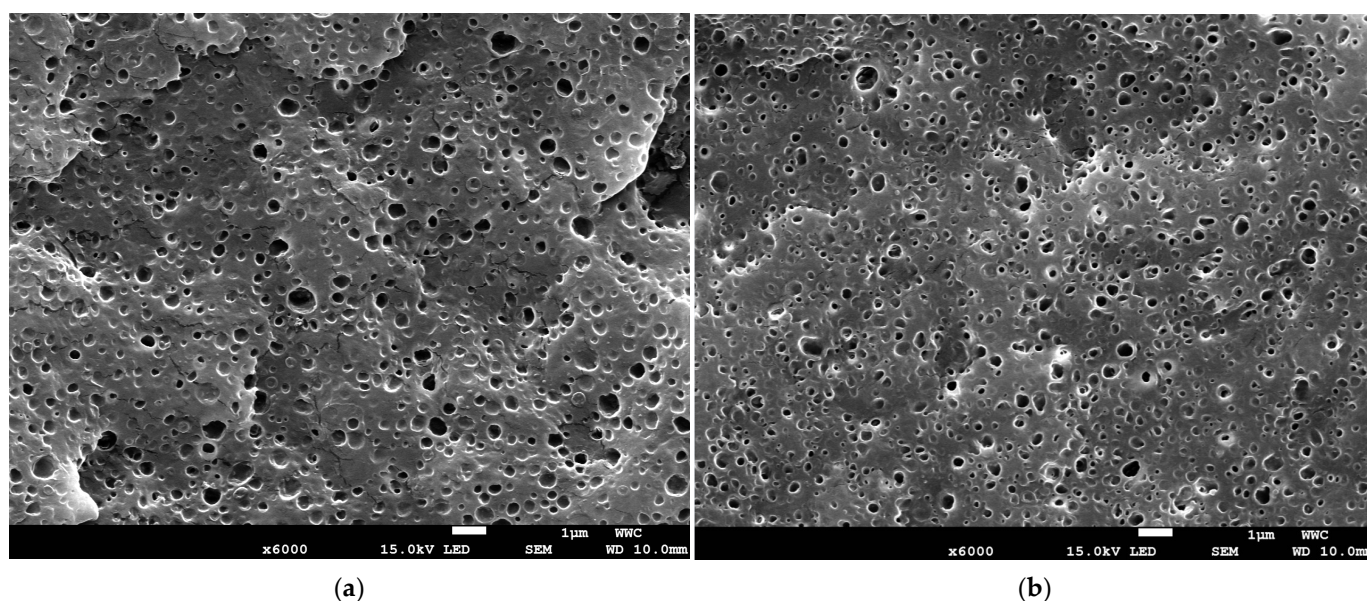


Figure 6. Exemplary SEM micrographs of cryo-fractured and xylene-etched surfaces: (a) PA-EOR-13-0.5 and (b) PA-EOR-13-1.

At constant c_{MAH} , all particle sizes and, consequently, the ID are comparable (see Table 3), and c_{oct} shows no notable influence on the microstructure, as discussed in our previous study [41].

Increasing c_{MAH} from 0.5 wt% to 1.0 wt% decreases $\bar{d}_n$ from (178 ± 4) nm to (153 ± 3) nm (see Table 3). This reduction is attributed to the lower interfacial tension resulting from higher c_{MAH} , as suggested in ref. [37]. It should be noted that both $\bar{d}_w$ and $\bar{d}_v$ decrease significantly, indicating that the larger particles are particularly affected. This also results in a slightly narrower particle-size distribution, as reflected by the reduced PDI . Please note that EOR-16-0.5 exhibits a slightly higher c_{MAH} than EOR-13-0.5 and EOR-15-0.5 (Table 1), resulting in somewhat smaller particle sizes and lower PDI .

Nevertheless, the particle diameters for $c_{MAH} = 0.5$ wt% ($\bar{d}_w \approx 226 \pm 9$ nm) and 1.0 wt% ($\bar{d}_w \approx 184 \pm 3$ nm) remain within the optimal size range of $d_{w,opt} \approx 150$ –250 nm, which is suitable for achieving both low BDTT and high NIS [1]. In addition, the ID of each compound stays well below the $ID_c = 300$ nm reported in refs. [36,37], ensuring that all investigated compounds meet the necessary conditions for effective toughening.

Furthermore, the variation in particle size is relatively small, indicating that the subtle differences in microstructure are unlikely to account for the observed discrepancies in the impact test results.

3.2.2. Compound Viscosity

Both NIS and flowability during processing are particularly important for the intended application of injection molding. Therefore, the η of the compound was measured at 240 °C. Figure 7 shows η as a function of $\dot{\gamma}$ for the representative samples PA-EOR-13-0.5 and PA-EOR-13-1. The corresponding results for PA-EOR-15 and PA-EOR-16 are presented in the Supporting Information (Figure S6). All compounds exhibit shear-thinning behavior as the PA6 chains orient along the flow direction under shear, thereby reducing the resistance to flow. For injection molding, the shear rates typically range between approximately 10^3 and 10^4 s⁻¹, depending on the part geometry and flow rate [71]. Within this range, the η of PA-EOR-13-0.5 is about 19% lower than that of PA-EOR-13-1. The corresponding decreases in η are 12% and 11% for PA-EOR-15 and PA-EOR-16, respectively. This suggests that reducing c_{MAH} lowers the number of covalently bound PA6 chains and thus the number of entanglements between EOR-g-MAH particles and the PA6 matrix, reducing η . This is also discussed in refs. [72,73]. The η decrease is further supported by the larger particle size at lower c_{MAH} , which reduces the total interfacial area. Conversely, higher c_{MAH} yields more entanglements and smaller particles with larger interfacial area—both effects act to increase η .

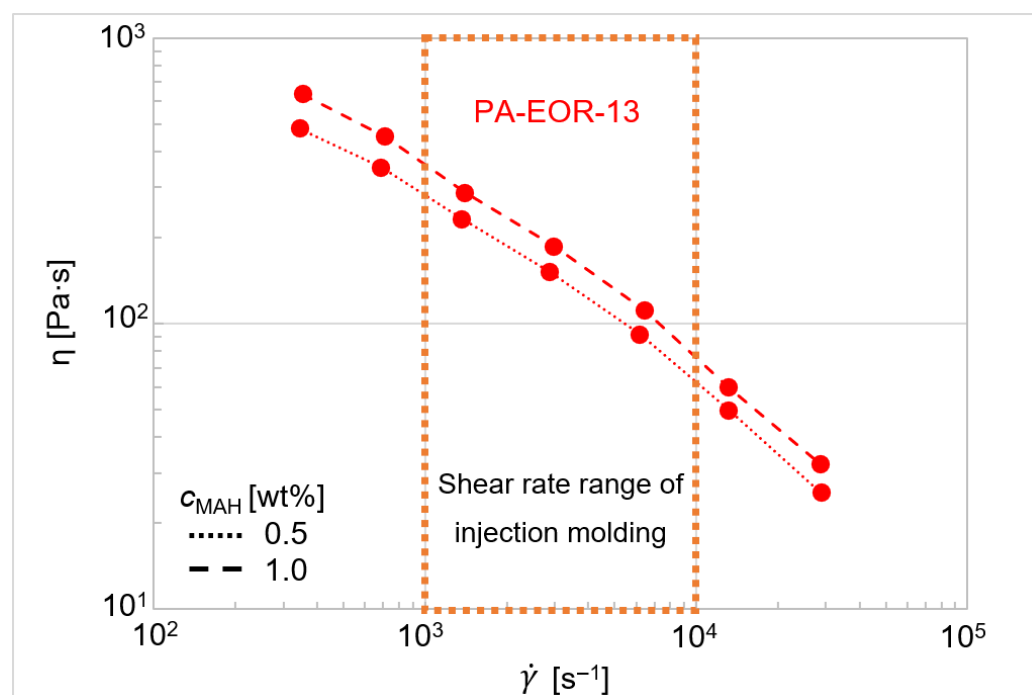


Figure 7. Log–log plot of viscosities η as a function of shear rate $\dot{\gamma}$ at 240 °C for PA-EOR-13 compounds. The dashed orange lines indicate the typical $\dot{\gamma}$ range of injection molding [71]. Data for PA-EOR-13-1 are taken from ref. [41].

3.2.3. Impact Toughness and Energy Dissipation

Instrumented impact testing distinguishes between energy dissipated during crack initiation E_{init} and energy dissipated during crack propagation E_{prop} , providing detailed insight into fracture mechanisms. Below the BDTT, in the brittle fracture regime, there is essentially no resistance to crack propagation, and NIS is primarily governed by E_{init} . Energy dissipation occurs via elastic deformation of the matrix and, above the modifiers'

T_g (here -55 to -50 °C, well below the low T limit of the impact test), also through plastic deformation and, eventually, modifier particle cavitation [7,42].

At the BDTT, the fracture mechanism changes, E_{prop} becomes dominant, and energy dissipation occurs primarily through matrix shear yielding [10]. Stress transfer from the matrix to the particles induces particle deformation and, at a certain stage, leads to cavitation at the particle centers, where the stress is concentrated [7,10]. Particle cavitation converts the triaxial stress state into a uniaxial one, thereby enabling extensive shear yielding of the surrounding matrix, provided that the particle strength is sufficiently high to hinder crack propagation [8,10] and that the particles exhibit high deformability [2,8,10,38–41], allowing for effective activation of shear yielding. It turns out that at low T , the modifier's deformability, as reflected by a low storage modulus E' , is essential for high NIS , whereas at higher T , a balance between strength and ductility, i.e., σ_b together with ε_b , also becomes important.

Figure 8 presents the impact test results as a function of T for PA6 and the PA6 compounds PA-EOR-13, PA-EOR-15, and PA-EOR-16, with modifiers grafted at approximately $c_{MAH} = 0.5$ or 1.0 wt%. Figure 8a shows the overall NIS , whereas Figure 8b and c compare E_{init} and E_{prop} for compounds containing modifiers with different c_{oct} at the same c_{MAH} . Figure 8d–f, in turn, compare compounds containing modifiers with different c_{MAH} but the same c_{oct} . Since all samples exhibit comparable microstructures (particle size, ID , and PDI ; see Section 3.2.1) and adequate adhesion between the modifier and matrix [13], differences in NIS cannot arise from these factors.

The discussion begins with the general trends of the overall NIS in relation to c_{MAH} and c_{oct} , as presented in Figure 8a.

Pure PA6 exhibits brittle behavior across the entire T range. The NIS of the modified compounds is higher than that of neat PA6, even below the BDTT, due to energy dissipation via modifier particle deformation and cavitation. All impact-modified compounds exhibit a BDTT around -20 °C, marked by a sharp increase in NIS , which corresponds to the onset of matrix shear yielding.

As previously shown, increasing c_{oct} from 8 to 13 mol% shifts the BDTT by approximately -5 °C toward lower T (see ref. [41]). This shift is attributed to the lower T_g and lower X_c of the modifier with $c_{oct} = 13$ mol% ($T_g = -50$ °C, $X_c = 14.7 \pm 0.1\%$) compared to the modifier with $c_{oct} = 8$ mol% ($T_g = -44$ °C, $X_c = 24.6 \pm 0.4\%$). DSC and DMTA results for the 8 mol% modifier are provided in Section S2 (Supporting Information) for direct comparison. The increase in c_{oct} enhances particle deformability, as reflected by the lower E' values obtained from DMTA measurements, and promotes cavitation. This leads to a more efficient stress release, which in turn facilitates shear yielding of the surrounding matrix. Further increase in c_{oct} does not shift the BDTT, although using EOR-16 further improves the NIS at the BDTT. This aligns with the fact that the T_g of EOR-13 ($T_g = -50$ °C) and EOR-15 ($T_g = -51$ °C) are similar, whereas EOR-16 has a lower $T_g = -55$ °C (see Table 1). However, the higher deformability of EOR-16 is likely partly offset by a reduction in particle strength, due to its lower X_c and/or MW reduction resulting from β -scission (see also the discussion below).

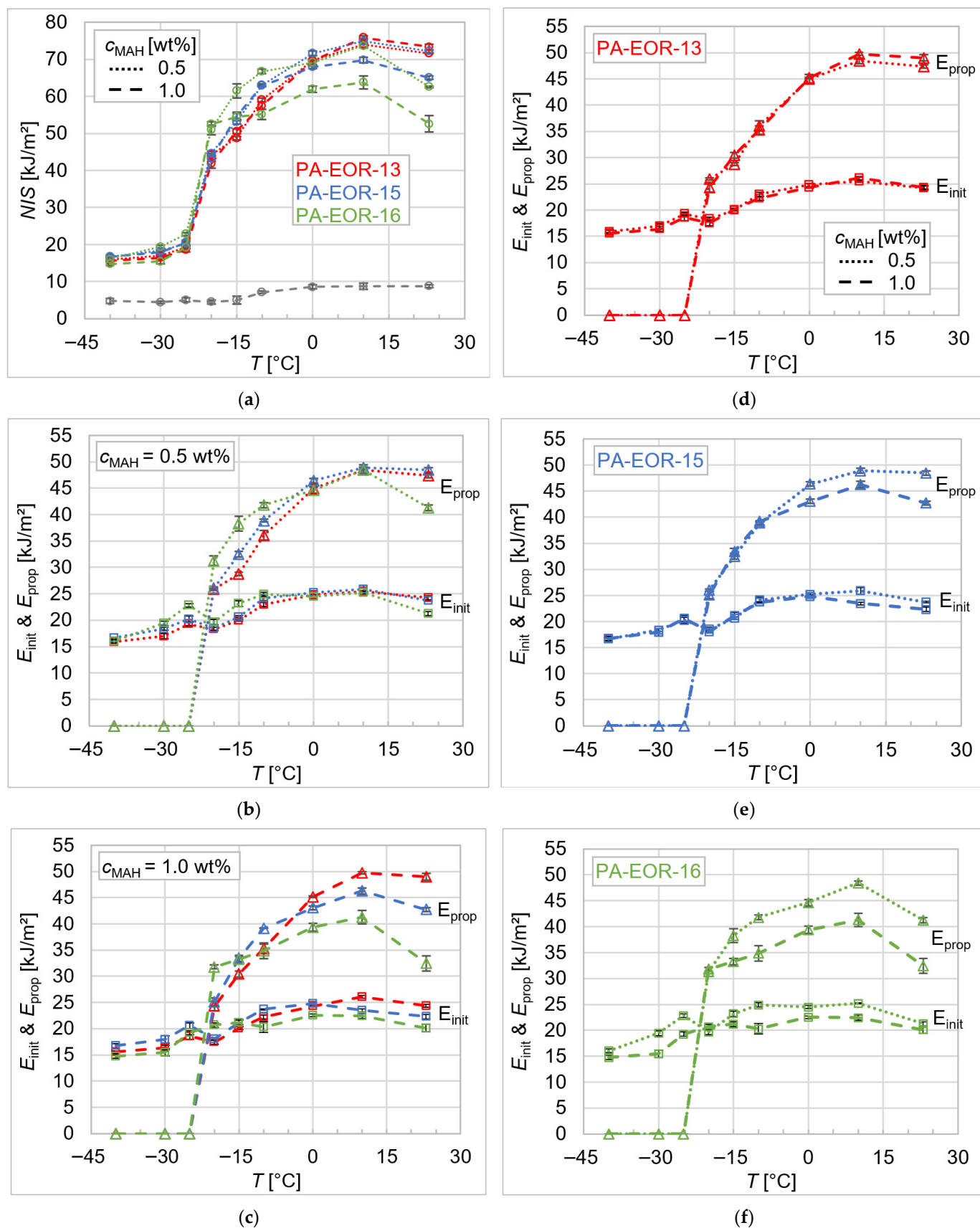


Figure 8. Notched impact test results as a function of temperature T for pristine PA6 (gray) and all studied compounds: (a) overall NIS, (b–f) comparison of the energy dissipated during crack initiation E_{init} ($\square$) and crack propagation E_{prop} (Δ) for modifiers with different octene content c_{oct} at constant MAH content c_{MAH} (b,c), and for varying c_{MAH} at constant c_{oct} (d–f). Data for PA-EOR-13-1 and PA-EOR-15-1 are taken from ref. [41].

For the subsequent detailed discussion, the influence of c_{MAH} on the NIS is analyzed for compounds containing modifiers at the same c_{oct} values.

According to Figure 8d, EOR-13-based compounds show no measurable influence of c_{MAH} on E_{init} and E_{prop} . This is consistent with the comparable E' obtained from DMTA of the pure modifiers and with their tensile test properties. The lower M_n of EOR-13-1 compared to EOR-13-0.5, resulting from β -scission, appears to be compensated by the presence of the additional high- MW chains formed by cross-linking. Despite differences in yielding behavior, both materials exhibit similar deformability (E') and comparable σ_b and ε_b , reflecting a balanced combination of strength and ductility. Overall, the differences in the MWD of EOR-13-1 and EOR-13-0.5 do not lead to notable changes in the NIS of the corresponding compounds across the entire T range.

For PA-EOR-15-0.5 and PA-EOR-15-1, the mechanical responses at low T ($T \leq -10$ °C) are essentially identical (see Figure 8e), which is consistent with DMTA results indicating that grafting does not measurably affect the deformability (E') of the modifiers. At more elevated T ($T > -10$ °C), however, PA-EOR-15-1 exhibits lower E_{prop} and E_{init} than PA-EOR-15-0.5, in agreement with the tensile test results of the pure modifiers. While σ_b remains similar, ε_b and W of EOR-15-1 are markedly lower than those of EOR-15-0.5. Consequently, the strength–ductility balance is compromised, leading to lower E_{init} and E_{prop} . The lower ε_b at higher c_{MAH} is attributed to increased polar intermolecular interactions and steric hindrance, which restrict chain sliding in PA-EOR-15-1 compared to PA-EOR-15-0.5, particularly in the amorphous phase. As a result, in the latter system, the triaxial stress state is more efficiently converted into a predominantly uniaxial one, enabling the formation of a more extensive shear-yielding zone ahead of the crack tip due to its higher deformation, until failure at comparable particle strength. This larger shear-yielding zone involves the deformation of a greater number of EOR particles, thereby increasing E_{prop} , while higher local stresses cause premature particle failure, limiting E_{init} . We do not attribute the observed differences between PA-EOR-15-1 and PA-EOR-15-0.5 to changes in the MWD, as no such effect was observed for the PA-EOR-13 systems. The fact that an increase in c_{MAH} has no effect on the NIS in PA-EOR-13 is attributed to the higher X_c of EOR-13. This results in a higher σ_b and a smaller contribution of the amorphous regions to ε_b .

In contrast, the differences in E_{init} and E_{prop} observed between PA-EOR-16-1 and PA-EOR-16-0.5 (Figure 8f) are attributed to the significantly reduced MW of the modifier EOR-16-1. As demonstrated by GPC, the grafting process of EOR-16-1 is dominated by β -scission, rather than cross-linking, resulting in a pronounced decrease in MW , particularly in M_w . Consequently, the mechanical performance is inferior, as reflected by lower σ_b , ε_b and W . As a result, E_{prop} is significantly reduced, starting just above the BDTT (≈ -15 °C) and E_{init} is significantly reduced compared to PA-EOR-16-0.5 over the entire T range. The combination of reduced σ_b and ε_b promotes premature particle failure in PA-EOR-16-1, limiting the development of an extensive shear-yielding zone in the matrix and thus reducing E_{prop} . Premature particle failure also lowers the energy dissipated during crack initiation, resulting in a decreased E_{init} , even at lower T , despite the fact that the modifier deformability, as indicated by E' from DMTA, remains largely unchanged.

Finally, we compare the influence of c_{oct} on the NIS for compounds with the same c_{MAH} . At $c_{\text{MAH}} = 0.5$ wt% (Figure 8b), increasing c_{oct} leads to a slight increase in E_{init} , up to $T = 0$ °C. In the same T range but above the BDTT, a measurable increase in E_{prop} is also observed, with the effect being most pronounced for the highest c_{oct} of 16 mol%. Since the differences in MWD at $c_{\text{MAH}} = 0.5$ wt%, particularly with respect to the high- MW fraction, are small (see Table 1 and Figure S4, Supporting Information), the enhanced energy dissipation cannot be attributed to MWD effects. Instead, this behavior is attributed to the increased deformability, as indicated by the lower E' obtained from

DMTA, which increases with decreasing X_c . In addition, the higher ε_b with higher c_{oct} , likewise associated with reduced X_c , appears to compensate for the concomitant reduction in σ_b , assuming that the tensile properties are representative of the mechanical behavior in this T range.

Starting at approximately 0 °C, EOR-16-0.5 begins to lose its effectiveness in impact toughening, as reflected by reductions in both E_{prop} and E_{init} . At 23 °C, a slight decrease in these contributions to energy dissipation is observed for all compounds, including those with $c_{MAH} = 1.0$ wt%. This decline is attributed to a reduction in particle strength caused by the progressively increasing fraction of molten modifier. This effect becomes more pronounced with increasing c_{oct} , which is consistent with the DSC results.

At $c_{MAH} = 1.0$ wt% (Figure 8c), E_{prop} of PA-EOR-15-1 and PA-EOR-16-1 shows only a slight increase, just above the BDTT, and falls below that of PA-EOR-13-1 from 0 °C onward. E_{init} of PA-EOR-16-1 is reduced to values that are comparable to PA-EOR-13-1 up to -15 °C and becomes lower at higher T . For PA-EOR-15-1, E_{init} remains higher than that of PA-EOR-13-1, as observed at $c_{MAH} = 0.5$ wt%, but also drops below it above 0 °C.

At $c_{MAH} = 0.5$ wt%, changes in NIS as a function of c_{oct} can be mainly explained by the decrease in X_c with increasing c_{oct} . At $c_{MAH} = 1.0$ wt%, however, the differences between compounds with varying c_{oct} originate from different mechanisms. Up to approximately 0 °C, the behavior of PA-EOR-15-1 is similar to that of PA-EOR-15-0.5. At higher T , the response of PA-EOR-15-1 is dominated by a reduction in ε_b , which is attributed to increased polar intermolecular interactions and steric hindrance that restrict chain sliding, while the particle strength remains comparable to PA-EOR-15-0.5. The inferior performance of PA-EOR-16-1 can be particularly attributed to a reduced σ_b combined with insufficient ε_b , resulting from MW degradation during modifier grafting together with restricted chain sliding in the amorphous phase.

In summary, while for c_{oct} between 8 mol% and 15 mol% at a constant $c_{MAH} = 1.0$ wt%, it was sufficient to consider c_{oct} -dependent differences in elastic deformability to explain the changes in NIS [41]; this approach is no longer sufficient to explain the c_{MAH} -dependent changes at $c_{oct} \geq 15$ mol%. In particular, the changes observed from the BDTT onward, upon increasing the c_{MAH} content from 0.5 wt% to 1.0 wt%, can only be explained by a reduction in plastic deformability resulting from enhanced polar interactions, together with the consideration of the adequacy of the modifier strength.

4. Conclusions

This study demonstrates that the NIS of PA6/EOR-g-MAH compounds is governed by the interplay between c_{MAH} , c_{oct} , and the competition between β -scission and cross-linking reactions during grafting. By keeping the initial modifier MW comparable and the blend microstructure similar, the influence of grafting-induced changes in the MWD and modifier properties on impact performance could be isolated and clearly evaluated. The instrumented impact test was valuable, as it distinguished E_{init} from E_{prop} , revealing the parameters and their correlations controlling compound toughness at different T .

MAH grafting shifts the MWD toward lower MW due to β -scission, with degradation becoming more pronounced at higher c_{MAH} and c_{oct} . At $c_{MAH} = 0.5$ wt%, chain scission dominates for all modifiers, while cross-linking remains negligible. At $c_{MAH} = 1.0$ wt%, the balance becomes strongly c_{oct} -dependent: EOR-13 and EOR-15 show some compensation of degradation by cross-linking, whereas for EOR-16, β -scission clearly prevails, leading to a pronounced reduction in MW . These MW changes are important because the original materials cannot be easily replaced due to economic and availability constraints. Moreover, shifting the MWD to higher MW may not compensate for β -scission as effectively as the small fraction of very long chains that preserve the modifier performance.

These MW scenarios directly reflect the observed impact performance. While, for c_{oct} between 8 mol% and 15 mol% at a constant $c_{MAH} = 1.0$ wt%, the changes in NIS can be adequately rationalized by c_{oct} -dependent differences in elastic deformability [41], this approach is no longer adequate to explain the c_{MAH} -dependent changes at $c_{oct} \geq 15$ mol%. In particular, the changes in toughness observed from the BDTT onward upon increasing the c_{MAH} from 0.5 wt% to 1.0 wt% require considering both the reduction in plastic deformability caused by enhanced polar interactions, particularly restricting chain sliding in the amorphous phase, and the adequacy of the modifier strength. As β -scission is partially compensated by cross-linking in EOR-15, the impact response of PA-EOR-15-1 is primarily determined by the loss in ductility. In contrast, for EOR-16, MW degradation dominates and, together with reduced ductility, results in the inferior toughness of PA-EOR-16-1. Additionally, reduced X_c and the earlier onset of successive melting further contribute to the diminished performance of PA-EOR-16-1 and PA-EOR-15-1 compared to PA-EOR-13-1 and -0.5. Both PA-EOR-13 variants exhibit nearly c_{MAH} -independent performance, as grafting-induced cross-linking maintains strength, while ductility remains largely unaffected by c_{MAH} due to the higher X_c .

At $c_{MAH} = 0.5$ wt%, changes in NIS as a function of c_{oct} can be mainly explained by the decrease in X_c with increasing c_{oct} , thereby enhancing the modifiers' elastic and plastic deformation capability and their ability to promote cavitation-driven shear yielding. This effect increases the NIS of PA-EOR-15-0.5 and PA-EOR-16-0.5 at low and intermediate T up to about 0 °C above the performance of both PA-EOR-13 variants. Only for PA-EOR-16-0.5 at RT does the loss in strength due to successive melting produce a significant drop in NIS compared to the other two compounds.

Overall, the impact performance of PA6/EOR-g-MAH compounds results from a balance between c_{oct} , c_{MAH} , and grafting-induced MW changes. A moderate $c_{MAH} = 0.5$ wt% and $c_{oct} = 15$ mol% offers an optimal compromise between strength, elastic deformability, and ductility, delivering low BDTT and high NIS across a broad T range, while also maintaining good compound processability by avoiding excessive viscosity caused by an increased number of PA6 chains that are covalently anchored to the modifier particles. While core-shell and other sophisticated polymer alloy concepts might achieve higher performance in certain applications, the approach presented here is aimed at reducing the material design complexity and processing requirements at a high cost efficiency.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/polym18050590/s1>. Figure S1: FTIR spectrum of EOR-13-0 (solid line), EOR-13-0.5 (dotted line), and EOR-13-1 (dashed line) normalized to same area underneath the CH_2 -band at 2919 cm^{-1} . Figure S2: Exemplary DSC endotherms (heat flow from the 2nd heating runs) as a function of temperature T for all investigated modifiers with the addition of EOR-8 (a), together with the corresponding cumulative residual crystallinities X_c (b). Data for EOR-8-1, EOR-13-1, and EOR-15-1 are taken from ref. [41]. Table S1: Properties of the ungrafted and grafted EOR copolymers used in this and our previous study [41]: ρ = density, c_{oct} = octene content, c_{MAH} = MAH content, T_g = glass transition temperature, T_m = melting temperature, $X_c^{(a)}$ = uncorrected crystallinity, $X_c^{(b)}$ = crystallinity corrected for the process additive contribution, M_n = number-average molecular weight, and M_w = weight-average molecular weight. Values are reported as mean values with standard deviations where applicable. Data for EOR-8-1, EOR-13-1, and EOR-15-1 are taken from ref. [41]. Figure S3: Loss modulus E'' and storage modulus E' (log-scale) versus temperature T , measured by DMTA for all investigated modifiers, with the addition of EOR-8. The brittle-ductile transition temperature (BDTT) range obtained from impact tests is shown as orange dashed lines. The shifted temperature $T_{shifted}$ accounts for the high strain rates experienced during impact testing [8]. Data for EOR-8-1, EOR-13-1, and EOR-15-1 are taken from ref. [41]. Figure S4:

Molecular weight distributions (MWD) of all investigated modifiers. Figure S5: Exemplary SEM micrographs of cryo-fractured and xylene-etched surfaces: (a) PA-EOR-15-0.5, (b) PA-EOR-15-1, (c) PA-EOR-16-0.5, and (d) PA-EOR-16-1. Figure S6: Log–log plot of viscosities η as a function of shear rate $\dot{\gamma}$ at 240 °C for PA-EOR-15 (a) and PA-EOR-16 (b). The dashed orange lines indicate the typical $\dot{\gamma}$ range of injection molding [71]. Data for PA-EOR-15-1 are taken from ref. [41].

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Abbreviations

The following abbreviations are used in this manuscript:

ABS	Acrylonitrile-butadiene-styrene
ASTM	American Society for Testing and Materials
BDTT	Brittle–ductile transition temperature
c_{MAH}	MAH content
c_{oct}	Octene content
DMTA	Dynamic mechanical thermal analysis
DIN	Deutsches Institut für Normung
DSC	Differential scanning calorimetry
$\bar{d}_n$	Number-average particle diameter
$\bar{d}_v$	Volume-average particle diameter
$\bar{d}_w$	Weight-average particle diameter
$d_{w,opt}$	Optimal weight-average particle diameter
D_i	Inner screw diameter
D_o	Outer screw diameter
EN	European Standard
EOR	Ethylene/1-octene rubber
EOR-g-MAH	Maleic anhydride grafted ethylene/1-octene copolymer
EPDM	Ethylene-propylene-diene monomer rubber
EPR	Ethylene-propylene rubber
E	Elastic modulus (tensile test)
E_{init}	Crack initiation energy
E_{prop}	Crack propagation energy
E'	Storage modulus (DMTA)
E''	Loss modulus (DMTA)
FTIR	Fourier transform infrared spectroscopy
GPC	Gel permeation chromatography
IR	Infrared
ID	Interparticle distance

ID_c	Critical interparticle distance
ISO	International Organization for Standardization
MA	Maleic acid
MAH	Maleic anhydride
M_n	Number-average molecular weight
M_w	Weight-average molecular weight
MW	Molecular weight
MWD	Molecular weight distribution
NIS	Notched impact strength
PA	Polyamide
PA6	Polyamide 6
PDI	Polydispersity index
RT	Room temperature
SEBS	Styrene-ethylene-butylene-styrene
SEM	Scanning electron microscopy
T	Temperature
T_g	Glass transition temperature
$T_{g,shifted}$	Shifted glass transition temperature
T_m	Melting temperature
$T_{shifted}$	Shifted temperature
UV	Ultraviolet
W	Working capacity
X_c	Crystallinity
ε	Strain
ε_b	Strain at break
ε_y	Strain at yield
$\dot{\gamma}$	Shear rate
η	Viscosity (compound)
ρ	Density (modifier)
σ	Stress
σ_b	Stress at break
σ_y	Stress at yield

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