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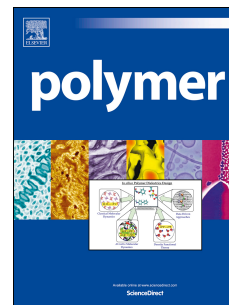
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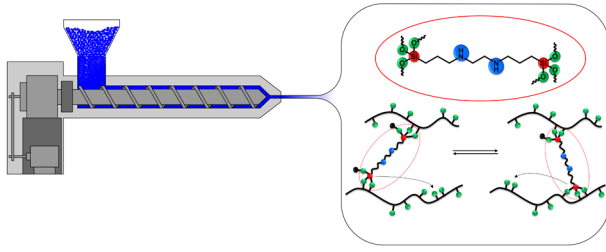
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CRediT authorship contribution statement

Arkadiusz Zych: Data curation, Formal analysis, Writing - original draft. Maria Soliman: Conceptualization, Supervision, Methodology Roberta Pinalli: Conceptualization, Methodology, Writing - review & editing., Project administration. Jérôme Vachon: Conceptualization, Methodology, Supervision, Writing - review & editing, Project administration. Enrico Dalcanale: Conceptualization, Methodology, Supervision, Writing - review & editing, Project administration.

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Polyethylene vitrimers via silyl ether exchange reaction

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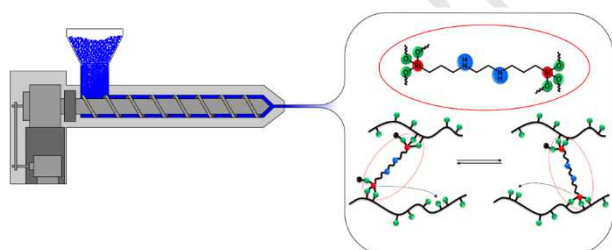
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Abstract

Functional polyethylene (PE) bearing pendant hydroxyl groups was dynamically crosslinked via reactive extrusion using commercially available *N,N'*-Bis[3-(trimethoxysilyl)propyl] ethylenediamine (TMSPEDA). This fast and efficient way allowed to produce PE vitrimers without synthetic effort or use of solvent, which makes the process environmentally friendly and easy to upscale. The dynamic crosslinking transformed thermoplastic PE into an elastic solid with greatly improved melt strength as revealed by DMTA and rheology. Mechanical properties could be tuned by varying the amount of TMSPEDA crosslinker. All prepared vitrimers were sparingly soluble in xylene and were not affected by moisture demonstrating crosslinked character, improved solvent resistance and excellent hydrolysis resistance which is of great importance for industrial applications. Despite the crosslink nature of the material, the dynamic silyl ether exchange enabled processability and recyclability of this system using industrially relevant techniques like injection and compression molding.

Graphical Abstract



Keywords

Polyethylene vitrimer; Silyl ether exchange reaction; Reactive extrusion

Introduction

Polyethylene (PE) is a widely used commodity thermoplastic due to its good solvent resistance, excellent flexibility, low cost and ease of processing [1,2]. However, its use is limited by low melting point, stress cracking as well as poor solvent and wear resistance. To overcome those issues and expand its applications, crosslinking of polyethylene is commonly used. Crosslinking forms a high molecular weight network, which improves impact strength, creep and abrasion resistance, without altering significantly tensile strength and density [3]. Crosslinked polyethylene (PEX) is produced using either chemical (e.g. with peroxides) [4] or physical methods (e.g. with radiation) [5].

Despite the numerous advantages of PEX and its widespread applications, recycling is a major drawback. Because of the permanent and fixed crosslinks between the chains, PEX does not flow

after melting and cannot be recycled and reprocessed like thermoplastics. Most of the PEX waste is currently landfilled or incinerated which is a major problem both for the environment as well as for a recovery of valuable materials [6,7]. Therefore, there is an urgent need to explore alternative technologies to manufacture reusable crosslinked polyolefins [8]. A rational solution to the problem comes from vitrimers [9], a new class of materials that behave like permanently crosslinked polymers at service temperatures, but flow like thermoplastics at elevated temperatures [10,11]. They are crosslinked using exchangeable covalent bonds, which enable them to change topology maintaining constant number of chemical bonds and crosslinks [12]. These cross-links undergo thermally triggered exchange reactions at high temperature, making their processability possible. Upon cooling, the shape can be fixed by slowing down the exchange reaction [13] or by quenching the motion of polymer molecules through glass transition or crystallization [14].

To date, a limited number of PE-based vitrimers are described in the literature. Nicolaÿ and Leibler grafted maleimides bearing dioxaborolane functionalities onto HDPE via two-step reactive extrusion [15]. The dioxaborolane metathesis allows fast reshuffling of the boronic esters crosslinks at temperatures above 60°C, leading to a PE vitrimer with melt flow index and tensile strength comparable to that of pristine HDPE. In a more recent paper, the same approach was further refined to achieve PE vitrimers via direct one-step reactive extrusion, using nitroxide dioxaborolanes as grafting agents [16].

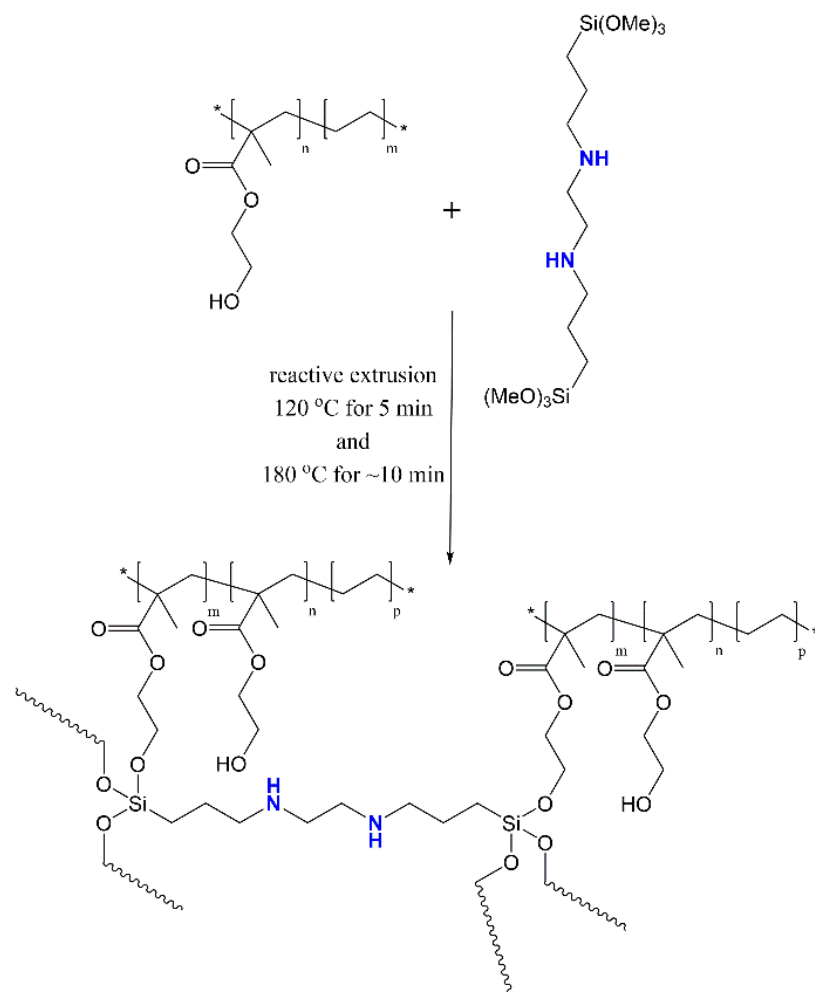
Transesterification has been adapted to polyolefins to form dynamic covalent polymer networks starting from poly(ethylene-co-vinyl acetate) in the presence of a suitable catalyst [17]. As alternative approach, glycidyl methacrylate units were introduced in HDPE as cross-linking units to be reacted with hydroxyl-terminated polytetrahydrofuran or polycaprolactone via reactive blending [18].

Guan and co-workers introduced bis-silyl ethers as dynamic cross-linkers for vitrimers. Initially they reported the direct crosslinking of polystyrene functionalized with pendant hydroxyl groups with commercially available silyl ether crosslinkers [19]. More recently, direct silyl ether metathesis was employed to generate polyethylene-co-vinyl alcohol vitrimers with exceptional thermal stability [20].

Recently we published an industrially relevant and easy to scale-up method for the preparation of cross-linked vinylogous urethanes PE vitrimers based on reactive extrusion [21]. Along this line, here we present the direct dynamic crosslinking via reactive extrusion of an hydroxyl functionalized PE, namely ethylene-hydroxyethylmethacrylate copolymer (PE-HEMA) with the commercially available TMSPEDA (N,N'-Bis[3-(trimethoxysilyl)propyl] ethylenediamine) silyl ether. The resulting PE vitrimers are hydrolytically stable and reprocessable.

Results and discussion

To prepare PE-silyl ether vitrimers, TMSPEDA was used as a dynamic crosslinker profiting from the dynamism and the high thermal and chemical stability of the silyl ether bonds. PE copolymerized with HEMA was used as polymer backbone exploiting the hydroxyl groups to prepare silyl ether connections. Reactive extrusion was employed to prepare the vitrimers, reacting PE-HEMA and TMSPEDA in presence of Irganox as antioxidant (Scheme 1). In this way, the use of costly or harmful solvents and long reaction times are avoided. Noteworthy, all the reagents are commercially available. The extrusion was performed in a 15 mL twin screw micro compounder at 120 °C for 5 min and at 180 °C till constant viscosity was reached (Figure S1). At the end, the process allowed to produce 10 g of PE-silyl ether vitrimer in around 10-15 min which is a great improvement in comparison to previously reported solution processes [19,20]. Using this protocol, four different vitrimers were prepared, in which theoretical crosslink density was varied from 3 to 9 crosslinks per chain (X/C) assuming that all 6 methoxy groups of TMSPEDA are involved in the reaction. Table 1 lists the four produced vitrimers, reporting the amount of the crosslinker used, the number of crosslinks per chain (X/C), melting (T_m) and beta transition (T_β) temperatures, as well as degree of crystallinity (X_{cr}).



Scheme 1. Preparation of PE silyl ether vitrimers via reactive extrusion.

As Table 1 shows, thermal properties did not change significantly after the crosslinking which suggests that TMSPEDA is excluded from PE crystalline phase (Figure S2).

Entry	PE-HEMA [g]	TMSPEDA [g]	X/C^a	T_m^b [°C]	T_β^c [°C]	X_{cr}^d [%]
Pristine*	-	-	-	73.9	-6.5	12.2
Vit 1	10	0.66	3	72.4	-4.9	1.8
Vit 2	10	0.88	4	72.1	-4.4	2.0
Vit3	8	1.06	6	71.0	-4.0	2.0
Vit 4	7	1.39	9	69.7	-1.9	2.2

Table 1. Overview of the pristine and prepared polymers: Pristine PE-HEMA characterization; amount of TMSPEDA crosslinker and PE-HEMA used for vitrimer preparation; thermal properties and theoretical links per chain of each PE vitrimers. *HEMA content = 12% mol (calculated from 1H NMR (120 °C, TCE d_2); M_n [g/mol] = 2900 (GPC reported in Figure S15), $\bar{D} = 2.2$. Both M_n and \bar{D} were determined by SEC in *o*-DCB at 150 °C with respect to polyethylene standards. ^a Theoretical number of crosslinks per chain (X/C) was calculated using M_n of PE-HEMA and the amount of TMSPEDA used assuming that all 6 methoxy groups of TMSPEDA can undergo the reaction with PE-HEMA hydroxyl groups. ^b Melting temperatures (T_m) were determined by DSC from the second heating scan. ^c β transition temperatures (T_β) were determined by DMTA from the maximum of $\tan \delta$. ^d Degrees of crystallinity (X_{cr}) were calculated with respect to the melting enthalpy of 100% crystalline PE (286.2 J/g) [22]. The melting enthalpy of each vitrimer was determined from the DSC second heating scan.

All the prepared vitrimers resulted partially soluble in xylene after soaking at 100 °C for 24 h (Figure S3) demonstrating the crosslinked character and improved solvent resistance of the material, while PE-HEMA completely dissolved under the same conditions (Table S1). The gel fraction of vitrimer 4 reached 40% surpassing the value of ~32 % reported for the HDPE vitrimer based on dioxaborolane metathesis [12]. Gel fraction of 40% is lower than that of commercial silane crosslinked PE (60-70 %); however, it facilitates good balance between performance and processability.

The processability and recyclability of the developed PE-vitrimers were evaluated using gel fraction measurements, FT-IR and industrially relevant techniques like injection and compression molding (Figure S4 and Figure S5). After the initial tensile test, the tensile bars of vitrimer 2 were cut into pieces and compress molded again 4 times. After each reprocessing step, gel fraction, FT-IR and tensile tests were repeated to exclude any change. Even after reprocessing the PE-HEMA vitrimer 4 times, no significant changes in crosslink density (Table S2), chemical structure (Figure S6) or mechanical performance (Figure 1) were observed thus showcasing the dynamic nature and robustness of TMSPEDA crosslinks.

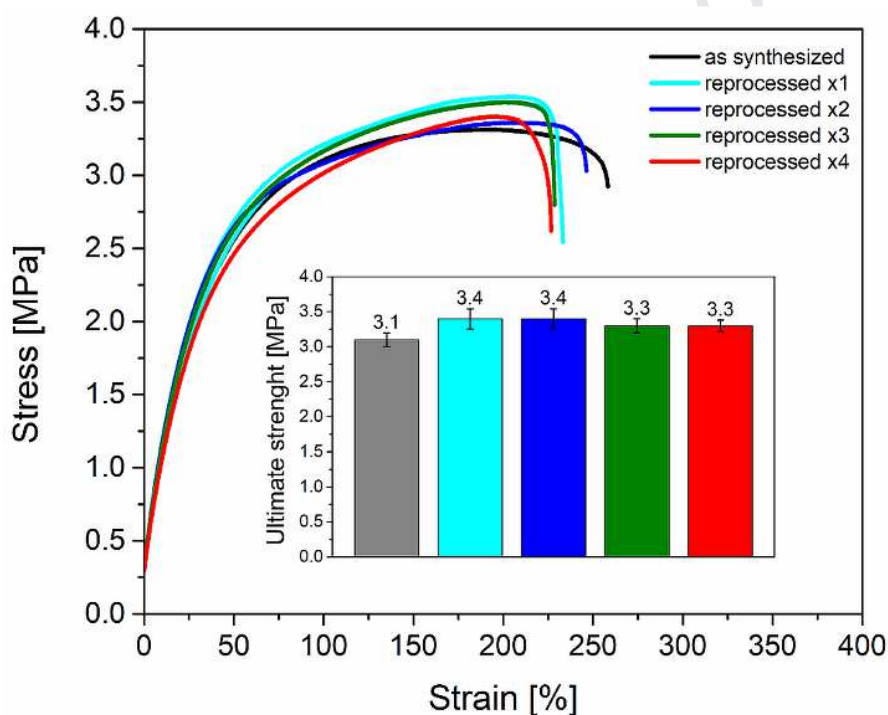


Fig. 1. Representative tensile curves and ultimate strength (inset) of vitrimer 2 tested as synthesized and after up to 4th reprocessing cycle.

Since silyl ether bonds are prone to hydrolysis [23], hydrolytic stability of the PE-vitrimers was assessed by soaking the specimens in water for 24 h at room temperature, and subsequently measuring water uptake, gel fraction and tensile properties. All vitrimers showed minimal water uptake (less than 1 %, Table S3), and the gel fraction as well as the tensile properties were not significantly affected by exposure to water (Table S4 and Figure S7, respectively).

The hydrophobic nature of the polyethylene backbone limits swelling and water uptake, protecting the silyl ether crosslinks from hydrolysis, which is of great importance for industrial applications like water pipes and electrical cables isolation.

Dynamic silyl ether crosslinking of PE-HEMA greatly improved dimensional stability at elevated temperatures and decreased creep in an exponential fashion with TMSPEDA amount (Figure S8) as revealed by the hot set test. While the hot set elongation of vitrimer samples after 10 min at 200 °C under 0.5g load were fairly low (below 25%), PE-HEMA completely melted and failed almost immediately (Figure 2).

To investigate the properties of the PE vitrimers in the melt, rheology measurements were performed (Figure 3). The frequency sweeps performed at 180°C indicated that PE HEMA displays a typical behavior of a low molecular weight polymer melt with a strong frequency dependence [24]. No crossover point between storage (G') and loss (G'') modulus was observed due to relatively long relaxation times compared to the probed time scales within the tested frequency range. The polymer was more viscous (G'' higher than G') than elastic (G' higher than G'') within the whole studied frequency range. Moreover, PE-HEMA was flowing out from between the plates of the rheometer at lower frequencies demonstrating a very low viscosity. After dynamic crosslinking with TMSPEDA, vitrimers behaved like an elastic solid with frequency independent G' and much lower G'' which is characteristic of crosslinked materials [25]. Plateau modulus (G_0) taken at the minimum of G'' increased in a linear fashion with increasing crosslink density (Figure S9) and ranged from around $2.8 \cdot 10^3$ (vitrimers 1) to around $1.2 \cdot 10^5$ MPa (vitriimer 4).

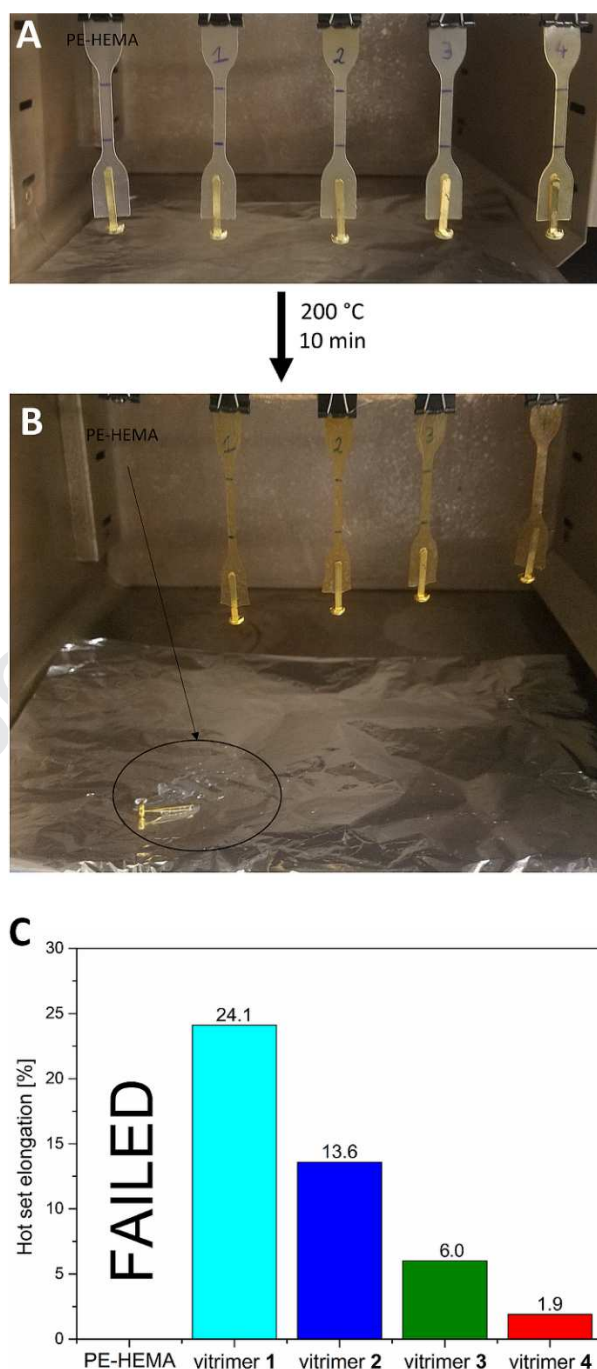


Fig. 2. Hot set test of PE-HEMA and vitrimers 1-4; (A) samples before the test, (B) samples after the test and (C) hot set elongation.

While PE-HEMA reached the zero-shear viscosity at around 10 Pa•s, vitrimers 1-4 had viscosities a few orders of magnitude higher before they even reached their zero shear viscosities (Figure S10). This result indicates highly improved melt strength which is extremely important for processes like film blowing, blow molding, thermoforming and foaming [26,27].

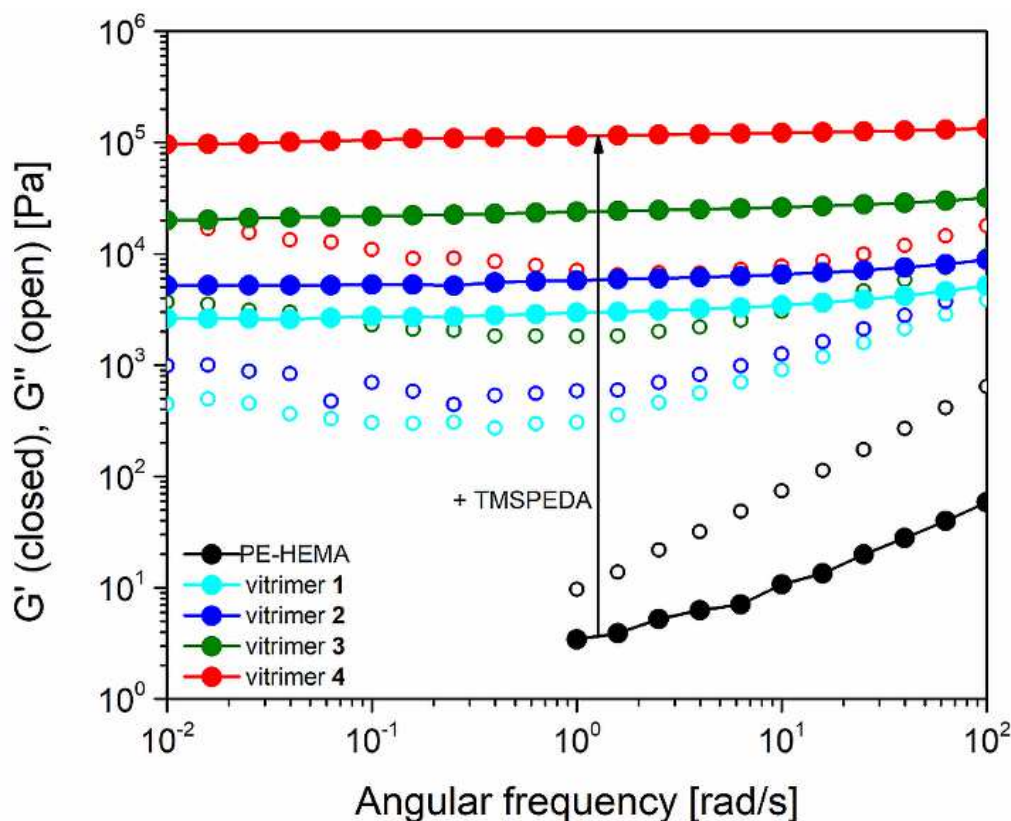


Fig. 3. Rheology frequency sweep curves at 180 °C of PE HEMA and vitrimers 1-4.

Stress relaxation curves of vitrimer 2 have a typical shape characteristic for vitrimers where stress relaxation is governed by the exchange reactions [21]. The experimental data did not fit well to the Maxwell model (Figure S11) and were fitted using a modified Maxwell equation (1), where an exponent a is introduced [28].

$$G(t) = G_0 e^{-\left(\frac{t}{\tau}\right)^a} \quad (1)$$

The exponent a represent a deviation from Maxwell law ($a = 1$) caused by different crosslinks with unequal strengths. In our case, $a \sim 0.25$ which can be attributed to the presence of chain entanglements, trapped loops of the polymer backbone, and hydrogen bonding between the hydroxyl groups of HEMA besides the silyl ether crosslinks [29,30]. Based on the stress relaxation (Figure 4), activation energy of the topological rearrangement (E_a) and topology-freezing transition temperature (T_v) were determined using Arrhenius plot of the relaxation times (Figure S12). E_a of 155 kJ/mol and T_v of 87 °C were calculated for vitrimer 2, this last one much higher than previously reported for PS and PE based silyl ether vitrimers [19,20]. This is also reflected in longer relaxation times, which might be caused by the use of different polymer matrixes and unequal crosslink density [21]. T_v of vitrimer 2 is just few degrees higher than its melting point (~ 72 °C) facilitating processability at relatively low temperatures. In contrast PE-HEMA relaxes stress extremely fast at those temperatures, (below 0.1s, Figure S16). From the industrial point of view, long relaxation times of vitrimers make processing more challenging. However they also ensure good performance and safety in application such as wires and cables by not dripping at elevated temperatures even without classical chemical cross-linking.

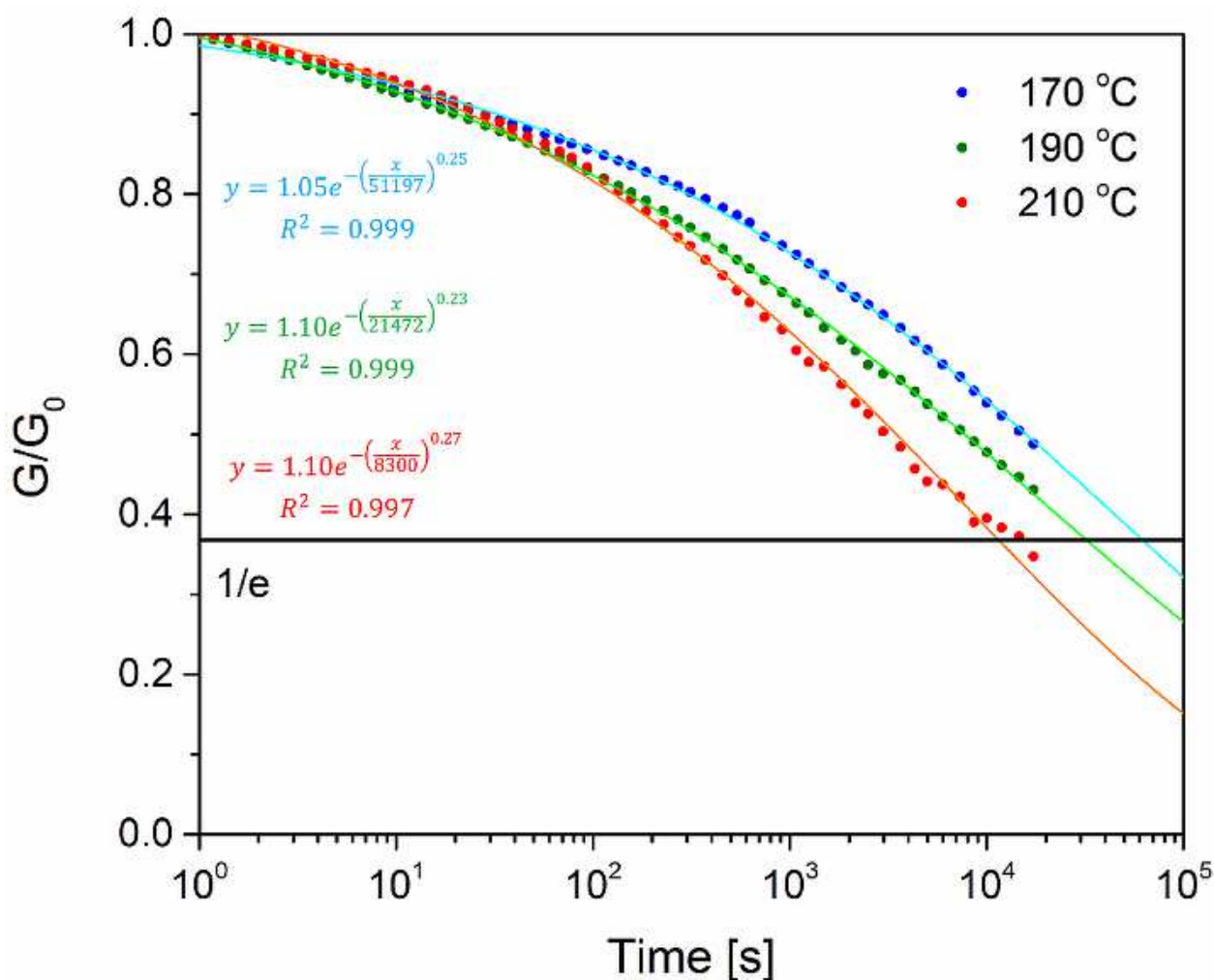


Fig. 4. Stress relaxation curves of vitrimer 2 and fitting performed according to the equation (1). For comparison, stress-relaxation curves for PE-HEMA are reported in Figure S16.

The semi-crystalline nature of our vitrimers can be advantageous, as it can impart increased strength due to the presence of crystal domains. Therefore, the need of extra network formation coming from the dynamic crosslinker is reduced compared to an amorphous polymer as both networks (crystallinity and dynamic crosslink) will be combined in the material at typical use temperature resulting into an enhanced mechanical profile and chemical resistance. Further, the processability of the semi-crystalline vitrimers is improved when compared with amorphous vitrimers. In particular, our semi-crystalline vitrimers have a relatively low melting point (60 °C to 80 °C). This allows the vitrimers to be produced via extrusion at 120 °C to 180 °C in about 10 to 15 minutes. The mechanical properties of the vitrimers were carefully analyzed via DMTA and stress-strain analyses. Semi-crystalline PE usually undergoes three characteristic temperature transitions upon heating [31,32].

γ transition, involving rotation of CH_2 groups in the amorphous and crystalline phases, is observed at around -130 °C and it is independent of the branching content as well as the degree of crystallinity. β transition, occurring at higher temperatures, can be related to movements involving longer parts of the polymer chains and branch points (T_β). Finally, the α transition is associated with a large movement of molecules that arises as the crystalline phase undergoes melting. In the case of PE-HEMA copolymers, an additional transition around -60 °C was observed which most likely results from hydrogen bonds breaking and reforming between hydroxy groups present in the HEMA units (Figure 5) [33].

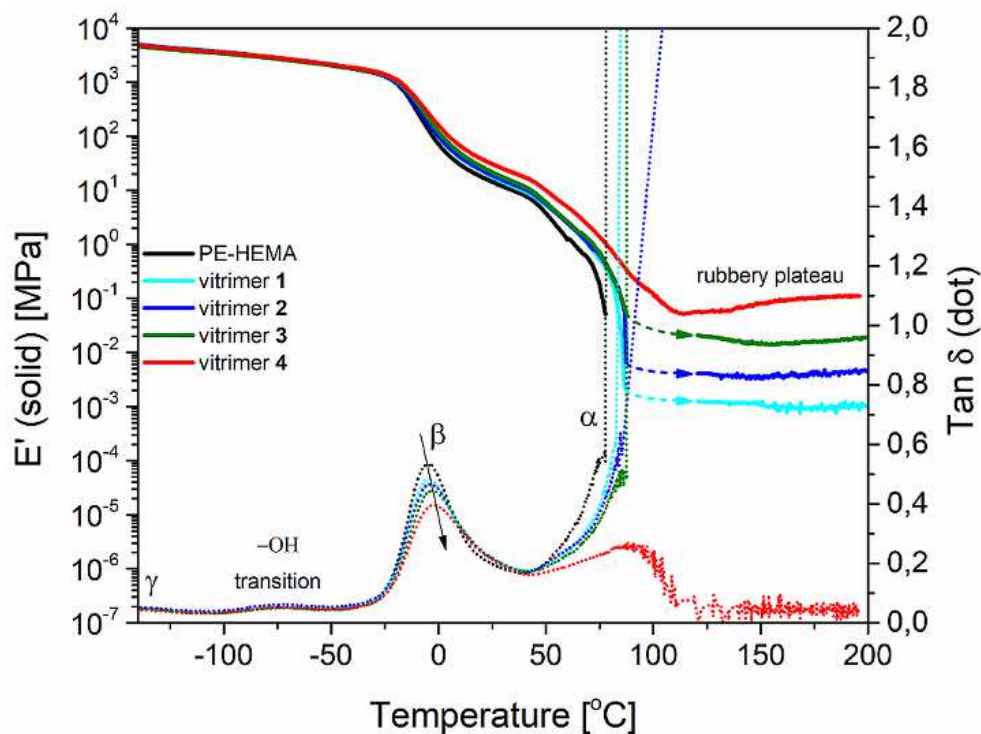


Fig. 5. DMTA curves of PE-HEMA and vitrimers 1-4.

No influence of dynamic crosslinking on γ transition was observed since this transition is independent of the branching content, as already pointed out. DMTA revealed a linear dependence of crosslink density on β transition (Figure S13) since crosslinking creates branched points restricting movement of chains which increases the temperature of β transitions [31,32]. Upon further heating, PE-HEMA and vitrimers 1-4 undergo to an α transition corresponding to the melting of the crystalline phase. While PE-HEMA flows after the melting transition, vitrimers 1-4 display a rubbery plateau with low moduli characteristic of crosslinked materials, indicating improved melt strength of these dynamic cross-linked polyolefins. Plateau modulus of vitrimer 4 of around 0.1 MPa was directly recorded by DMTA, while for the softer vitrimers 1-3 with lower crosslink densities, plateau modulus had to be adapted from rheology temperature sweeps (Figure S14) according to Hooke's law reported in eq. 2 for PE ($\nu \cong 0.5$):

$$E' = 3G' \quad (2)$$

where E' is the storage modulus and G' the shear modulus (Figure 5, colored arrows).

Stress and strain curves show that PE-HEMA exhibits tensile properties characteristic of a semicrystalline thermoplastic, displaying an initial elastic deformation before the neck is formed followed by cold drawing and fracture (Figure 6) [34]. Since PE-HEMA has low molecular weight and low crystallinity (Table 1), low ultimate strength (2.1 MPa) and Young's modulus (7.4 MPa) were observed. The ratio between PE-HEMA and TMSPEDA crosslinker (and thus the amount of crosslinks per chain X/C) has a high impact on the future mechanical properties on the vitrimer. For instance, increasing the amount of TMSPEDA gradually improved ultimate strength and Young's modulus of the vitrimer material up to 134 % and 148% respectively for 9 X/C. However, a higher number of crosslinks (such as for vitrimers 3 and 4) leads to an increase of brittleness as indicated by decreased toughness (strain at break % in Figure 6).

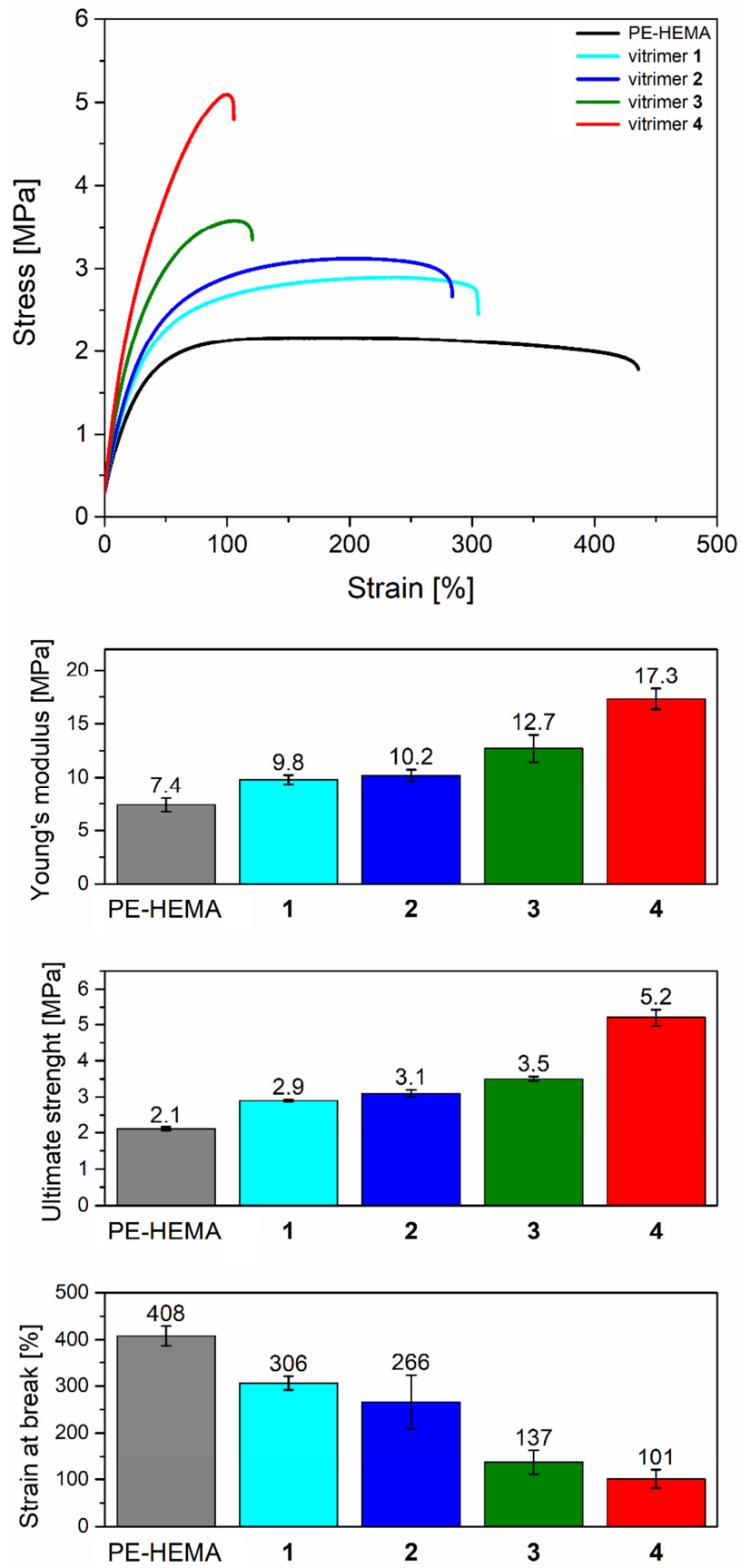


Fig. 6. Representative stress-strain curves and Young's modulus (top), ultimate strength (middle) and strain at break (down) of PE HEMA and vitrimers 1-4.

Conclusions

Dynamic crosslinked PEs were developed introducing exchangeable silyl ether bonds into PE-HEMA. These PE-based vitrimers were directly synthesized via reactive extrusion, using the commercially available TMSPEDA as dynamic cross-linker and Irganox as antioxidant. The silylation reaction proceeds easily thanks to the presence of hydroxyl pendant groups on the PE-backbone. This process allowed to produce the vitrimers in a fast and efficient way, avoiding the use of expensive or toxic solvents, thus making the synthesis environmentally friendly and easy to upscale. We demonstrated that the thermoplastic PE-HEMA could be transformed into an elastic material with improved melt strength and creep resistance. This enhanced property is crucial for processes like film blowing, blow molding, thermoforming and foaming, where permanent covalent crosslink is often used to achieve the same performance. Additionally, mechanical properties could be tuned by varying the amount of TMSPEDA cross-linker. Increasing crosslink density, a gradual improvement of ultimate strength (up to 134 %) and Young's modulus (up to 148 %) was obtained. All prepared vitrimers were sparingly soluble in xylene and were moisture insensitive, demonstrating crosslinked character and solvent and hydrolysis resistance, essential properties for industrial applications. Dynamic silyl ether cross-linking enables processability and recyclability via industrial relevant techniques like injection and compression molding.

Materials and methods

Materials.

Xylene, 1,2 dichlorobenzene (*o*-DCB) and Irganox 1010 (98%) were purchased from Sigma-Aldrich. N,N'-Bis[3-(trimethoxysilyl)propyl] ethylenediamine (TMSPEDA, 95 %) was purchased from BOC Sciences. PE-HEMA copolymer was kindly provided by SABIC (characterization in Table 1 and Figures S15-16). All materials were used as received unless otherwise stated.

Typical procedure for reactive extrusion of PE-HEMA with TMSPEDA dynamic crosslinker. PE-HEMA, TMSPEDA and Irganox 1010 (1000 ppm) were mixed in a metal cup and subsequently fed into a 15 mL co-rotating twin-crew micro extruder. The reaction mixture was processed at 120 °C for 5 min and at 180 °C until constant viscosity was reached (5-10 min) with a screw speed of 100 RPM, after which the discharge valve was opened. The amount of TMSPEDA in the final product was determined from the weight ratio of the PE-HEMA and TMSPEDA fed into the extruder.

Methods.

Reactive extrusion was performed using 15 mL twin crew EXPLORE micro compounder. PE-HEMA and TMSPEDA were mixed in a metal cup and subsequently fed into the micro compounder connected to a computer monitoring melt viscosity. The reaction mixture was processed under nitrogen, with a screw speed of 100 RPM, at 120 °C for 5 min and at 180 °C until the constant melt viscosity was reached (around 10 min, Figure S1).

Injection molding was performed using 12 mL EXPLORE injection molder. Melt temperature, 180 °C, mold temperature 80 °C, injection pressure 10 bar.

Fourier transform infrared spectra (FT IR) were obtained using a Varian 610 IR spectrometer at room temperature in attenuated total reflection (ATR) mode.

The molecular weight and dispersity were studied by size exclusion chromatography (SEC) measurements performed at 150 °C on a Polymer Char GPC IR[®] built around an Agilent GC oven model 7890, equipped with an auto sampler and the Integrated Detector IR4. *o*-DCB was used as eluent at a flow rate of 1 mL/min. The SEC data were processed using Calculations Software GPC One[®]. The molecular weights were calculated with respect to polyethylene as standard.

Melting temperatures (T_m) and enthalpies of the transition (ΔH_m) were measured by differential scanning calorimetry (DSC) using a DSC Q100 from TA Instruments. The measurements were carried out at a heating and cooling rate of 10 °C/min from -20 °C to 150 °C. The transitions were deduced from the second heating.

To determine the gel fraction a small piece (~200 mg) of cross-linked polymer was weighed and placed in a vial to which around 200 mL of xylene were added. The vial was closed and heated at 100 °C for 24 h. The xylene was then removed and the remaining undissolved polymer was washed with acetone, dried under vacuum at 80 °C for 24h and weighed again. Gel fraction was calculated from the mass ratio of the polymer after and before heating in xylene (**Error! Reference source not found.**).

To investigate the water uptake of PE-HEMA-TMSPEDA vitrimers, samples of around 200 mg were weighed and submerged in deionized water for 24h. Subsequently the samples were dried with a paper towel and weighed again. Water uptake was calculated by dividing the initial mass by the mass after water immersion (**Error! Reference source not found.**).

Resistance to hydrolysis was evaluated by measuring the gel fraction of the samples previously used for the water uptake experiment (**Error! Reference source not found.**). Additionally, tensile bars of PE-HEMA and vitrimers **1-4** were submerged in deionized water for 24 h at room temperature, and subsequently tensile test of the sample was performed (Figure S7).

Hot set test was performed using dumbbell-shaped samples (ISO 527-2 type 5A, 0.5 mm thickness prepared by compression molding at 180 °C. The samples were allowed to creep for 10 min at 200 °C by applying a weight of 0.5g. The final length L_{hot} was measured to calculate the hot set elongation $\epsilon_{hot} = (L_{hot} - L_0)/L_0$.

Tensile tests were performed according to ASTM D638-03 with a Zwick Z100 tensile tester equipped with a 100 N load cell, ± 0.001 N resolution. The tests were performed on compression molded tensile bars (ISO 527-2 type 5B, 0.5 mm thickness). The samples were pre-stressed to 0.3 MPa, then loaded with a constant cross-head speed of 50 mm/min. The Young's modulus was determined between 0.05 and 0.25 % strain by regression method in the Zwick testXpert II software. The calculation is based on 8-10 data points.

Rheology was measured using TA Instruments DHR 2 equipped with parallel plate geometry. Compression molded discs with diameter of 25 mm and thickness of 1 mm were prepared at 180 °C. Frequency sweeps were measured from 100 to 0.01 rad/s (strain amplitude of 0.4 %) at a temperature of 180 °C. Stress relaxation measurements were performed at 170 °C, 190 °C and 210 °C, applying a step strain of 1 %, then monitoring the stress for 20000 s.

Dynamical mechanical thermal analysis (DMTA) was measured using TA Instruments Q800 in tensile mode. The specimens were compression molded at 180 °C. Samples were measured from 140 to 200 °C with a heating speed of 3 °C/min and a fixed oscillation (amplitude 10 micron, frequency 1 Hz).

CRedit authorship contribution statement

Arkadiusz Zych: Data curation, Formal analysis, Writing - original draft. **Maria Soliman:** Conceptualization, Supervision, Methodology **Roberta Pinalli:** Conceptualization, Methodology, Writing - review & editing., Project administration. **Jérôme Vachon:** Conceptualization, Methodology, Supervision, Writing - review & editing, Project administration. **Enrico Dalcanele:** Conceptualization, Methodology, Supervision, Writing - review & editing, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary data: DMTA, DSC, ATR and tensile testing data.

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- Production of PE vitrimers via reactive extrusion, a process that is fast, solventless and does not require the use of catalysts.
- The dynamic crosslinking transformed thermoplastic PE into an elastic solid with greatly improved melt strength as revealed by DMTA and rheology.
- The PE vitrimers show excellent hydrolysis resistance which is of great importance for industrial applications.
- Reprocessing of the materials has been positively tested without decrease of the mechanical properties.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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