

Article

Tailoring Impact Toughness of PA6: Isolated Effects of Modifier Octene Content and Molecular Weight in MAH-Grafted EOR Copolymers

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Abstract

The impact modification of polyamide 6 (PA6) using maleic anhydride grafted ethylene/1-octene copolymers (EOR-g-MAH) is well-established, yet the isolated influence of intrinsic modifier parameters—specifically octene content c_{oct} and molecular weight MW —remains insufficiently understood due to confounding microstructural effects. This study presents a systematic approach to decouple these variables by maintaining constant grafting degree, modifier content, and compound morphology. A series of PA6/EOR-g-MAH compounds was prepared with controlled variations in c_{oct} (8–15 mol%) and MW (34–42 kg/mol). Instrumented Charpy impact testing across a temperature range from $-40\text{ }^{\circ}\text{C}$ to $+23\text{ }^{\circ}\text{C}$ enabled quantification of crack initiation and propagation energies (E_{init} and E_{prop}), providing mechanistic insight into the brittle–ductile transition. Complementary thermal, rheological, and tensile analyses of the modifiers revealed how c_{oct} governs cavitation behavior and low-temperature toughness, while MW in particular influences particle integrity and energy dissipation at elevated temperatures. The results demonstrate that targeted adjustment of c_{oct} and MW allows for the precise tuning of brittle–ductile transition temperature (BDTT) and impact resistance. The compound containing a high- MW modifier with intermediate c_{oct} (13 mol%) exhibited the most favorable balance of toughness and strength retention at elevated temperatures. These findings offer design principles for engineering thermoplastics with enhanced performance across broad service conditions.

Keywords: impact strength; maleic anhydride; ethylene/1-octene copolymers; octene content; molecular weight



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1. Introduction

Polyamide 6 (PA6) is one of the most widely used engineering plastics and finds application across various industries, including the automotive, household and sports sectors. This popularity is largely due to its high stiffness, high strength and good chemical resistance. However, despite these advantages, PA6 exhibits a relatively low notched impact strength NIS , which limits its range of applications [1]. In safety-relevant components, for example, NIS is a crucial parameter, as even minor surface scratches can drastically alter the material's failure behavior and lead to brittle fracture. Consequently, improving the NIS of PA6 is vital to broaden its application potential.

To enhance the NIS of PA6, the polymer is commonly melt-blended with impact modifiers that form a dispersed, toughened phase within the matrix. Various types of maleic

anhydride (MAH)-grafted (co)polymers have proven effective in this regard. These include styrene-ethylene-butylene-styrene (SEBS-g-MAH) [2–5], acrylonitrile-butadiene-styrene (ABS-g-MAH) [6,7], ethylene-propylene-diene monomer rubber (EPDM-g-MAH) [8–11], ethylene-propylene rubber (EPR-g-MAH) [2–5,8,10–12] and ethylene/1-octene rubber (EOR-g-MAH) [2,13–15]. These modifiers promote ductile fracture behavior and significantly increase the *NIS* of PA6, both at room temperature [15] and even at sub-ambient temperatures [2–5,10–13].

Olefin-based modifiers, compared with styrene-based modifiers (e.g., SEBS-g-MAH, ABS-g-MAH), offer good resistance to automotive-relevant chemicals (e.g., cleaning agents), a favorable volatile organic compound (VOC) profile, and robust weathering behavior, including UV-stability [16,17]. EOR-g-MAH is the focus of the present study due to its particular advantages, notably a broader range of tunable properties than other olefin-based modifiers. A wide variety of high-volume industrial grades is available at a competitive cost, making EOR-g-MAH suitable for large-scale PA6 components [18,19]. Properties such as crystallinity X_c and glass transition temperature T_g can be readily adjusted through the octene content c_{oct} [20,21], while molecular weight *MW* serves as an independent parameter for tuning performance.

At temperatures T below the modifier's T_g , both the matrix and the modifier deform purely elastically. When T exceeds the modifier's T_g , the modifier undergoes plastic deformation; however, this alone is insufficient to trigger shear yielding of the matrix. As a result, the material exhibits brittle failure behavior and relatively low *NIS* [8–10,12,13]. The transition from brittle to ductile fracture occurs at the so-called brittle–ductile transition temperature (BDTT), where particle cavitation initiates shear yielding in the matrix. This process leads to ductile fracture and a significant increase in *NIS*, while the energy dissipated through particle cavitation and fracture plays only a secondary role [3,8–10,12].

Numerous studies have investigated how various factors influence the microstructure and, consequently, the *NIS* of PA6. These factors include the MAH content c_{MAH} of the modifier [2,3,5,9,13,14,22], the overall modifier content [1,8,9,12,13,15,23,24], and the processing parameters [1,2,11,22–24], particularly the processing temperature [1,11,22–24] and extrusion method [1,2,11,22,23].

Previous studies have established general trends in impact modification but mostly compared different modifier types rather than systematically varying individual parameters within a single system. The focus was primarily on EPR, EPDM, and SEBS, or on comparing EORs with these modifiers. As a result, the modifiers in these studies typically differed in more than one material parameter [2–5,11].

Differences in *NIS* and BDTT observed between various modifier types often originated from variations in microstructure, which were, in turn, influenced by factors such as melt flow behavior, e.g., melt elasticity and viscosity [2–5]. Microstructural variations reported across different studies further complicate the comparison and interpretation of the results. These discrepancies mainly arise from differing processing conditions, such as the use of single-screw [3,9,13,24,25] versus twin-screw extruders [9,11,13], as well as differences in the properties of the PA6 matrix (e.g., low *MW* [1,3,5,13,25,26] versus high *MW* [3–5,10,11,25,26]) and modifier characteristics, particularly in terms of c_{MAH} [2,3,5,13,14] and *MW* [5,25,26].

Despite variations in materials and processing conditions across studies, several consistent conclusions can be drawn regarding the influence of modifier properties on the *NIS* of PA6: Achieving ductile fracture and high *NIS* requires shear yielding, which is initiated by a transition from a plane-strain to plane-stress state via modifier particle cavitation within an optimized microstructure. This demands a homogeneous dispersion of spherical modifier particles with a defined size and spacing regime. Particles that are

too small cannot cavitate, while excessively large particles lead to increased interparticle distances ID that limit stress transfer and plastic deformation [1,2,5,8]. Within the optimal size and spacing range, particle size itself has only a small influence on the toughening efficiency [2,5]. For PA-based systems, a critical interparticle distance, $ID_c \approx 300$ nm, has been identified [1,24]. The critical value is largely independent of the specific modifier material and should not be exceeded. Furthermore, for EOR-based PA6 compounds, an optimal modifier particle size of about $d_{w,opt} \approx 150$ nm (weight-average value) has been reported [2].

Increasing c_{MAH} of the modifiers reduces interfacial tension, resulting in smaller particles [2,3,5,9,13,14]. Smaller particles as well as larger modifier content both lower the ID and shift the BDTT to lower values [2,3,5,9,11,13,22].

At T below the BDTT, a low T_g of the modifier is crucial for relatively high NIS [3,27,28]. A lower elastic modulus of the modifier compared to the matrix is also essential for cavitation-induced shear yielding [3,8,11,27]. Modifiers with a low modulus, i.e., high deformability and, consequently, with high cavitation ability lead to lower BDTT and higher NIS [3,10,11,27,29,30], whereas highly crystalline modifiers, characterized by higher stiffness and T_g , result in elevated BDTT and reduced NIS [2,4,25,28,30]. While ref. [11] reported no clear correlation between tensile properties, e.g., tensile strength or strain at break and NIS , refs. [29,31] suggested that modifiers with lower stress at break, attributed to low X_c , promote cavitation and thereby enhance NIS . Limited attention has been given to the influence of modifier MW on impact properties, and it is often excluded from material characterization. Previous studies have attributed low NIS to poor microstructures arising from MW -related differences in flowability and viscosity η : low- MW modifiers, characterized by lower η , tend to form particles that are too small to cavitate [4,5] or may even develop a continuous phase [25]. In contrast, high- MW modifiers with higher η generally result in improved NIS . However, the intrinsic mechanical properties of modifiers, which are strongly governed by MW , have received little consideration, despite their potential influence on NIS [11,32]. MW also affects the tensile properties, as an increase in MW results in a higher entanglement density, thereby enhancing the tensile strength [32].

Furthermore, a correlation between the T -dependent modifier properties and the NIS across different testing temperatures is often lacking. Thermo-mechanical analysis (DMTA) has been conducted either on isolated modifiers [2,5,10,11,25] or on the compound [4,16], but these approaches have not been correlated or considered together. Interpretation commonly focuses on the stiffness of the modifier and its T_g within the compound [4,16]. It has been shown that ductile fracture occurs at T where the storage modulus ratio between the matrix and the modifier falls below 10 [2,5,10,11,25]. The role of residual X_c at the respective testing temperatures is frequently overlooked. Since modifiers typically exhibit low X_c and possess low melting temperatures T_m [32], their strength decreases with increasing T within the application range. This may negatively impact the NIS . The thermal and mechanical properties of EOR modifiers can also be tailored by adjusting c_{oct} [20,21,32]. Increasing c_{oct} lowers T_g and X_c , thereby not only reducing T_m but also altering the tensile properties of the modifiers across the entire T range up to T_m , which in turn affects the T dependence of the NIS [20,21,32].

Thus, despite extensive research, the relationship between the properties of EOR-g-MAH modifiers, such as c_{oct} and MW in particular, and their influence on the T -dependent impact properties, as well as the underlying mechanism, remain not fully understood. Therefore, a detailed and systematic investigation of the effects of c_{oct} and MW on the impact properties across a wide T range is warranted.

While core-shell and more complex polymer alloy concepts, together with new compatibilization strategies, are currently widely discussed [33], this work instead focuses on cost reduction and process simplification by targeting industrial-scale PA6/EOR-g-MAH compounds with a controlled microstructure. The main aim is to disentangle the impact of modifier properties on the *NIS* of the compound from microstructural effects. To reduce complexity, c_{MAH} in the EOR-g-MAH was fixed at 1.0 wt%. The *MW* of the modifiers was restricted to 34,000–42,000 g/mol to minimize potential microstructural changes arising from variations in the viscosity ratio between the modifier and the matrix material, which determines the efficiency of droplet break-up and dispersion during melt mixing [22,34,35]. The effect of c_{oct} on viscosity is moderate, with *MW* remaining the dominant factor controlling the microstructure. This choice was further guided by economic considerations and material availability, as ethylene- α -olefin modifiers with higher *MW* are less commonly at scale. This reflects the fact that the primary application sector for this class of modifiers is packaging, where low to moderate *MW* are favored to enable low melt viscosity, high processing stability at elevated throughputs, and a cost-efficient large-scale production. The c_{oct} was varied between 8 and 15 mol%, with only one parameter altered at a time, while the other remained constant, enabling a clear assessment of their individual effects on the *NIS* of the compound, starting from capturing the relevant variation in chain flexibility and particle cavitation without introducing excessive softening and melting of the modifier. Furthermore, high c_{oct} levels would exacerbate feeding difficulties and extrusion instabilities due to pronounced softening and stickiness, e.g., causing granules to agglomerate, block the feeder, or stick to the extruder screw, and are associated with higher synthesis costs and limited large-scale availability. In contrast to previous studies, an instrumented Charpy impact tester was employed to analyze fracture behavior in detail by separating the total *NIS* into the energy for crack initiation E_{init} and crack propagation E_{prop} . The testing *T* was systematically varied between -40 and 23 °C. Key modifier properties, including residual X_c , T_g , storage modulus and tensile properties (at 23 °C), were measured and correlated with the impact results. This approach provided valuable insights into how *T*-dependent changes in modifier properties influence the *NIS* of the compound and allowed the identification of the dominant material parameters governing *NIS* across different *T* ranges, thereby supporting the design of tailor-made materials for industrial applications.

2. Materials and Methods

2.1. Materials

A heat-stabilized, medium-viscosity polyamide 6 (PA6) (AKROMID® B3 1 natural) supplied by AKRO-PLASTIC GmbH (Niederzissen, Germany) was used as matrix material. In all compounds, the content of maleic anhydride (MAH)-grafted ethylene/1-octene copolymer (EOR-g-MAH) was kept constant at 20 wt%, and the grafting degree (MAH content c_{MAH}) was fixed at approximately 1 wt%. The chemical structure of EOR-g-MAH is shown in the ref. [18]. In Series I and Series II, the octene content c_{oct} and the molecular weight *MW* were varied, respectively, as illustrated schematically in Figure 1. The nomenclature for the modifier is as follows: EOR-“ c_{oct} [mol%]”-“number-average molecular weight M_n [kg/mol]”. The nomenclature for the compound is as follows: PA-EOR-“ c_{oct} [mol%]”-“ M_n modifier [kg/mol]”. The properties of the modifiers, determined by the methods described below, are summarized in Table 1.

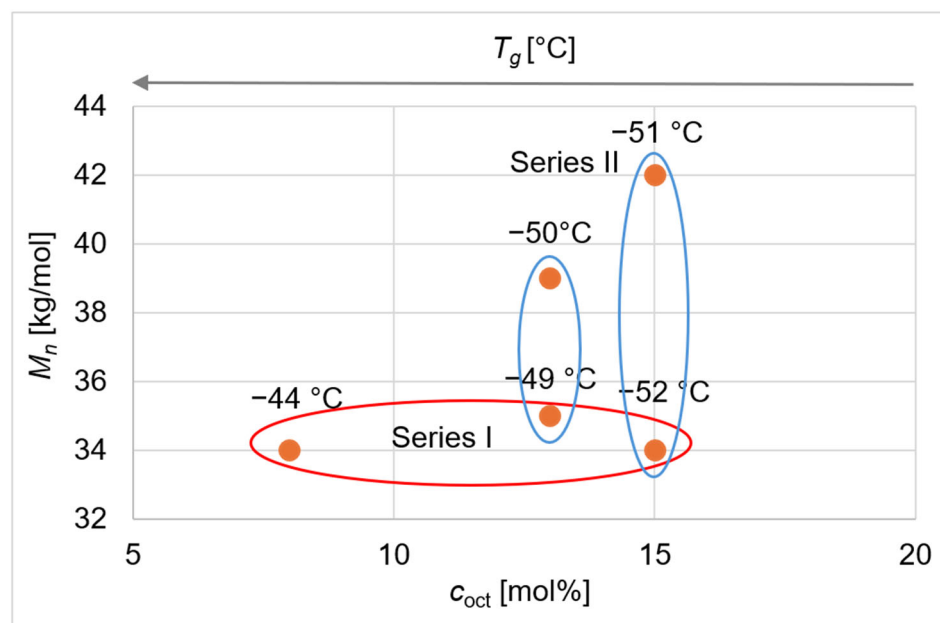


Figure 1. Selection scheme of the EOR-g-MAH modifiers used in this study. The indicated temperatures correspond to the glass transition temperatures T_g . M_n and c_{oct} denote the number-average molecular weight and octene content of the modifiers, respectively.

Table 1. Properties of the modifiers 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 = crystallinity, M_n = number-average molecular weight and M_w = weight-average molecular weight.

Designation	Gravimetry		FTIR	DMTA		DSC	GPC	
	c_{oct} [mol%]	ρ [g/cm ³]	c_{MAH} [wt%]	T_g	T_m	X_c	M_n	M_w
EOR-8-34	8.4 ± 0.4	0.8863 ± 0.0015	0.86 ± 0.04	−44	80.7 ± 1.0	24.6 ± 0.4	34	108
EOR-13-35	12.8 ± 0.4	0.8712 ± 0.0010	1.00 ± 0.03	−49	61.0 ± 0.2	16.4 ± 0.4	35	107
EOR-13-39	13.0 ± 0.2	0.8705 ± 0.0004	0.95 ± 0.04	−50	54.5 ± 0.1	14.7 ± 0.1	39	146
EOR-15-34	14.5 ± 0.3	0.8658 ± 0.0006	0.89 ± 0.04	−52	37.8 ± 0.2	11.5 ± 1.1	34	119
EOR-15-42	14.9 ± 0.2	0.8647 ± 0.0004	0.95 ± 0.02	−51	48.5 ± 0.4	11.5 ± 0.1	42	138

2.2. Characterization of the Modifiers

2.2.1. Gravimetry

The granules' density ρ [g/cm³] of the ungrafted modifier was used to determine c_{oct} [mol%] of the modifiers, according to the procedure described in ref. [21]:

$$c_{oct}[\text{mol}\%] = 17.6345 - 37.0185 \rho[\text{g}/\text{cm}^3] + 19.4252 \rho^2[\text{g}/\text{cm}^3]^2 \quad (1)$$

ρ was measured at 23 °C using a density kit (Mettler-Toledo XP205, Mettler-Toledo GmbH, Greifensee, Switzerland) with ethanol (purity 96%, relative density d_{20 °C}/4 °C = 95.1–96.9%) as immersion medium. The density of ethanol was measured using a pycnometer. For each modifier, five independent ρ measurements were performed to determine the mean and standard deviation, from which c_{oct} values and their uncertainties were calculated via error propagation. The measured ρ and the calculated c_{oct} are summarized in Table 1.

2.2.2. Fourier Transform Infrared Spectroscopy

Measurements of c_{MAH} on pressed films were performed using a Fourier transform infrared (FTIR) spectrometer (Thermo Scientific™ Nicolet™ iS™50, Thermo Fisher Scientific Inc., Waltham, MA, USA) according to the procedure described in refs. [22,36].

Films were prepared according to ASTM D6645 [37]. The granules were placed between two polytetrafluoroethylene (PTFE) foils in a heated hydraulic lab press (Manual Press, Graseby Specac, now Specac Ltd., Orpington, UK). After reaching a temperature $T = 50\text{ }^{\circ}\text{C}$ above the modifier's melting temperature T_m , a pressure of two tons was applied. After 60 s, T was reduced below T_m , while maintaining a constant pressure of two tons. To convert maleic acid into MAH, the pressed films were dried for at least 16 h at $110\text{ }^{\circ}\text{C}$ in a vacuum oven at 20 mbar. This step was necessary because maleic acid and its anhydride exhibit different absorption bands and extinction coefficients [22,36]. For each spectrum, 32 scans were measured in transmission under dry air atmosphere. The absorption spectra were recorded in a wavenumber range of $4000\text{--}600\text{ cm}^{-1}$ with a step size of 0.2411 cm^{-1} . All spectra are baseline corrected, and a background scan was performed prior to each measurement. According to [36], c_{MAH} was calculated as follows:

$$c_{\text{MAH}}[\text{wt}\%] = K \cdot \frac{A_{1791\text{ cm}^{-1}}}{A_{2019\text{ cm}^{-1}}} \quad (2)$$

Because the correction factor K may vary depending on the spectrometer used, it was determined from materials with known c_{MAH} to be $K = 0.07347$ [36]. The peak band at 1791 cm^{-1} corresponds to the symmetrical C=O stretching vibration of MAH, while the peak at 2019 cm^{-1} corresponds to the methylene (CH_2) combination band [18,36,37]. $A_{1791\text{ cm}^{-1}}$ and $A_{2019\text{ cm}^{-1}}$ refer to the respective peak areas. $A_{2019\text{ cm}^{-1}}$ was used to correct for variations in sample thickness. This band is frequently employed because it is primarily influenced by the copolymer and only negligibly by MAH [37]. Peak areas were determined by integrating the total area between the peak and the baseline using OriginLab (OriginLab Corporation, Northampton, MA, USA). The resulting c_{MAH} of the modifiers are reported in Table 1 as mean values with standard deviations derived from at least two independent measurements. Representative FTIR spectra for EOR-13-39 (ungrafted, $c_{\text{MAH}} = 0.5$ and $1.0\text{ wt}\%$) are shown in the Supporting Information of ref. [38].

2.2.3. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was used to investigate the melting behavior of the modifiers, allowing the determination of the temperature-dependent crystallinity $X_c(T)$ and T_m . Thermograms were recorded using a DSC instrument (DSC 1, Mettler-Toledo AG, Schwerzenbach, Switzerland) over a T range of -80 to $200\text{ }^{\circ}\text{C}$ with heating and cooling rates of 10 K/min . To ensure homogeneous T distribution, the samples were held at $-80\text{ }^{\circ}\text{C}$ for 80 min and $200\text{ }^{\circ}\text{C}$ for 5 min, respectively. Measurements were conducted under a nitrogen atmosphere with a flow rate of 80 mL/min . Indium, tin, and lead standards were used for calibration. The results were normalized to the sample weight and baseline corrected. X_c was calculated by normalizing the measured enthalpy from the 2nd heating run ($-30\text{ }^{\circ}\text{C}$ to the end of the melting region) to the enthalpy of an ideal polyethylene crystal (290 J/g) [20,39]. T_m was assigned to the peak temperature. The values of X_c and T_m listed in Table 1 represent mean values with the corresponding standard deviations obtained from two independent measurements.

2.2.4. Gel Permeation Chromatography

To obtain the molecular weight distributions (MWD) of the modifiers, from which the number-average M_n and weight-average M_w molecular weights can be derived, high-

temperature gel permeation chromatography (GPC) measurements were performed externally. The GPC system (ALLIANCE GPC/V 2000, Waters Corp., Milford, CT, USA) was equipped with four columns (PLgel 20 μ m MIXED-A, 300 $\times$ 7.5 mm, Agilent Technologies Inc., Santa Clara, CA, USA). Calibration was carried out using 20 polystyrene standards with narrow MWD and MW between 600 and 6,000,000 g/mol.

The modifiers were dissolved at a concentration of 0.2 wt% in 1,2,4-trichlorobenzene (TCB) at 160 °C for at least 3 h under continuous stirring. Measurements were conducted at a column temperature of 145 °C and a detector temperature of 150 °C, with an eluent flow rate of 1.0 mL/min. The resulting M_n and M_w values are summarized in Table 1.

2.2.5. Dynamic Mechanical Thermal Analysis

A dynamic mechanical thermal analyzer (DMTA, Gabo Eplexor 500 N, Gabo Qualimeter Testanlagen GmbH, Ahlden, Germany) equipped with a 150 N force transducer was used to determine the thermo-mechanical behavior of the modifiers. Measurements were conducted in strain-controlled mode under tensile loading at a frequency of 1 Hz, with a preload of 1.0 N, a maximum static strain of 0.10%, and a maximum dynamic strain of 0.8%. The sample dimensions were 10 mm in width, 18 mm in length, and 1 mm in thickness. The initial measurement length L_0 was set to 15 mm.

T was varied from -100 to 25 °C at a heating rate of 2 K/min. Cooling was achieved using vaporized liquid nitrogen. To ensure homogeneous T distribution, the measurement was initiated 5 min after reaching -100 °C. The glass transition temperature T_g was determined from the peak position of the loss modulus E'' by fitting a Lorentzian function. The results for T_g are summarized in Table 1. Specimen preparation is described in Section 2.3.

2.2.6. Rotational Rheometry

A rotational rheometer (MCR502, Anton Paar Group AG, Graz, Austria) equipped with a parallel-plate geometry was used to measure the complex viscosity η^* of the modifiers at 240 °C in oscillation mode. Measurements were performed for angular velocities ω between 0.1 and 370 rad/s, using a strain amplitude of 10% and a gap width of 1 mm. Circular specimens with a diameter of 25 mm were punched from 1 mm-thick injection-molded plates. After the desired T had been reached, the samples were placed between the plates, and any excess polymer was trimmed off. The measurements were initiated three minutes after the target temperature was reached to ensure thermal equilibration of the samples.

2.2.7. Tensile Test

Tensile tests were performed in accordance with DIN EN ISO 527-1 [40] at 23 °C and 50% relative humidity using a universal testing machine (ZwickRoell Z020, ZwickRoell GmbH & Co. KG, Ulm, Germany) equipped with a 2.5 kN force transducer. The elastic modulus E was determined at a deformation rate of 5 mm/min in the strain range between 0.05 and 0.25%. Subsequently, the specimens were strained to failure at a traverse speed of 50 mm/min. Elongations up to 150% were measured using an extensometer (multiXtens, ZwickRoell GmbH & Co. KG, Ulm, Germany); higher elongations were recorded via traverse displacement. A minimum of five samples were tested, and all tensile properties are reported in Section 3.1.2 as mean values with standard deviations.

2.3. Specimen Preparation for Mechanical Tests and Shear Rheology

Specimen preparation for mechanical testing and shear rheology was performed using an injection molding machine (ARBURG 420 C 1000-250, ARBURG GmbH & Co. KG, Loßburg, Germany). For PA6-containing materials, the barrel and nozzle temperature were set between 240 and 255 °C, and the mold temperature was set to 80 °C. The pure modifier

was processed at a barrel and nozzle temperature of 160 °C and a mold temperature of 35 °C.

PA6-containing granules were dried in a vacuum oven at 80 °C prior processing to achieve a residual moisture content of (0.05 ± 0.01) wt%, as determined by Karl Fischer titration (C30 Coulometric KF Titrator, Mettler-Toledo GmbH, Greifensee, Switzerland).

Specimens for impact testing were produced by manufacturing type A1 tensile bars according to DIN EN ISO 294-1 [41], following the geometry specifications of DIN EN ISO 527-2 [42], and subsequently cutting the shoulders in accordance with DIN EN ISO 179-1 [43]. The samples were then notched and conditioned in a climate chamber at 23 °C and 50% relative humidity for 16–24 h prior to testing in accordance with DIN EN ISO 179-1 [43]. Samples that could not be tested on the same day were sealed airtight in polyethylene-coated aluminum bags and removed immediately before testing.

For tensile testing of the pure modifier, type A5 tensile bars were produced in accordance with DIN EN ISO 527-2 [42]. Additionally, plates of $100 \times 100 \times 1$ mm were prepared for punching samples for shear viscosity measurements and for cutting samples for DMTA.

2.4. Preparation and Characterization of the Compounds

2.4.1. Compounding

The impact-modified PA6/EOR-g-MAH compounds were prepared using a co-rotating twin-screw extruder equipped with distributive and dispersive mixing elements to ensure a reproducible microstructure and fine dispersion. The extruder had an outer screw diameter D_o of 26 mm (FED 26 MTS, FEDDEM GmbH & Co. KG, Sinzig, Germany), with an outer-to-inner screw diameter ratio $D_o/D_i = 1.55$. Extrusion was carried out at a barrel temperature of 250 °C and a screw speed of 660 rpm with a feed rate of 50 kg/h. PA6 and the modifier were simultaneously fed into the extruder in granular form. PA6 was supplied with a moisture content below 0.1 wt%, which was routinely verified by Karl Fischer titration (C30 Coulometric KF Titrator, Mettler-Toledo GmbH, Greifensee, Switzerland) prior to compounding.

2.4.2. Instrumented V-Notched Charpy Impact Tests

The impact response of the compounds was evaluated using an instrumented pendulum impact tester (HIT25P, ZwickRoell GmbH & Co. KG, Ulm, Germany) equipped with a 25 J hammer with force transducer. The instrumented striker records the force F experienced by the specimen throughout the entire test. The resulting force-deflection curve $F(s)$ exhibited a distinct maximum; the area under the curve before this maximum corresponds to the energy dissipated during crack initiation E_{init} , while the area after the maximum represents the energy dissipated during crack propagation E_{prop} . To account for oscillations in the F signal, a Lorentzian function was fitted to $F(s)$ to determine the force maximum.

The specimens were notched with a 45° V-notch and a notch radius of (0.25 ± 0.05) mm in accordance with DIN EN ISO 179-1/1eA, using a manual notching device (Notchvis, Ceast, Italy, now part of Instron Corp., Norwood, MA, USA) [43]. Tests were conducted following DIN EN ISO 179-2 [44]. The cross-sectional area behind the notch was measured for each specimen using a precision dial indicator (MarCator 1075 R, Mahr GmbH, Göttingen, Germany) equipped with a V-shaped measuring tip, and the measured values were used to calculate the NIS .

For low- T measurements, the specimens were conditioned in a climate chamber for at least 3 h to ensure a homogeneous T distribution. For testing, the samples were removed from the climate chamber using tweezers and tested within 5 s of removal, following the

procedure described for metals in DIN EN ISO 148-1 [45]. At least five specimens were tested for each material and T . The presented NIS values represent mean values, with the error bars indicating the standard deviations.

2.4.3. High-Pressure Capillary Viscometry

The viscosities η of all compounds were measured as a function of shear rate $\dot{\gamma}$ using a high-pressure capillary viscometer (Göttfert RG50, Göttfert GmbH, Buchen, Germany) equipped with capillaries with a length-to-diameter ratio of $L/D = 20/1$ and $40/1$. Prior to the measurements, the granules were dried in a vacuum oven at $80\text{ }^{\circ}\text{C}$ to achieve a residual moisture content of $(0.05 \pm 0.01)\text{ wt\%}$, as determined by Karl Fischer titration (C30 Coulometric KF Titrator, Mettler-Toledo GmbH, Greifensee, Switzerland).

Prior to each measurement, the compounds were melted for 10 min. Measurements were conducted at $240\text{ }^{\circ}\text{C}$ over a $\dot{\gamma}$ range from $3.5 \times 10^2\text{ s}^{-1}$ to a maximum of $3.0 \times 10^4\text{ s}^{-1}$, covering the values typically encountered in injection molding ($10^3\text{--}10^4\text{ s}^{-1}$), which depend on part geometry and flow rate [46]. All η data were corrected according to the Bagley and Weißenberg–Rabinowitsch methods.

2.4.4. Scanning Electron Microscopy

Scanning electron microscopy (SEM, Jeol JSM-7200F, JEOL Ltd., Tokyo, Japan) was employed to investigate the microstructure of the compounds, specifically the dispersion of the modifier phase within the PA6 matrix. The acceleration voltage was set to 15 kV. Samples were cryo-fractured and subsequently immersed in boiling xylene overnight to dissolve the dispersed EOR-g-MAH phase. Prior to imaging, all samples were sputter-coated with a 6 nm iridium layer using a sputter coater (Safematic CCU-010, Safematic GmbH, Zizers, Switzerland).

The dimensions of the dispersed EOR-phase were determined from the diameters d of the resulting voids. At least $n \geq 500$ voids (indexed $i = 1, \dots, n$) were analyzed using image analysis software (Image-Pro Premier Ver. 9.2, Media Cybernetics, Inc., Rockville, MD, USA). From the void diameter distribution, the number-average $\bar{d}_n$, weight-average $\bar{d}_w$, and volume-average $\bar{d}_v$ particle diameters were calculated for each compound [26]:

$$\bar{d}_n = \frac{\sum_{i=1}^{i=n} d_i}{n} \quad (3)$$

$$\bar{d}_w = \frac{\sum_{i=1}^{i=n} d_i^2}{\sum_{i=1}^{i=n} d_i} \quad (4)$$

$$\bar{d}_v = \frac{\sum_{i=1}^{i=n} d_i^4}{\sum_{i=1}^{i=n} d_i^3} \quad (5)$$

The interparticle distance ID is calculated from $\bar{d}_n$ following the procedures described in ref. [1]:

$$ID = \bar{d}_n \left[k \left(\frac{\pi}{6\phi_r} \right)^{\frac{1}{3}} - 1 \right] \quad (6)$$

Here, ϕ_r is the volume fraction of the modifier, calculated from the ρ values of the modifiers listed in Table 1 and the density of PA6 ($(1.13 \pm 0.01)\text{ g/cm}^3$). The PA6 density was measured following the procedure in Section 2.2.1, using distilled water (density at $20\text{ }^{\circ}\text{C}$: 1 g/cm^3) with one drop of a wetting agent (PERVITRO 75%) as the immersion medium. The geometry factor k was set to one, corresponding to a cubic lattice, as suggested by ref. [1]. Average particle diameters and ID , together with the corresponding standard

deviations obtained from the evaluation of at least two SEM micrographs are reported 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_{oct} and MW were analyzed by DSC and DMTA. Figure 2a shows the DSC thermograms of the 2nd heating runs, while Table 1 summarizes the corresponding T_m and X_c . All modifiers exhibit broad melting ranges, with melting initiating just above T_g . DMTA measurements yield T_g values of -44 °C, -49 °C, and -52 °C for EOR-8-34, EOR-13-35, and EOR-15-34, respectively (Table 1).

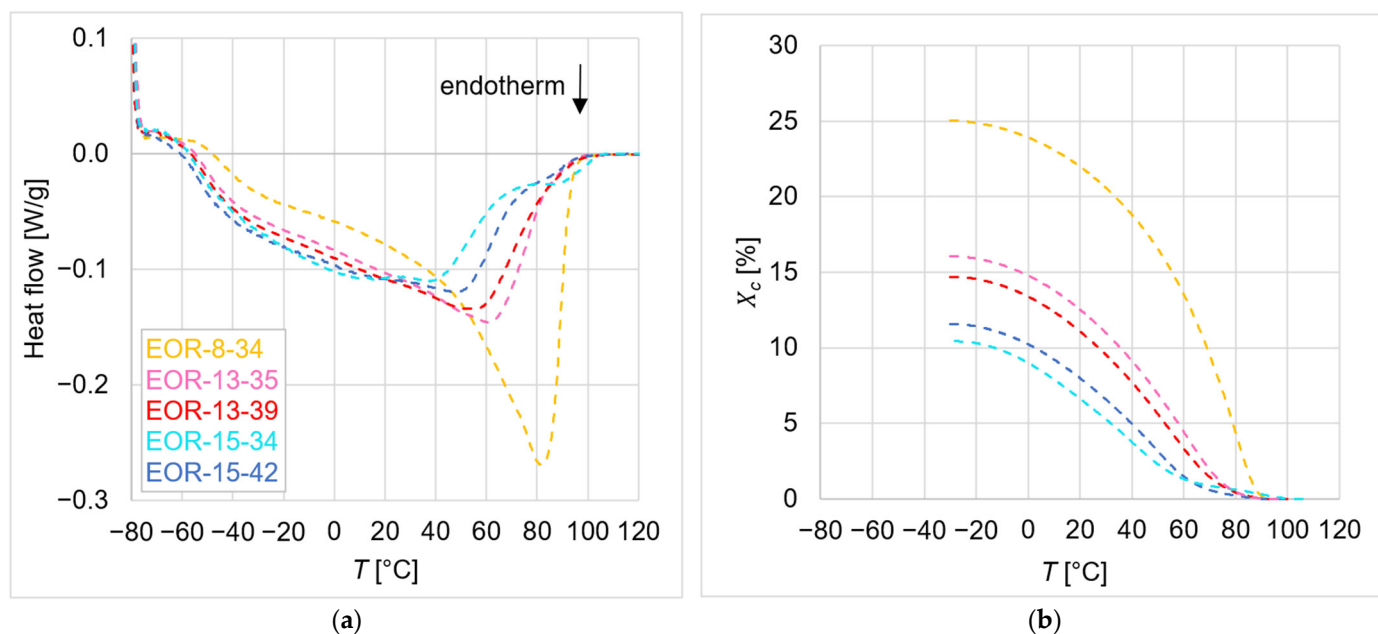


Figure 2. Exemplary DSC endotherms (heat flow from the 2nd heating runs) as a function of temperature T for all investigated modifiers (a), along with the corresponding cumulative residual crystallinities X_c (b).

With increasing c_{oct} , the copolymers contain a higher number of side chains, which hinder crystallization and progressively increase the free volume relative to polyethylene. Simultaneously, the length of ethylene sequences capable of crystallizing decreases, resulting in thinner lamellae and consequently lower X_c [20]. This behavior causes a shift in the entire melting region toward lower T as c_{oct} increases from 8 to 13 and 15 mol%. While T_m and X_c values of EOR-8-34 are significantly higher than those of the materials with higher c_{oct} , the differences between EOR-13-35 and EOR-15-34 are relatively small (Table 1).

It should be noted that X_c determined from the total area under the relatively broad melting peak does not reflect the residual X_c at T above T_g . Figure 2b illustrates the residual X_c as a function of T . The onset of melting just above T_g results in a continuous decrease in X_c up to T_m . At room temperature ($T = 23$ °C), X_c of EOR-8-34 decreases from approximately 25 to about 21%, while for EOR-15-34 it declines from roughly 12 to around 7%. The melting and associated loss of X_c in the modifiers reduces their mechanical strength at elevated T , limiting shear yielding in the PA6 matrix and thereby decreasing the overall toughness of the compound (see discussion below). In contrast to the influence of

c_{oct} , the overall melting behavior, including the overall X_c of the copolymers, is not affected by the MW (Table 1).

Figure 3 presents the storage modulus E' and loss modulus E'' as a function of T . The T range was chosen to cover conditions relevant for the impact tests. To account for the strain-rate difference between DMTA and impact tests, the T -scale of the DMTA measurements was shifted upward to $T_{\text{shifted}} = T + 9\text{ }^{\circ}\text{C}$ [11]. T_g is identified as the peak in E'' , with the results summarized in Table 1.

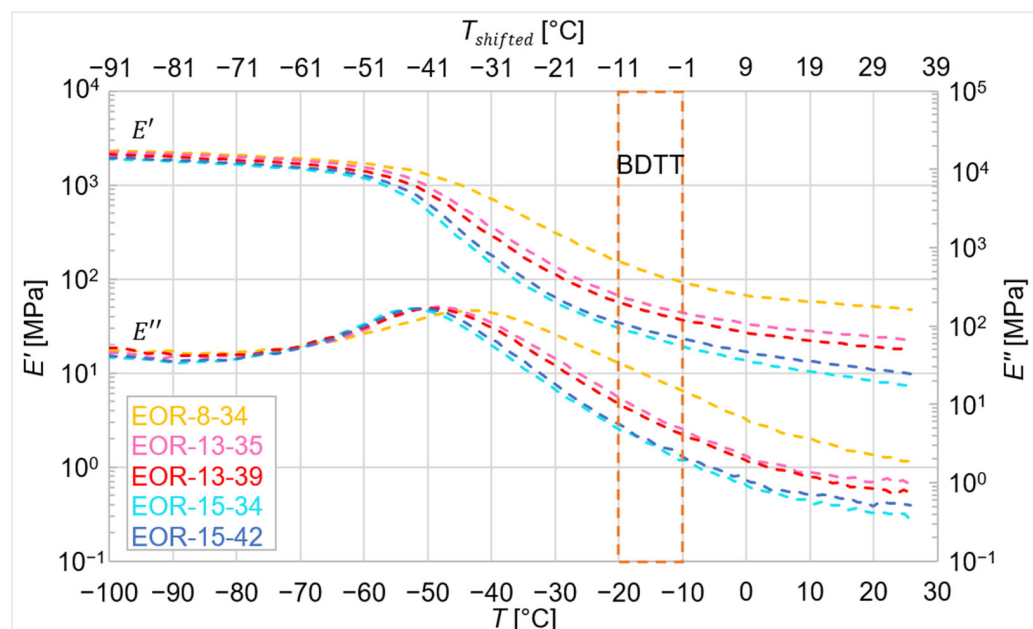


Figure 3. Loss modulus E'' and storage modulus E' (log-scale) versus temperature T measured by DMTA for all investigated modifiers. The brittle–ductile transition temperature BDTT range obtained from impact tests is shown as orange dashed lines. The shifted temperature T_{shifted} accounts for the high strain rates experienced during impact testing [11].

Below T_g , chain mobility is limited, whereas above T_g , E' (as a measure of the material stiffness) decreases due to increased mobility of the amorphous phase and the progressive melting of the crystalline domains, which starts just above T_g according to the DSC results. Both T_g and E' above T_g decrease systematically with increasing c_{oct} (Table 1), reflecting increased chain mobility due to increased free volume, with E' additionally affected by lower X_c . In contrast, MW shows little influence on the dynamic mechanical behavior in the range studied.

Even after applying the $9\text{ }^{\circ}\text{C}$ T shift, the shifted T_g values $T_{g,\text{shifted}}$ of all modifiers (EOR-8-34: $-35\text{ }^{\circ}\text{C}$, EOR-13-35: $-40\text{ }^{\circ}\text{C}$, EOR-15-34: $-43\text{ }^{\circ}\text{C}$, EOR-13-39: $-41\text{ }^{\circ}\text{C}$, EOR-15-42: $-42\text{ }^{\circ}\text{C}$) remain well below the brittle–ductile transition temperatures (BDTT) determined from impact tests (EOR-8-34: $-10\text{ }^{\circ}\text{C}$, EOR-13-35: $-15\text{ }^{\circ}\text{C}$, EOR-15-34: $-15\text{ }^{\circ}\text{C}$, EOR-13-39: $-20\text{ }^{\circ}\text{C}$, EOR-15-42: $-20\text{ }^{\circ}\text{C}$) (see Section 3.2.3).

3.1.2. Tensile Properties

Figure 4 shows the stress σ –strain ϵ curves determined by tensile tests for all EOR-g-MAH materials investigated in this study. The corresponding results for 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 are summarized in Table 2. For EOR-8-34 and EOR-13-35, ϵ_y was determined from the minimum of the first derivatives of the stress–strain curve and σ_y was taken as the corresponding σ at this ϵ . EOR-15-34, EOR-13-39, and EOR-15-42 exhibited no distinct minimum in the first derivative. For these materials, ϵ_y was estimated as the

intersection point of the slopes of the first derivative in the two approximately linear regions immediately before and after the marked change in slope. The σ_y was taken from the corresponding σ at this intersection point.

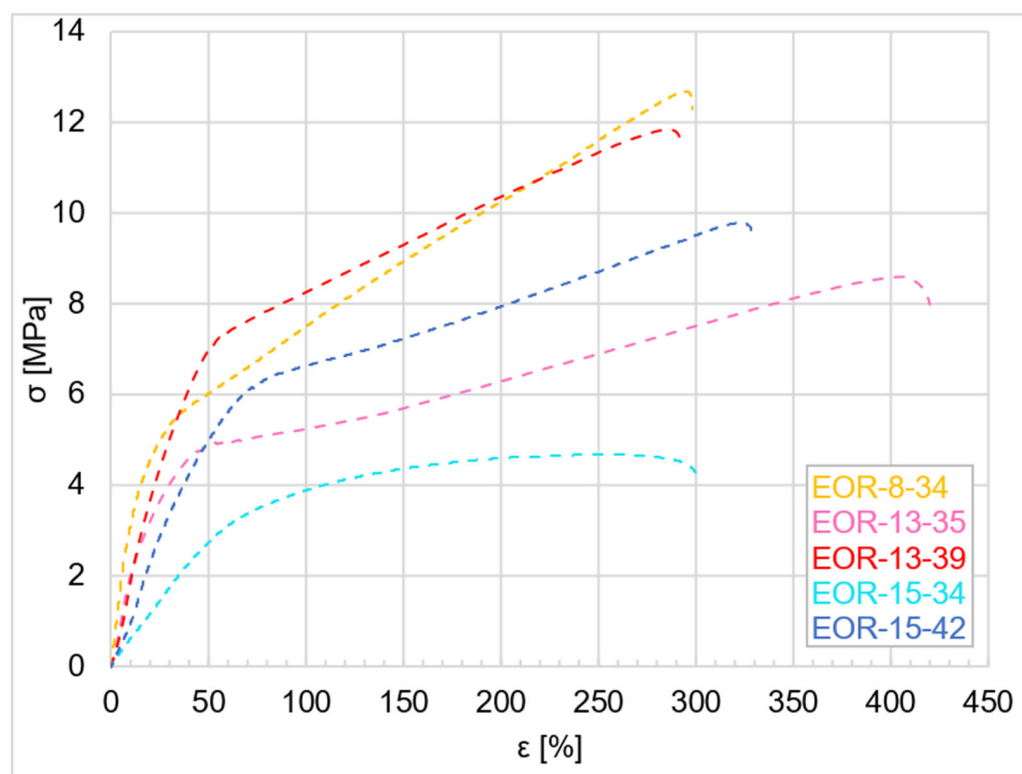


Figure 4. Representative stress σ -strain ε curves obtained from tensile tests at 23 °C of all investigated modifiers.

Table 2. Summary of the tensile test results of the modifiers: elastic modulus E , working capacity W , stress at yield σ_y and strain at yield ε_y , stress at break σ_b and strain at break ε_b .

Designation	E [MPa]	W [J]	σ_y [MPa]	ε_y [%]	σ_b [MPa]	ε_b [%]
EOR-8-34	35.1 ± 0.5	4.3 ± 0.2	6.0 ± 0.1	52 ± 1	12.4 ± 0.2	307 ± 7
EOR-13-35	17.3 ± 0.5	4.0 ± 0.3	4.9 ± 0.1	77 ± 2	8.0 ± 0.1	403 ± 15
EOR-13-39	13.2 ± 0.2	4.3 ± 0.1	7.4 ± 0.1	63 ± 1	11.5 ± 0.2	291 ± 5
EOR-15-34	5.8 ± 0.4	2.1 ± 0.1	3.3 ± 0.1	73 ± 1	4.0 ± 0.1	302 ± 8
EOR-15-42	8.0 ± 0.4	4.3 ± 0.1	6.2 ± 0.1	84 ± 2	9.4 ± 0.2	348 ± 6

Unlike the ungrafted EOR reported in [38], necking is not observed in the grafted copolymers. At 1 wt% grafting and $c_{\text{oct}} = 8\text{--}15$ mol%, polar interactions between MAH and hydrolysis-formed MA groups [47–52], arising during processing [53], are primarily responsible for suppressing necking. Additionally, increased free volume, reduced entanglement density, and greater steric hindrance compared to the ungrafted EOR, facilitate more uniform chain deformation [49,52,54]. Increasing c_{oct} also reduces X_c , which further contributes to necking suppression [20,39,55]. As a result, the chains align less effectively along the loading direction, and the yield point is directly followed by strain hardening, indicated by a monotonic increase in σ until failure.

At constant MW (Series I), modifiers with higher c_{oct} values exhibited lower E , lower σ_y and a lower σ_b compared to modifiers with lower c_{oct} . This behavior is attributed to reduced X_c , as indicated by the DSC results and discussed in ref. [20]. As c_{oct} increases, the comonomer side chains increasingly hinder the regular packing of the polymer backbone,

leading to lower X_c [20,39]. Consequently, an increase in c_{oct} leads to enhanced deformability but reduced mechanical strength. The observed decrease in stiffness with increasing c_{oct} from 8 mol% to 13 mol% and 15 mol% is consistent with the reduction of E' above T_g observed in the DMTA results.

ε_y and ε_b increase as c_{oct} rises from 8 mol% to 13 mol%, whereas ε_y remains constant within the error bars and ε_b decreases when c_{oct} is further increased to 15 mol%. The lower ε_b of EOR-15-34 is attributed to the high fraction of molten material at 23 °C (Figure 2b), in combination with its low MW, as further considered in the subsequent discussion.

Modifiers with the same c_{oct} but different MW (Series II) exhibit similar deformation behavior in the elastic region, compared to the pronounced differences between modifiers with different c_{oct} , indicating that X_c is the dominant factor governing the response in this regime. At higher ε , significant differences emerge between low- and high-MW modifiers. High-MW modifiers exhibit increased σ_y and σ_b , mainly reflecting the greater interconnectivity between fringed micelles, with contributions from a higher entanglement density compared to their low-MW counterparts. This increase is significantly stronger for EOR-15 compared to EOR-13, i.e., for the material with lower X_c and larger MW difference. Consistently, ε_b and ε_y decrease for EOR-13 upon increasing MW. However, for EOR-15, both ε_b and ε_y are lower for the low-MW variant, most likely due to the combined effects of high fraction of molten material, insufficient interconnectivity, and low entanglement density in this material, which promote premature failure.

Since W corresponds to the area under the stress–strain curve up to fracture, it reflects the combined effects of the stresses σ_y and σ_b and the associated strains ε_y and ε_b . Despite reduced σ_y and σ_b of EOR-13-35 compared to EOR-13-39, both materials exhibit similar W within the experimental error, owing to the higher ε_b and ε_y of EOR-13-35 (Table 2). In contrast, EOR-15-34 shows not only reduced σ_y and σ_b but also lower ε_y and ε_b relative to EOR-15-42, resulting in a markedly lower W .

3.2. Compound

3.2.1. Rheology of the Blend Components and Compound Microstructure

In general, the microstructure of the compounds, specifically the particle size distribution, is governed by the interfacial forces between the components and the viscosity ratio $\lambda = \eta_{\text{modifier}}^* / \eta_{\text{matrix}}^*$ of the compounding partners, i.e., the modifier (EOR-g-MAH) and the matrix material (PA6) [22,34]. As shown in Table 1, the differences in c_{MAH} among the modifiers are small; therefore, the interfacial forces are assumed to be comparable [34].

Figure 5 presents the η^* of the EOR-g-MAH copolymers as a function of ω , measured at 240 °C. All modifiers exhibit a decrease in η^* with increasing ω . This shear-thinning behavior originates from disentanglement and alignment of the macromolecules in flow direction, which reduces the resistance to flow. It can also be observed that the differences in η^* are more pronounced at low ω and diminish at higher ω . At constant MW, the decrease in η^* with increasing c_{oct} can be attributed to enhanced chain mobility in the melt, resulting from a lower entanglement density and reduced intermolecular constraints. At constant c_{oct} , the modifiers with higher MW show an increase in η^* compared to those with lower MW. This behavior can be attributed to longer relaxation times associated with increased chain length and entanglement density. Within the investigated range, the effect of the modifier's MW on η^* appears to be more significant than that of c_{oct} between 13 and 15 mol%.

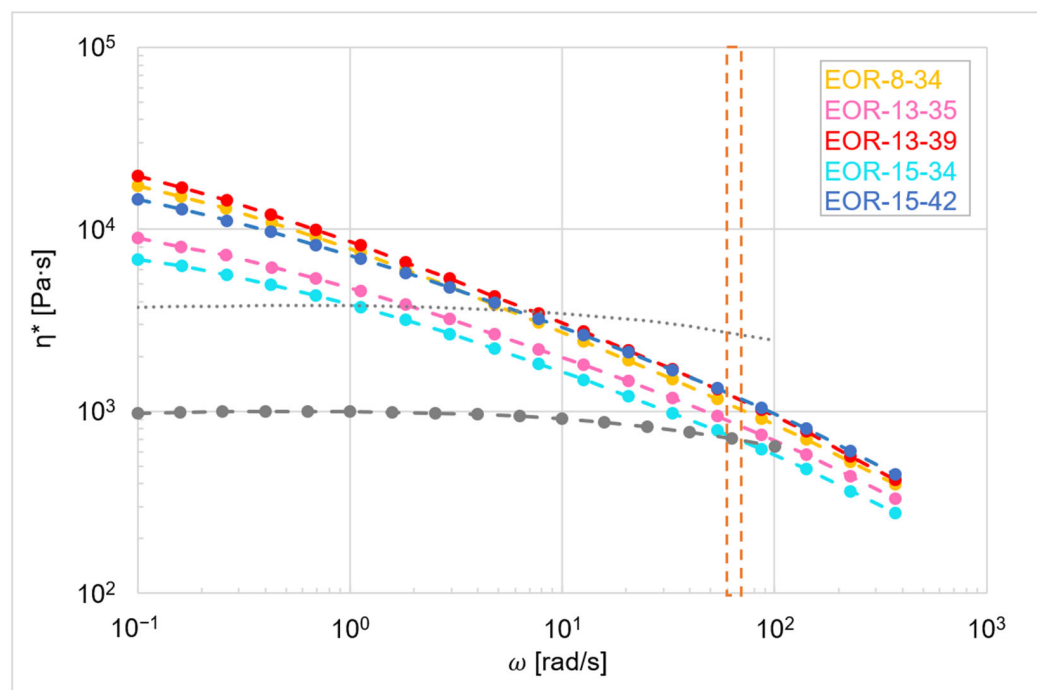


Figure 5. Log–log plot of the complex viscosities η^* of PA6 (gray) and pure modifiers versus angular velocity ω at 240 °C. Below the dotted black line, the viscosity ratio $\lambda < 3.8$. Dashed orange lines indicate the estimated ω range corresponding to the apparent shear rate during extrusion.

According to ref. [34], the smallest particle sizes are obtained when the viscosity ratio λ equals unity. With increasing η^*_{modifier} the particle size increases. At $\lambda \geq 3.8$, the shear field can deform the particles but cannot induce droplet breakup [35]. As shown in Figure 5, $\lambda = \eta^*_{\text{EOR-g-MAH}}/\eta^*_{\text{PA6}}$ is a function of ω . While at $\omega = 0.1$ rad/s λ ranges between approximately 7 and 20, it decreases significantly at higher ω .

To identify the operational range relevant for η^* comparison, the apparent average shear rate $\bar{\dot{\gamma}}$ in the co-rotating twin-screw extruder was determined according to the following equation [56]:

$$\bar{\dot{\gamma}} = \frac{2\pi NR}{60h} \quad (7)$$

In this study, the screw rotational speed was $N = 660 \text{ min}^{-1}$, and the channel depth of the screw was $h \approx 4.6 \text{ mm}$, calculated from the known outer-to-inner screw diameter ratio $D_o/D_i = 1.55$ and $D_o = 26 \text{ mm}$. This results in $\bar{\dot{\gamma}} = 400 \text{ s}^{-1}$ during extrusion. To allow for comparison with the rheological results, ω was converted into $\bar{\dot{\gamma}}$, using the following equation for a plate–plate geometry:

$$\bar{\dot{\gamma}} = \omega \frac{r}{2h} \quad (8)$$

with $r = 12.5 \text{ mm}$ (plate radius) and $h = 1 \text{ mm}$ (gap height). Thus, the shear rate during extrusion ($\bar{\dot{\gamma}} = 400 \text{ s}^{-1}$) corresponds to $\omega = 64 \text{ rad/s}$ in the rheological measurement. In this range, λ lies between 1.1 and 1.8 (Figure 5), indicating that the formation of small modifier particle sizes is likely.

Since c_{MAH} (Table 1) remains essentially constant, the interfacial forces are expected to remain unchanged. In addition, the differences in η^* at higher ω are minor, with little impact on λ . Consequently, no significant influence on the particle size distribution is expected when varying the modifiers.

Figure 6a shows a representative SEM micrograph of the cryo-fractured and xylene-etched surface of the PA-EOR-8-34 specimen. Figure 6b presents the histograms and corresponding cumulative particle size distributions for compounds containing modifiers of Series I (Figure 1) with $c_{oct} = 8, 13$ and 15 mol% and low MW. SEM micrographs, histograms, and cumulative plots for all other compounds are provided in the Supporting Information (Figures S1 and S2). The mean particle diameters ($\bar{d}_n$, $\bar{d}_w$ and $\bar{d}_v$) for all compounds are summarized in Table 3.

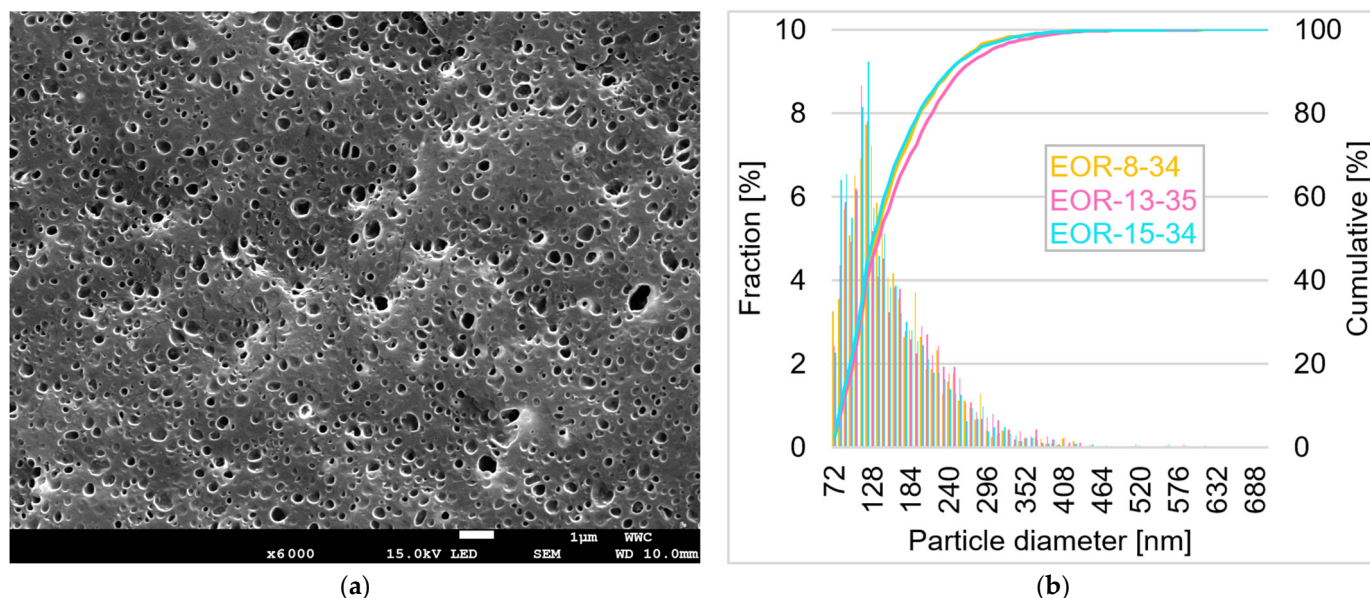


Figure 6. Exemplary SEM results: (a) SEM micrograph of the cryo-fractured and xylene-etched surface of PA-EOR-8-34. (b) Histograms and cumulative distributions of particle diameters for Series I compounds.

Table 3. Microstructural parameters derived from SEM micrographs: number-average particle diameter $\bar{d}_n$, weight-average particle diameter $\bar{d}_w$, volume-average particle diameter $\bar{d}_v$, and interparticle distance ID .

Designation	Particle Size [nm]			ID [nm]
	$\bar{d}_n$	$\bar{d}_w$	$\bar{d}_v$	
PA-EOR-8-34	151 ± 4	180 ± 5	254 ± 5	44 ± 2
PA-EOR-13-35	158 ± 7	192 ± 11	276 ± 13	46 ± 2
PA-EOR-13-39	154 ± 4	184 ± 6	263 ± 6	47 ± 2
PA-EOR-15-34	148 ± 4	178 ± 5	257 ± 2	42 ± 2
PA-EOR-15-42	156 ± 5	188 ± 6	261 ± 6	45 ± 2

As discussed in the introduction, the particle size distribution and ID can strongly influence the toughness of impact-modified compounds. Particles that are too small are unable to cavitate, whereas excessively large particles lead to ID that are too large to effectively initiate matrix shear yielding. Variations in c_{oct} and MW resulted in morphologies with mean diameters of $\bar{d}_n \approx (153 \pm 2)$ nm, $\bar{d}_w \approx (184 \pm 3)$ nm and $\bar{d}_v \approx (262 \pm 4)$ nm, respectively. All $\bar{d}_w$ values are close to the optimal modifier particle size of $d_{w,opt} \approx 150$ nm reported for EOR-based PA6 compounds in ref. [2]. Furthermore, the interparticle distance ($ID = (45 \pm 1)$ nm) of all compounds is well below the critical value ($ID_c = 300$ nm) reported in refs. [1,24] for PA (Table 3). These findings confirm that all materials investigated in this study meet the microstructural requirements for effective toughening. By maintaining

comparable particle sizes and ID across different formulations, the influence of modifiers' c_{oct} and MW on the NIS could be assessed independently of microstructural effects.

3.2.2. Compound Viscosity

In addition to mechanical performance, processability is a crucial consideration for practical applications. Figure 7 presents the η of all compounds as a function of $\dot{\gamma}$ within the range typically encountered during injection molding (10^3 – 10^4 s $^{-1}$) [46]. All compounds exhibit shear-thinning behavior, and comparable η , independent of variations in c_{oct} or MW . Since all modifiers have the same c_{MAH} and similar particle size, the surrounding shell of covalently bonded PA6 is expected to be comparable for all compounds. Consequently, increasing c_{oct} or MW at constant c_{MAH} does not negatively affect processability under the conditions studied. This behavior is consistent with the comparable particle size distributions of the modifiers used in this study.

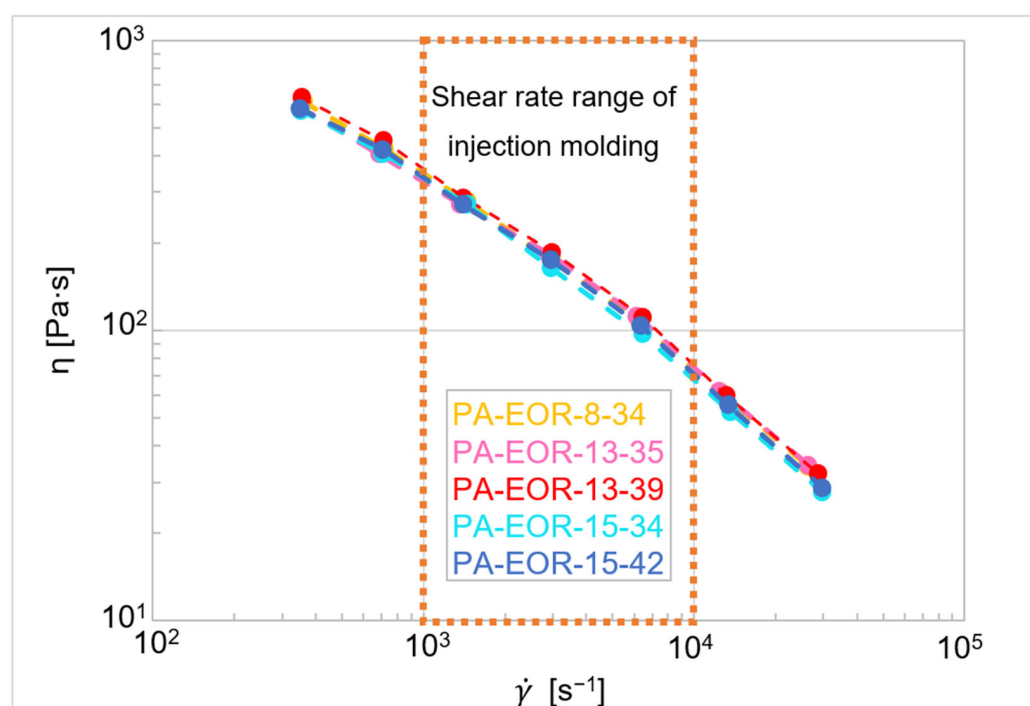


Figure 7. Log–log plot of compound viscosities η as a function of shear rate $\dot{\gamma}$ at 240 °C for all compounds investigated in this study. The dashed orange lines indicate the typical shear rate range of injection molding [46].

3.2.3. Impact Toughness and Energy Dissipation

In this chapter, we first discuss the effect of c_{oct} for low- MW modifiers of Series I. This is followed by an analysis of the influence of increased MW at two constant c_{oct} values in Series II on the energy dissipation during impact testing. Finally, we examine the differences in energy dissipation for materials of low and high MW containing different c_{oct} to elucidate the combined influence of c_{oct} and MW . Using an instrumented Charpy impact testing device enabled a deeper insight into the energy dissipation processes during the impact test by separating the NIS into E_{init} and E_{prop} .

Effect of c_{oct} at constant MW (Series I): Figure 8 depicts the results for unmodified PA6 and compounds containing modifiers of $c_{oct} = 8, 13$ and 15 mol% and comparable, relatively low MW . At low T , where the specimens fracture in a brittle manner, only E_{init} can be identified. Here, E_{init} is about two to three times higher for all impact-modified compounds compared to neat PA6. Since no significant plastic deformation of the matrix occurs in this

brittle regime, the increase in E_{init} can be attributed to energy dissipation by elastic and plastic deformation and fracture of the modifier particles.

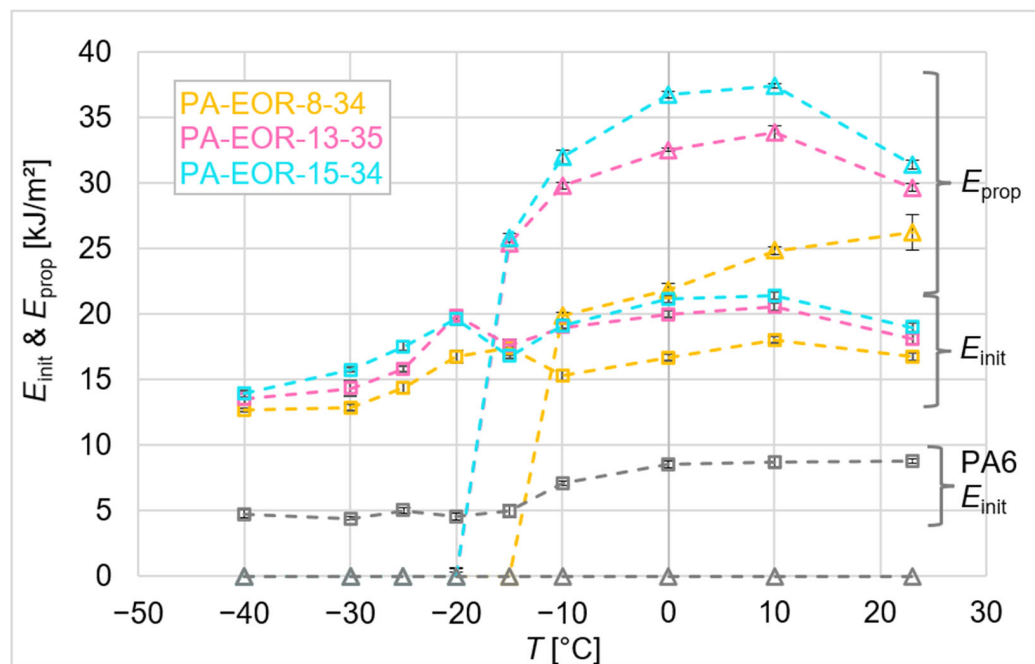


Figure 8. Energy dissipated during crack initiation (E_{init} □) and crack propagation (E_{prop} Δ), respectively, as a function of temperature T for PA6 (gray) and Series I compounds.

Among the impact-modified compounds of Series I, PA-EOR-8-34 exhibits the lowest E_{init} , while PA-EOR-13-35 and PA-EOR-15-34 exhibit progressively higher values with the increasing c_{oct} . This trend can be explained by their lower E' (DMTA results, Figure 3), which results from a higher amorphous fraction (DSC results, Figure 2) and lower T_g (Table 1). Enhanced chain mobility in the amorphous fraction leads to greater deformability (lower E') of EOR-13-35 and EOR-15-34 compared to EOR-8-34, thereby increasing the energy dissipated through particle deformation and fracture in the modifiers with increasing c_{oct} .

As T increases, the BDTT is reached, and E_{prop} becomes measurable for the impact-modified compounds (Figure 8). In contrast, neat PA6 remains brittle throughout the studied T range. During specimen deformation, stress is transferred from the matrix to the modifier particles, leading to particle elongation and cavitation. This process transforms the triaxial stress state in the matrix into a uniaxial one, thereby promoting matrix shear yielding [8,10].

In Figure 8, compounds containing modifiers with $c_{\text{oct}} \geq 13$ mol% exhibit a BDTT at -15 °C, while PA-EOR-8-34 shows a BDTT at -10 °C. The modifier particles in PA-EOR-8-34 apparently cannot cavitate at -15 °C, inhibiting matrix shear yielding and resulting in brittle failure. In contrast, the higher chain mobility of the modifiers in PA-EOR-13-35 and PA-EOR-15-34 (due to the modifiers' lower T_g and larger amorphous fraction) facilitates cavitation and shear yielding. Increasing c_{oct} from 13 to 15 mol% does not further lower the BDTT, likely due to only marginal reduction in T_g (EOR-13-35: $T_g = -49$ °C; EOR-15-34: $T_g = -50$ °C, see Table 1) and small differences in X_c at -15 °C ($\Delta X_{c,-15} = 5\%$).

Above the BDTT, E_{prop} increases with T as both the modifier and the matrix become more deformable, enabling more efficient stress relaxation and higher energy dissipation. The compound containing the modifier with the highest c_{oct} (PA-EOR-15-34) exhibits the largest E_{prop} , followed by PA-EOR-13-35, while PA-EOR-8-34 shows the lowest. As discussed in ref. [28], a lower modulus, here resulting from higher c_{oct} , facilitates particle

cavitation, which promotes more effective stress release and the formation of a more extended shear-yielding zone at the crack tip, which provides the main contribution to energy dissipation. Due to this enlarged shear-yielding zone, a greater number of modifier particles participate in the fracture process, additionally contributing to the total energy dissipated through deformation and cavitation, although this contribution remains small compared to that of matrix shear yielding. Consequently, compounds containing modifiers with higher c_{oct} exhibit greater overall energy dissipation.

At T above 10 °C, both E_{init} and E_{prop} decrease for PA-EOR-13-35 and PA-EOR-15-34. This drop can be attributed to decreasing particle strength due to partial melting, as indicated by DSC results (Figure 2b), which negatively affects the mechanical performance of the modifiers, particularly for higher c_{oct} .

Effect of MW (Series II): Figure 9 presents E_{init} and E_{prop} as a function of T for compounds containing modifiers of low and high MW ($c_{\text{oct}} = 13$ and 15 mol%). Across the entire T range, compounds containing modifiers with higher MW (PA-EOR-13-39, PA-EOR-15-42) outperform those with lower MW (PA-EOR-13-35, PA-EOR-15-34). These differences cannot be attributed to variations in X_c (Table 1), dynamic mechanical properties (Figure 3), or microstructure (Table 3), as these parameters are comparable among the modifiers at the same MW. Instead, the improved performance is likely due to the higher modifier strength associated with higher MW, as indicated by the tensile test results (Table 2).

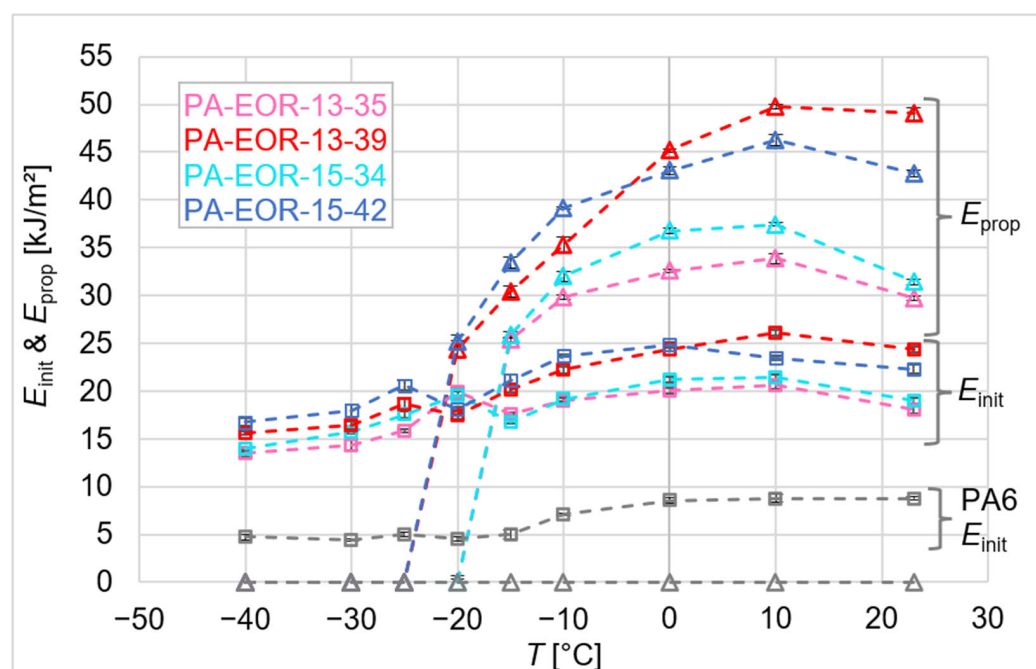


Figure 9. Energy dissipated during crack initiation (E_{init} $\square$) and crack propagation (E_{prop} Δ), respectively, as a function of temperature T for PA6 (grey) and Series II compounds.

E_{init} is mainly governed by the elastic and plastic deformation and fracture of the modifier particles. PA-EOR-13-39 and PA-EOR-15-42 show higher values than their low-MW counterparts (PA-EOR-13-35 and PA-EOR-15-34) at all T .

Although the apparent strain rates differ significantly between tensile and impact tests [11], tensile test results can nevertheless serve as an indicator of the role of the modifier particles in the fracture mechanism of the compound (see Section 3.1.2).

E_{init} shows no correlation with the strains ε_y and ε_b , consistent with the findings of refs. [11,29], nor with W , in agreement with the suggestions of refs. [11,29]. This indicates that particle extensibility is likely constrained by the matrix and cannot be fully accessed,

rendering W an unsuitable measure of a modifier's effectiveness in increasing NIS within this T range. Within a given c_{oct} , a higher E_{init} can be associated with a higher σ_y and σ_b , which increase with modifiers' MW according to the tensile test results (Table 2). Similar correlations between NIS at low T and stress values were also reported in refs. [11,12,29]. The improved interconnectivity between fringed micelles, together with higher entanglement density in high- MW modifiers, leads to increased stress values.

The BDTT of compounds containing high- MW modifiers is about 5 °C lower than that of compounds with low- MW modifiers (Figure 9). The higher strength of the high- MW modifiers enables effective crack shielding and matrix shear yielding already at −20 °C, whereas the lower strength of the low- MW modifiers results in brittle fracture at this T . At higher T , increased deformability of both matrix and modifiers allows even the low- MW modifiers to promote ductile fracture. However, the trend in E_{init} for the different compounds cannot be explained solely by the trend in the stresses. Instead, the behavior appears to be governed by a balance between efficient stress release due to higher elastic deformability (E') and sufficient resistance to prevent premature failure, leading to higher E_{init} for EOR-15 compared to EOR-13 at same MW (see also discussion below).

Above the BDTT, the superior strength of high- MW modifiers compared to low- MW counterparts becomes increasingly apparent, resulting in significantly higher E_{init} and E_{prop} values up to room temperature. SEM micrographs of fracture surfaces after impact testing at 10 °C support these observations; PA-EOR-13-35 (Figure 10a) exhibits a relatively smooth fracture surface, whereas PA-EOR-13-39 (Figure 10b) shows a much rougher topography, indicative of enhanced plastic deformation and higher energy absorption, consistent with the 1.5× higher E_{prop} of PA-EOR-13-39 compared to PA-EOR-13-35.

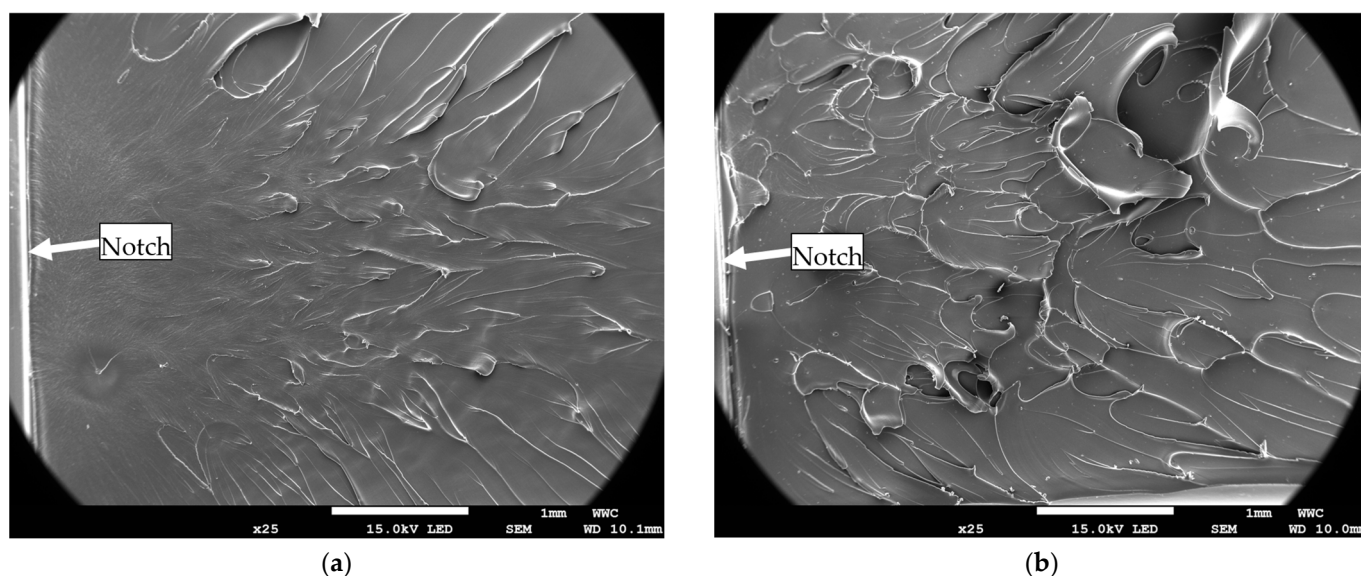


Figure 10. SEM micrographs of V-notched Charpy impact specimens with low- and high- MW modifiers from Series II, tested at 10 °C: (a) PA-EOR-13-35 and (b) PA-EOR-13-39.

At $T \geq 0$ °C, E_{init} and E_{prop} of PA-EOR-13-39 continue to increase, whereas the corresponding values for other compounds start to level off or decline. This behavior is likely attributable to the combination of high MW and relatively high residual X_c (Figure 2b), both of which contribute to increased particle strength.

Combined influence of c_{oct} and MW : Further discussion is focused on the overall impact performance of the compounds. Therefore, Figure 11 summarizes the NIS as a function of T for all PA6/EOR compounds, without separating the contributions of E_{init} and E_{prop} .

However, starting with the BDTT, NIS is mainly governed by E_{prop} . For clarity, the results are divided into three distinct T regions to facilitate discussion.

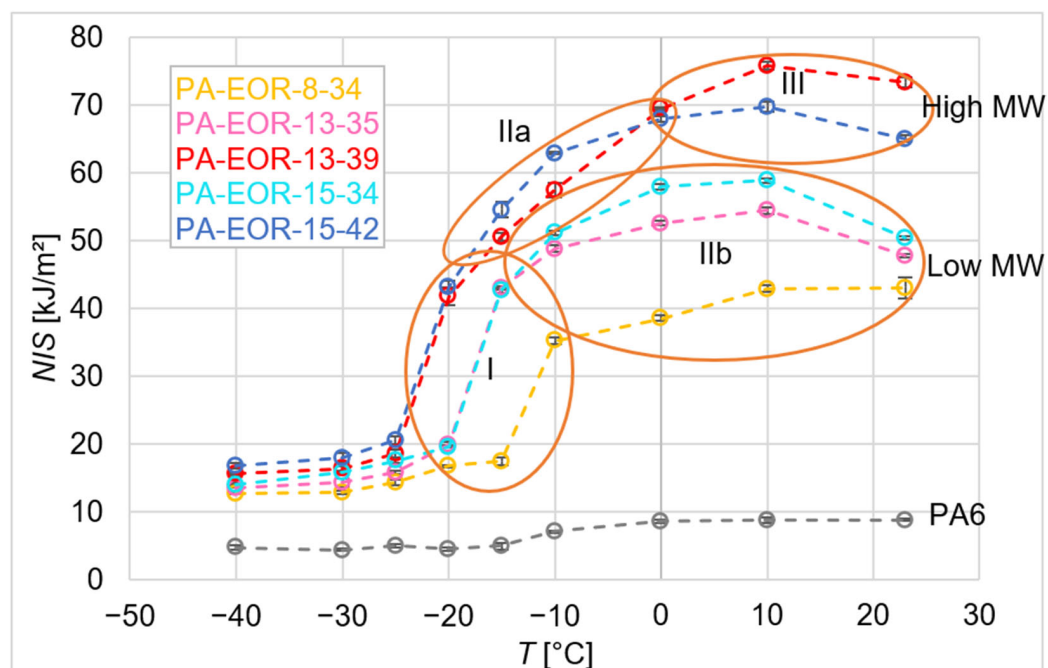


Figure 11. Notched impact strength NIS as a function of temperature T for PA6 (gray) and all investigated compounds. The circled areas indicate the failure Regions I–III discussed in the text.

In Region I, around the BDTT, the fracture behavior changes from brittle to ductile, accompanied by a sharp increase in NIS . Increasing c_{oct} from 8 to 13 mol% reduces the BDTT by approximately 5 °C, as the higher amorphous fraction and lower T_g of the modifier increase chain mobility and deformability (E'), facilitating particle cavitation and the onset of matrix shear yielding. A further increase in c_{oct} beyond 13 mol% produces no additional reduction in BDTT, consistent with the negligible decrease in T_g and the only small reduction in X_c between $c_{oct} = 13$ and 15 mol%. In contrast, increasing the MW leads to a further reduction in the BDTT, which can be attributed to the higher particle strength of the high-MW modifiers that effectively promote shear yielding and hinder crack propagation.

In Region II, above the BDTT, higher c_{oct} enhances impact toughness by increasing the deformability of the modifier, enabling more efficient stress relaxation and promoting extensive matrix shear yielding. This effect is observed across the full T range above the BDTT when comparing PA-EOR-15-34 with PA-EOR-13-35, and up to approximately 0 °C when comparing PA-EOR-15-42 with PA-EOR-13-39. In this range, the deformability of the modifier (at sufficient strength) and its ability to release stress are crucial for the overall energy dissipation process.

At the same time, the influence of MW becomes increasingly significant in Regions II and III (the latter following Region IIa at T above 0 °C). Compounds containing high-MW modifiers exhibit superior performance, with higher NIS values than those containing low-MW modifiers. The higher strength of the high-MW modifiers prevents premature particle failure and enables more efficient energy dissipation through shear yielding as the matrix softens with increasing T .

In Region III, the beneficial effect of higher c_{oct} diminishes for compounds containing high-MW modifiers, as excessively high c_{oct} adversely affects particle strength. The compound containing EOR-13-39 (high MW, moderate c_{oct}) exhibits the highest NIS , owing to

the higher residual X_c of the modifier, which preserves particle integrity, and enables more extensive matrix shear yielding compared to the more amorphous modifier EOR-15-42 with reduced mechanical strength.

The results indicate that a high c_{oct} is beneficial for achieving elevated NIS at lower T up to about 0 °C. Increasing particle strength through the use of high-MW modifiers reduces the BDTT. In contrast, a c_{oct} above 13 mol% does not lead to additional BDTT reduction and may be detrimental at T above 0 °C. The use of high-MW modifiers results in higher NIS values both below and above the BDTT. Overall, PA-EOR-13-39, containing a high-MW modifier with $c_{\text{oct}} = 13$ mol%, exhibits the most balanced performance across the entire T range investigated.

4. Conclusions

This study systematically investigated the isolated influence of the intrinsic properties of MAH-grafted EOR copolymers—namely c_{oct} or MW —on the NIS of PA6 compounds. By keeping c_{MAH} , modifier content, and compound microstructure constant, the effects of c_{oct} or MW could be clearly attributed. Instrumented Charpy impact testing enabled detailed separation of E_{init} and E_{prop} , revealing distinct roles of c_{oct} or MW across the BDTT.

Increasing c_{oct} from 8 to 13 mol% significantly lowered the BDTT (from approximately −10 °C to −15 °C), driven by enhanced chain mobility, reduced X_c , and improved cavitation ability of the modifier particles. This led to increased E_{init} at low T , where fracture is dominated by particle deformation, and cavitation-induced matrix shear yielding. However, further increasing c_{oct} to 15 mol% did not yield additional improvement and even reduced particle strength at elevated T due to partial melting and diminished residual X_c .

A range of industrially relevant MW was selected to maintain a comparable microstructure. Furthermore, this range was chosen with regard to cost efficiency, as modifiers with higher MW are less economical to manufacture and less readily available at large scale. Raising MW improved particle strength and mechanical integrity, reducing BDTT by approximately 5 °C compared to low- MW systems. High- MW modifiers absorbed more energy before failure, promoted earlier and more extensive matrix shear yielding, and maintained higher NIS values across the entire T range. Their contribution was most evident in E_{prop} at and above BDTT, where matrix shear yielding governs energy absorption.

A combined evaluation revealed that high c_{oct} facilitates cavitation and matrix shear yielding at low T , while high MW ensures particle integrity and mechanical support at higher T . The optimal balance between deformability and strength was achieved with the compound PA-EOR-13-39, containing a high- MW modifier with moderate c_{oct} (13 mol%), which exhibited the highest overall NIS and the broadest T range of ductile behavior.

Overall, the study demonstrates that tailoring the interplay between c_{oct} and MW of EOR-g-MAH modifiers enables precise control over the BDTT and NIS of PA6 compounds, providing robust, industry-relevant design guidelines for high-performance, impact-resistant engineering thermoplastics operating across a wide T range.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/polym18050584/s1>. Figure S1: Exemplary SEM micrographs of cryo-fractured and xylene-etched surfaces for Series II compounds: (a) PA-EOR-13-35, (b) PA-EOR-13-39, (c) PA-EOR-15-34, and (d) PA-EOR-15-42; Figure S2: Histograms and cumulative distributions of particle diameters for Series II compounds.

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Abbreviations

The following abbreviations are used in this manuscript:

ABS-g-MAH	Maleic anhydride grafted 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_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
EPR-g-MAH	Maleic anhydride grafted 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
ID	Interparticle distance
ID_c	Critical interparticle distance
ISO	International Organization for Standardization
k	Geometry factor
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
PTFE	Polytetrafluoroethylene
SEBS	Styrene-ethylene-butylene-styrene
SEBS-g-MAH	Maleic anhydride grafted styrene-ethylene-butylene-styrene
SEM	Scanning electron microscopy
TCB	1,2,4-Trichlorobenzene
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
$\bar{\dot{\gamma}}$	Apparent average shear rate (extrusion)
η	Viscosity (compound)
η^*	Complex viscosity (modifier, matrix)
λ	Viscosity ratio $\eta^*_{\text{modifier}}/\eta^*_{\text{matrix}}$
ρ	Density (modifier)
σ	Stress
σ_b	Stress at break
σ_y	Stress at yield
ω	Angular velocity

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