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One-pot synthesis of robust silyl ether-based HDPE vitrimers with enhanced performance and recyclability

Subhaprad Ash [a,b], Rishi Sharma [a], Mohamed Shaker [a], Shalin Patil [c], Shiwang Cheng [c], Muhammad Rabnawaz [a,b,*]

[a] School of Packaging, Michigan State University, East Lansing, MI, 48824-1223, USA
[b] Department of Chemistry, Michigan State University, East Lansing, MI, 48824-1223, USA
[c] College of Engineering Building, Michigan State University, East Lansing, MI, 48824-1223, USA

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ABSTRACT

Vitrimers are thermally reversible crosslinked polymers that combine the performance of thermosets with the benefits of melt (re)processing. However, existing high-storage modulus vitrimers lack this melt-reprocessibility. This study reports on high storage modulus vitrimers obtained by grafting vinyltrimethoxysilane onto high-density polyethylene (HDPE) using silyl ether crosslinker, bis[3-(trimethoxysilyl)propyl]amine. We also explored the effects of 2,2,6,6-tetramethyl-4-piperidinol and diethyl maleate on the performance of these vitrimers. All vitrimers reported herein are prepared in one step via melt-extrusion without the use of any solvent or catalyst. These vitrimers were characterized via differential scanning calorimetry, Fourier-transform infrared spectroscopy, thermogravimetric analysis, dynamic mechanical analysis and mechanical testing. Selected vitrimers were melt-reprocessed six times and assessed for changes in their storage modulus and mechanical strength by industry-relevant extrusion processing. This study is the first of its kind to offer a solvent-free, single-step approach for the synthesis of vitrimers from HDPE. These vitrimers exhibit an impact strength five times higher relative to that of conventional HDPE, a very high storage modulus (1.58 MPa) at 180^{o}C, and full melt-reprocessability. Considering that extrusion and injection molding is used, the storage modulus achieved in this study is significantly higher than that of vitrimers generated by compression molding, which is commonly used in previous research.

1. Introduction

Prior to Leibler's discovery of vitrimers, there were two primary classes of polymeric materials. These included melt-reprocessable thermoplastics and thermosets that are not melt-reprocessable. However, in 2011, Leibler introduced a revolutionary concept by demonstrating traditional thermosets, such as epoxy thermosets, could be converted into remoldable and reprocessable thermosets [1]. This was achieved by integrating associative dynamic covalent bonds into the network structure of thermosets. Dynamic crosslinking was incorporated to create polymers that can flow like vitreous silica above their melting temperature without exhibiting an abrupt drop in viscosity. These special polymers were named vitrimers, and since then, there has been extensive research on the exchange chemistry to fine-tune the desired properties.

Despite more than a decade of efforts and significant progress in this field, several challenges persist in developing vitrimers suitable to replace conventional thermosets. One major hurdle is creating truly melt-reprocessable vitrimers with high storage modulus. When the material is densely crosslinked, it exhibits a high storage modulus and behaves more like a conventional thermoset, but it becomes difficult to melt-reprocess and vice versa. Typically, the storage modulus for reported vitrimers is less than 1 MPa. Occasionally, vitrimers with a storage modulus of around 2 MPa have been reported, which is really good. However, such high modulus vitrimers are only (re)processed by compression molding hot press or compression molding as opposed to more industrially relevant extrusion and injection molding approaches that are used for all commodity plastics [2–12]. Compression molding involves shaping material by heat and pressure, but it does not involve true melting like thermoplastics. Another challenge in creating vitrimers is the use of traditionally expensive chemicals, harmful solvents, niche polymers, and multistep synthesis. This relies on complicated and costly

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* Corresponding author. School of Packaging, Michigan State University, 448 Wilson Road, East Lansing, MI, 48824, USA.
E-mail address: rabnawaz@msu.edu (M. Rabnawaz).

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Table 1
Formulations (mol %) of materials used to produce HDPE vitrimers.

Sample	HDPE (mol %)	Dicumyl peroxide, DCP (mol %)	Vinyltrimethoxysilane, VTMS (mol %)	Bis[3-(trimethoxysilyl)propyl] amine, BTMSPA (mol %)	2,2,6,6-Tetramethl-4-piperidinol, T (mol %)	Diethyl maleate, D (mol %)
HDPE (control)	100.00	–	–	–	–	–
Samples without T or D (V series)						
$V_{0.25}$	99.48	0.03	0.25	0.25	–	–
$V_{0.5}$	98.97	0.03	0.50	0.50	–	–
$V_{1.0}$	97.96	0.03	1.00	1.00	–	–
Samples with 2,2,6,6-Tetramethyl-4-piperidinol (V-T Series)						
$V_{0.25}$-T	99.41	0.03	0.25	0.25	0.06	–
$V_{0.5}$-T	98.92	0.03	0.50	0.50	0.06	–
V_{1}-T	97.91	0.03	1.00	1.00	0.06	–
Samples with diethyl maleate (V-D Series)						
$V_{0.25}$-D	99.16	0.03	0.25	0.25	–	0.30
$V_{0.5}$-D	98.67	0.03	0.50	0.50	–	0.30
V_{1}-D	97.67	0.03	1.00	1.00	–	0.30

$V_{0.25}$-T *denotes a sample of* ***HDPE*** *grafted with* 0.25 mol% *vinyltrimethoxysilane* ***(VTMS)*** *and* 0.06 mol% 2,2,6,6-*tetramethyl-4-piperidinol* ***(T)*** *with the aid of a radical initiator dicumyl peroxide* ***(DCP)*** *and crosslinked with a secondary amine crosslinker bis[3-(trimethoxysilyl)propyl]amine* ***(BTMSPA)****.*

routes, further restricting the application scope of vitrimers. Most of these chemistries involve the use of external catalysts, which will have the problem of leaching out of the system. Importantly, most of the vitrimeric systems are not prepared by a continuous single pot synthesis, which is one of the prime needs considering the industrial scales.

To make commercially viable vitrimers, plastics that are both low-cost and abundant should be used as feedstock. Polyethylene (PE) fits these criteria well, being both cheaper and more abundant than many other materials. In fact, PE represents nearly 31 % of all polymers [13]. Developing vitrimers from PE could provide numerous advantages, such as creating low-cost vitrimers for widespread use and offering a solution for managing waste or discarded PE. Most of the PE vitrimers have been prepared using boronic ester metathesis [2,3,14–21]. This is because boronic esters have good compatibility with different functional groups, thereby eliminating the need for catalysts. However, these vitrimers undergo faster degradation in hydrophilic environments and are prone to hydrolysis. This poses the need for a thermally and oxidatively stable chemical moiety. Transesterification-mediated PE vitrimers have been studied extensively because of tunable fast activation energies for the exchange reaction because of the catalysts [4,22–24]. However, the catalyst loading in these systems is so high that they leach over time, hinting at the requirement of a catalyst-free fast exchange mechanism. Recently, PE vitrimers were developed using vinylogous urethane [25], but the studies showed that such systems required higher activation energy for the exchange reaction to occur. To overcome the stated difficulties, silyl ether chemistry has turned out to be a better option, owing to the more stable Si–O bond as compared to the C–O bond (128 kcal mol^{-1} vs 91 kcal mol^{-1}) [26]. Inspired by this, fast exchanging and thermally robust silyl ether vitrimers were produced with good processability [5,27–29]. Despite the progress in PE vitrimers, past attempts to create PE vitrimers encountered issues such as a low storage modulus due to low crosslinking density, the use of compression molding for reprocessing, complicated and environmentally unfriendly synthesis protocols. Addressing these challenges is crucial for the successful development and adoption of PE-based vitrimers.

This report describes the development of high storage modulus vitrimers achieved by grafting vinyltrimethoxysilane onto high-density polyethylene (HDPE) in conjunction with bis[3-(trimethoxysilyl)propyl]amine, which served as crosslinker. We also investigated the impact of 2,2,6,6-tetramethyl-4-piperidinol and diethyl maleate on the performance of these vitrimers. The first methodology relies on the use of aminoxyl radicals to suppress the self-polymerization of HDPE macroradicals [30]. The second method employs the use of a maleate system to maintain the surface energy of the system [31]. Notably, all vitrimers were prepared via a continuous single pot melt-extrusion process, thereby eliminating the need for solvent use. Previously, silyl ether-based vitrimers were prepared from poly(ethylene-*co*-vinyl alcohol) and ethylene-hydroxyethyl methacrylate copolymer [5,27–29]. In another study by Hu et al. [32], crosslinked functionalized PE with polysilsesquioxane and carbamate linkages was reported. However, the silyl ether metathesis requires the metal catalyst zinc trifluoromethanesulfonate [$Zn(OTf)_2$]. In another report on silyl ether vitrimers, a hydroxyl-functionalized PE system was used for PE vitrimers [5]. These vitrimers have several desirable features, as they are reprocessable, are produced by a solvent-free approach, and can withstand hydrolysis. However, they had a low storage modulus and required compression molding for reprocessing (not melt-processing). Moreover, silyl ether systems have not been directly studied for HDPE, which is the most abundant plastic produced and used globally [13]. Our study marks a significant advancement in this field. For the first time, we report the creation of melt-reprocessable vitrimers with a storage modulus reaching as high as 1.52 MPa at 180 °C, using a solvent-free single-step approach.

2. Experimental

2.1. Materials and methods

HDPE was obtained from Dow Chemical, USA, labeled DOWLEX™ IP 1026232, having a melt flow index (MFI) of 9g/10min at 190 °C with a load cell of 2.16 kg. Vinyltrimethoxysilane (VTMS, 98 %), dicumyl peroxide (DCP, 98 %), diethyl maleate (D, 97 %), and 2,2,6,6-tetramethyl-4-piperidinol (T, 98 %) were purchased from Sigma Aldrich, Milwaukee, WI. Bis[3-(trimethoxysilyl)propyl]amine (BTMSPA, 97 %) was purchased from TCI AMERICA, USA. These chemicals were used as received from the commercial suppliers without any further purification.

2.2. Procedure for continuous melt extrusion of vitrimers

A summary of the HDPE vitrimers generated by the two methodologies with their compositions are listed in Table 1. All the chemicals were mixed together physically and fed into a 15 cc DSM micro extruder with co-rotating conical twin screws. The screws were rotated at 100 rpm, with the reaction proceeding in a molten state under a nitrogen environment. The residence time for the polymer was kept at 4 min at 190 °C, where the torque of the system was equilibrated to a constant value. Then the samples were extruded and injection molded with an Xplore Injection Molder IM5.5 #0802 at 190 °C to create samples for tensile strength, impact strength, and DMA analysis. The mold temperature was maintained at 45 °C, and a pressure of 6 bar was used to inject the molten material into the mold.

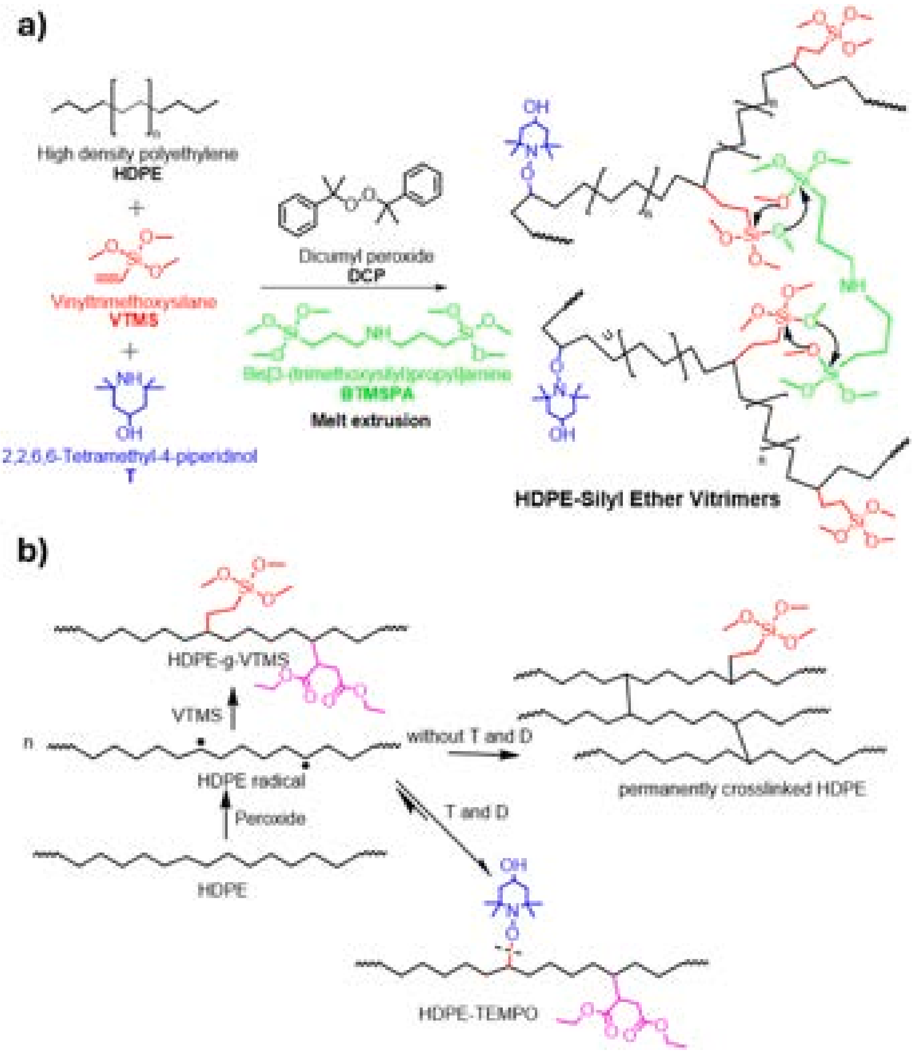

Fig. 1. **a)** Schematic illustration of HDPE-silyl ether vitrimers prepared in this study; and **b)** The formation of HDPE-*g*-VTMS in the absence and presence of T and D.

2.3. *Differential scanning calorimetry*

Differential scanning calorimetry (DSC) was used to investigate thermal properties. Typically, 8.0 ± 1.0 mg of the injection molded sample under a continuous flow of nitrogen at a rate of 100 mL min^{-1}. Aluminum DSC pan with lid were used for DSC analysis. All samples were heated from 25 to 200 °C at 10 °C min^{-1}, and were subsequently cooled at the same rate before they were subjected to a second heating cycle.

2.4. *Thermogravimetric analysis*

Thermogravimetric studies were formed on the vitrimers with a TA Q50 instrument. In a similar way as DSC, 8.0 ± 1.0 mg of sample was taken and placed in an aluminum pan for heating from 25 to 600 °C. A heating rate of 10 °C min^{-1} under nitrogen was used for the TGA analysis.

2.5. *Ultimate tensile testing*

Ultimate tensile testing was performed on the samples after keeping them for 48 h at 23 °C. These tests were performed on an Instron 5565P6021 following the protocol in ASTM D638 [33]. Type V specimens were generated by injection molding so that their dimensions of width, thickness, and gauge length were 3.25 mm, 3.25 mm, and 12.5 mm, respectively, and these samples were subsequently tested at an extension rate of 10 mm min^{-1}. Five replicates of each sample were studied, and the mean value was reported with standard deviation error.

2.6. *Dynamic mechanic analysis*

Dynamic mechanical analysis (DMA) tests were conducted via RSA-G2 system (TA Instruments). For DMA analysis, rectangular specimens were prepared by injection molding with dimensions of 12.5 mm × 6.25 mm × 3.25 mm. These specimens were then subjected to a temperature sweep of 2 °C min^{-1} from 40 to 220 °C at a frequency of 1 Hz with 0.01 % strain in the tensile mode. HDPE sample was analyzed over a temperature range from 40 °C to 140 °C because of its melt flow behavior. The DMA system was equilibrated at 40 °C for 5 min prior to analysis of each sample.

2.7. *Impact testing*

Rectangular specimens were prepared by injection molding with dimensions of 12.5 mm × 6.25 mm × 3.25 mm and tested for impact strength on a Ray Ran Test Equipment Ltd RR/IMT instrument after initial aging for 48 h at 23 °C. Izod impact strength tests were performed on notched samples following the ASTM D256 test method [34]. Five replicates of each sample were studied for stiffness, and the mean value with standard deviation error was reported.

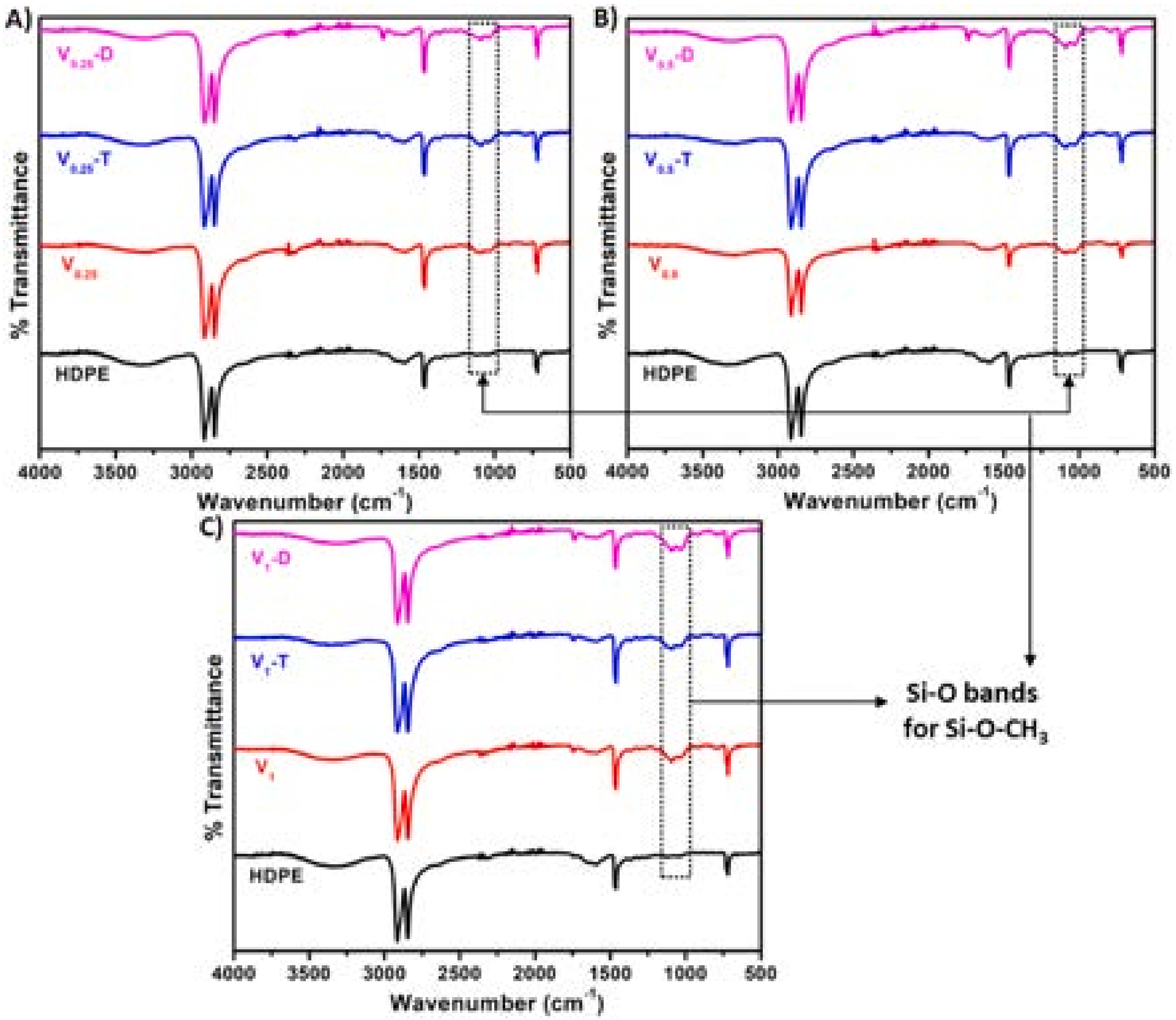

Fig. 2. FT-IR spectra of vitrimers showing strong Si–O bands (1100-1080 cm^{-1}) indicating the presence of $Si–O–CH_3$ in 0.25 mol% **(A)**, 0.5 mol% **(B),** and 1 mol% **(C)** in VTMS samples.

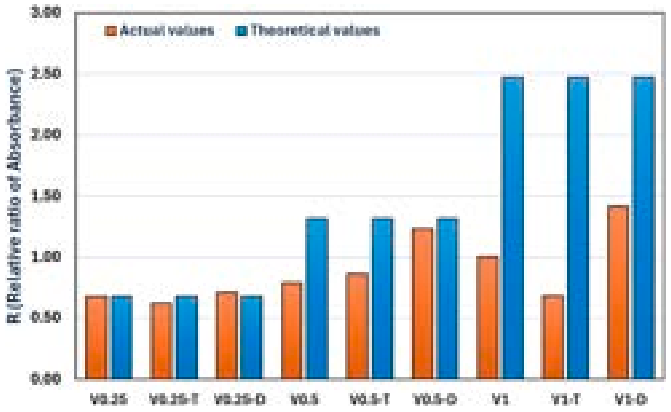

Fig. 3. Relative ratio of absorbance of VTMS at 1092 cm^{-1} to that of HDPE at 719 cm^{-1} for different vitrimers.

2.8. *Fourier-transform infrared spectroscopy*

Fourier-transform infrared (FT-IR) spectroscopy characterization was performed on a Jasco FTIR-6600 spectrometer that was equipped with an ATR Pro-One accessory with a 28-degree Michelson interferometer. Spectra were scanned over the wavelength range of 400–4000 cm-1 with the number of scans decided in auto mode, and the signals were processed with the Spectra Manager™ software program.

3. Results and discussion

Prior studies have established that silyl ether crosslinkers involving secondary amino groups increase the rate of exchange in silyl ether bonds by three orders of magnitude [29]. This is due to the neighboring group effect that enhances rapid exchange reactions and hence makes silyl ether crosslinked polymers malleable. Therefore, we decided to incorporate silyl ether chemistry into HDPE-based vitrimers. Using a one-pot melt-processing approach, HDPE was grafted with vinyltrimethoxysilane to prepare polyethylene-*graft*-vinyltrimethoxysilane (PE-*g*-VTMS) and concurrently crosslinked with bis[3-(trimethoxysilyl) propyl]amine (BTMSPA). The chemistry of the silyl ether exchange process is shown in Fig. 1, where the methoxy groups of the grafted VTMS tend to become exchanged with the methoxy groups of the crosslinker BTMSPA. In addition, we also explored the impact of 2,2,6, 6-tetramethyl-4-piperidinol (denoted with 'T') and diethyl maleate (denoted with 'D') on the performance of HDPE vitrimers with VTMS and BTMSPA.

We used 'T' to enhance the grafting of VTMS on HDPE and to minimize non-reversible crosslinking between HDPE polymer chains. The mechanism is shown in Fig. 1b. Briefly, a peroxide radical abstracts an H atom from HDPE, forming an HDPE macroradical. This HDPE

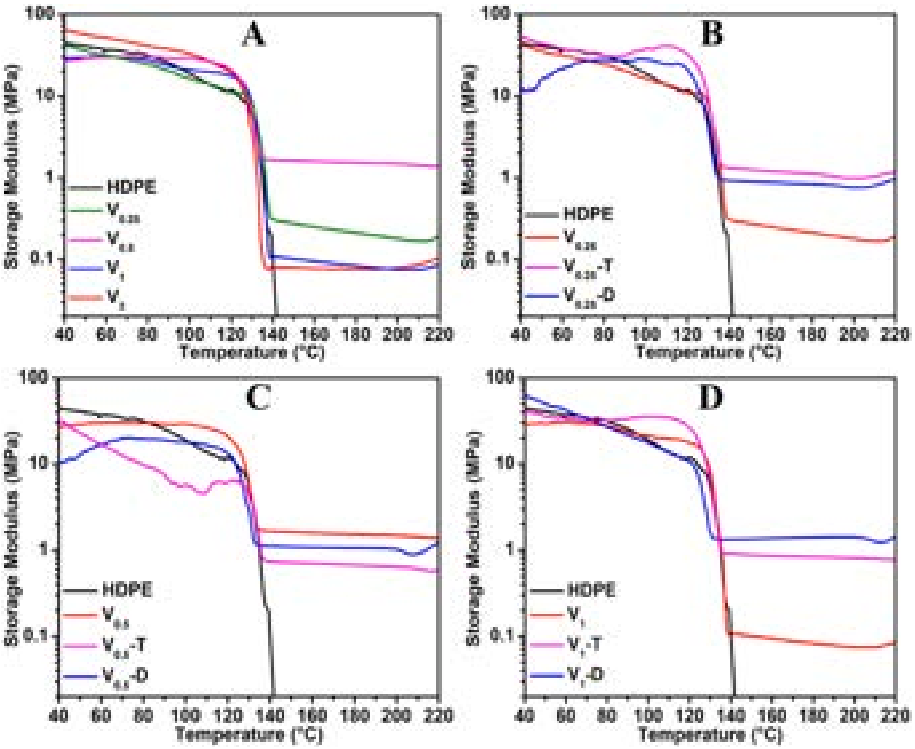

Fig. 4. Plots of storage modulus versus temperature for different vitrimeric systems measured via DMA. **A)** Plots showing the impact of varying mol% of VTMS with respect to PE. **B)** Effect of **T** and **D** on the storage moduli of various vitrimers containing 0.25 mol% of VTMS**. C)** Effect of **T** and **D** on the storage moduli of various viitrimers containing 0.5 mol% of VTMS. **D)** Effect of **T** and **D** on the storage moduli of various vitrimers containing 1.0 mol% of VTMS.

Table 2
Crosslinking densities for silyl ether vitrimers at 180 °C showing enhanced properties with addition of **T** and **V**.

Sample code	E' at *453.15* K (MPa)	Crosslinking density ν ($\times 10^{-5}$ mol cm^{-3})
HDPE	0.00	0.00
0.25 mol% Vinyltrimethoxysilane		
$V_{0.25}$	0.21	1.84
$V_{0.25}$-T	1.11	9.82
$V_{0.25}$-D	0.82	7.27
0.5 mol% Vinyltrimethoxysilane		
$V_{0.5}$	1.52	13.49
$V_{0.5}$-T	0.67	5.91
$V_{0.5}$-D	1.07	9.43
1.0 mol% Vinyltrimethoxysilane		
V_1	0.08	0.74
V_1-T	0.83	7.35
V_1-D	1.40	12.42
2 mol% ***Vinyltrimethoxysilane***		
V_2	0.08	0.74

Table 3
Effect of the reversible radical mediator **T** and co-grafting agent **D** on the crystallinity and melting temperature of silyl ether vitrimers as obtained from DSC measurements.

Sample	ΔH_m (J g^{-1})	ΔH_c (J g^{-1})	χ_c (%)	T_m (°C)	T_c (°C)
HDPE	192.5	205.8	65.6	133.7	112.3
Thermal properties obtained for the V-T systems					
$V_{0.25}$	143.6	153.8	48.9	139.7	110.5
$V_{0.25}$-T	148.3	153.5	50.5	134.0	111.1
$V_{0.5}$	160.9	166.1	54.8	132.2	111.9
$V_{0.5}$-T	164.2	174.9	55.9	134.1	113.2
V_1	172.0	192.1	58.6	138.2	111.4
V_1-T	148.7	151.2	50.6	133.4	109.4
Thermal properties obtained for the V-D systems					
$V_{0.25}$	143.6	153.8	48.9	139.7	110.5
$V_{0.25}$-D	164.8	167.5	56.1	133.7	108.6
$V_{0.5}$	160.9	166.1	54.8	132.2	111.9
$V_{0.5}$-D	144.1	145.9	49.1	130.5	106.8
V_1	172.0	192.1	58.6	138.2	111.4
V_1-D	128.1	135.0	43.6	127.2	110.1

macroradical then reversibly bonds with 4-hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl (4-hydroxy-TEMPO), as supported by literature [3]. As 4-hydroxy-TEMPO reversibly attaches to the HDPE radical, it reverts back to the HDPE radical and 4-hydroxy-TEMPO. The newly created HDPE radical can react again with 4-hydroxy-TEMPO or with VTMS. The equilibrium between 4-hydroxy-TEMPO and HDPE radical primarily favors the formation of HDPE-TEMPO. Consequently, the concentration of HDPE radicals remains low during the reaction, thereby minimizing non-reversible crosslinking between HDPE radicals and also facilitates the grafting of VTMS.

The role of 'D' is to enhance the grafting of VTMS through a different mechanism than TEMPO. D serves as a co-agent that reacts with HDPE radicals, capturing some of these radicals during the grafting process by reacting with them irreversibly (Fig. 1b) and thereby suppressing the coupling of HDPE radicals with each other. This modification facilitates the melt processing of the resulting vitrimers, even at higher VTMS loadings. Additionally, D, with its two dangling ethyl groups and a polar ester component, controls the surface energy. Specifically, the surface energy of D is comparable to that of HDPE (38 dyn/cm for D versus 36 dyn/cm for HDPE) [35]. It has been shown in the literature that the grafting of VTMS onto low-density polyethylene/ethylene vinyl acetate blend at a 5 wt% loading reduces the surface energy of that polymer from 30.90 to 27.63 mJ m^{-2} [31]. In our previous work [36], we were able to avoid this surface energy mismatch by using dimethyl maleate.

Once the vitrimers were prepared, they were characterized by FT-IR spectroscopic analysis. Strong peaks observed at 2919 and 2850 cm^{-1} correspond to the characteristic C–H asymmetric and symmetric stretching vibrations for HDPE. Meanwhile, C–H rocking vibrations for HDPE are signified by strong peaks at 730 and 720 cm^{-1}. The presence

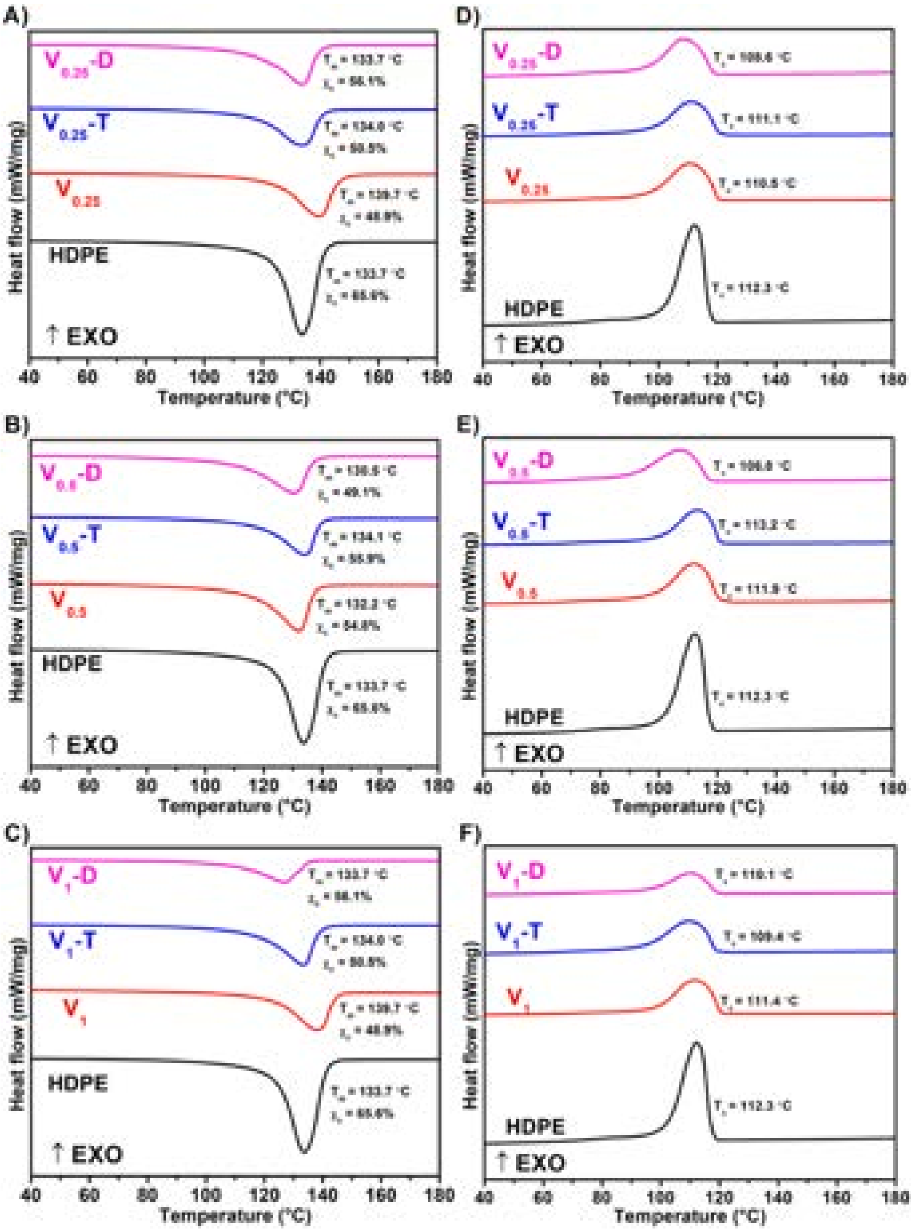

Fig. 5. Broadened DSC thermograms for the heating cycle showed similar melting temperatures and reduced degree of crystallinity with respect to HDPE for PE vitrimers with VTMS loadings of 0.25 mol% **(A)**, 0.5 mol% **(B)** and 1 mol% **(C)**, respectively Similarly, broadened curves for cooling cycles depict the crystallization temperatures for 0.25 mol% **(D)**, 0.5 mol% **(E)**, and 1 mol% **(F)** VTMS loading HDPE vitrimers respectively.

of VTMS is clearly shown by a strong Si–O band in the range 1100-1080 cm^{-1}, indicating the presence of Si–O–CH_3 groups in the vitrimers prepared. FT-IR spectra for all the specimens are shown in Fig. 2.

To further quantify the grafting density of VTMS onto HDPE, we employed a method described in the literature [37]. Initially, all HDPE-VTMS samples were extracted to remove any ungrafted VTMS (monomeric and oligomeric) by heating these samples in toluene at 110 °C for 2 h. The samples were subsequently dried in an oven for 24 h at 80 °C. This was followed by FTIR analysis in the transmittance mode, where the recorded values were converted into absorbance values.

Following the literature method, we determined the theoretical ratios of VTMS grafted onto HDPE [37]. The relative ratio of VTMS absorbance to that of HDPE was analyzed using an absorption peak at 1092 cm^{-1} for VTMS, corresponding to the characteristic methoxy groups of Si–O–CH_3, and a peak at 719 cm^{-1} for HDPE and corresponding to the CH_2 rocking vibration. The experimental relative ratio of absorbance (A_{1092}/A_{719}) is displayed in Fig. 3 as orange bars, while the theoretical values calculated via the literature method are shown as blue bars. This data suggests that as the VTMS concentration increases, the grafting density of VTMS also increases. However, beyond a certain threshold, further addition of VTMS may result in clustering formed by the VTMS self-oligomerization rather than the desired grafting of VTMS onto HDPE, as supported by the literature [38].

DMA offers valuable information in determining storage modulus and crosslinking density. Therefore, DMA analysis was conducted between 40 and 220 °C to determine the storage moduli and, thereby, the crosslinking densities for all samples. HDPE (unmodified) was used as a control/baseline. All vitrimeric specimens showed a rubbery plateau above their melting temperature, indicating the presence of crosslinks (Fig. 4), albeit to a different degree. Firstly, PE-vitrimers were screened by increasing the grafting of VTMS onto HDPE in the presence of an equimolar ratio of crosslinker. With increasing mol% of VTMS, the crosslinking degree of the system increased and then started to decrease, as depicted in the storage modulus graph (Fig. 4A). For example, the

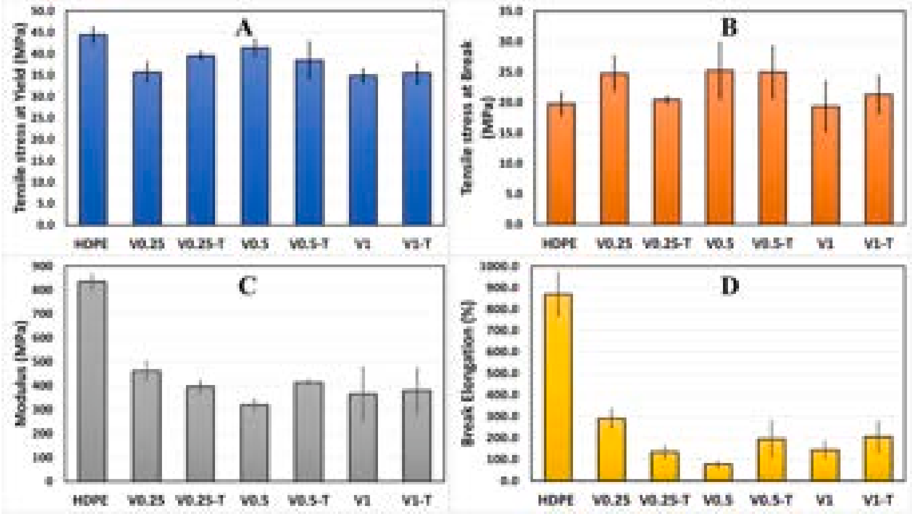

Fig. 6. Tensile properties for various V-T systems. Tensile stress at yield **(A)** and tensile stress at break **(B)** is similar to that of HDPE due to the effect of crystallinity, while Young's modulus **(C)** and elongation at break % **(D)** decrease due to enhanced crosslinking.

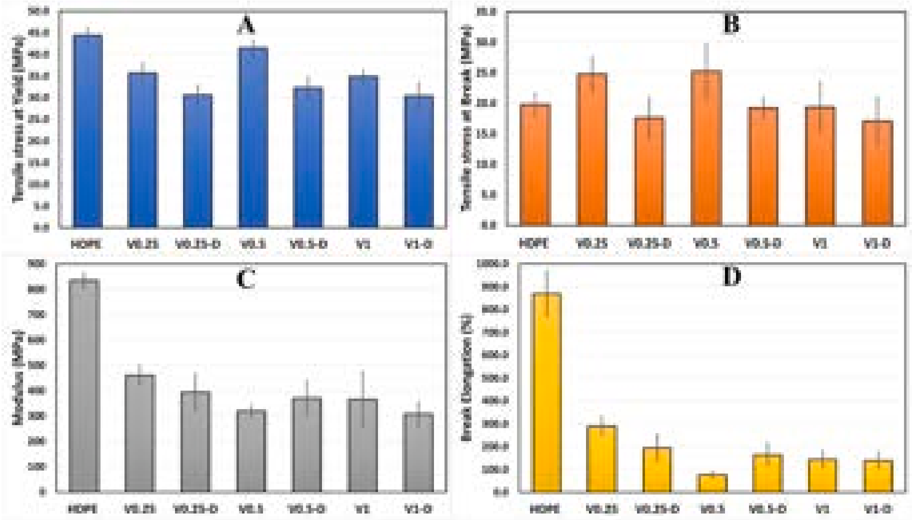

Fig. 7. Tensile properties for various V-D systems. A similar effect is observed as that obtained with the V-T systems. Tensile stress at yield **(A)** and tensile stress at break **(B)** is similar to that of HDPE due to the effect of crystallinity, while Young's modulus **(C)** and elongation at break % **(D)** decrease due to enhanced crosslinking.

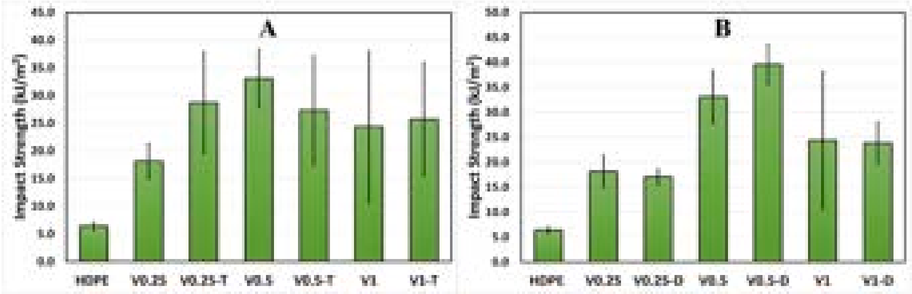

Fig. 8. Impact strengths of the V-T **(A)** and V-D **(B)** vitrimeric systems.

storage moduli for samples with 0.25, 0.5, 1, and 2 mol% VTMS at 180 °C were 0.21, 1.52, 0.08, and 0.08 MPa, respectively. This data suggests that as the VTMS concentration increases, it enhances effective crosslinking. However, beyond a certain threshold, further addition of VTMS may have led to cluster formation within the ungrafted VTMS, as evidenced by grafting densities saturating at 2.25 wt% in studies shown in the literature [38]. This clustering effect hinders the ability of VTMS to facilitate additional crosslinking, thus reducing the overall effectiveness of the material enhancement.

The storage moduli of vitrimers containing 2,2,6,6-tetramethyl-4-piperidinol **(T)** were determined, and these vitrimeric systems were denoted as V-T systems. For the V-T system, the storage moduli at 180 °C

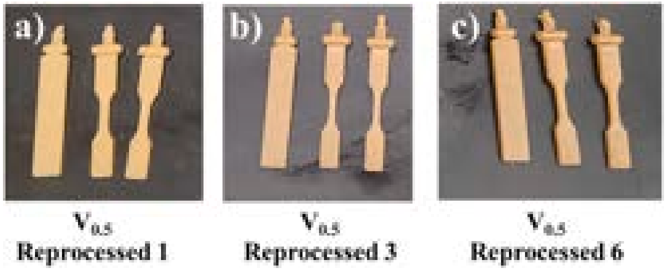

Fig. 9. $V_{0.5}$ samples that had been reprocessed one, three, and six times and which are labeled as $V_{0.5}$ Reprocessed 1 **(a)**, $V_{0.5}$ Reprocessed 3 **(b)**, and $V_{0.5}$ Reprocessed 6 **(c)**, respectively.

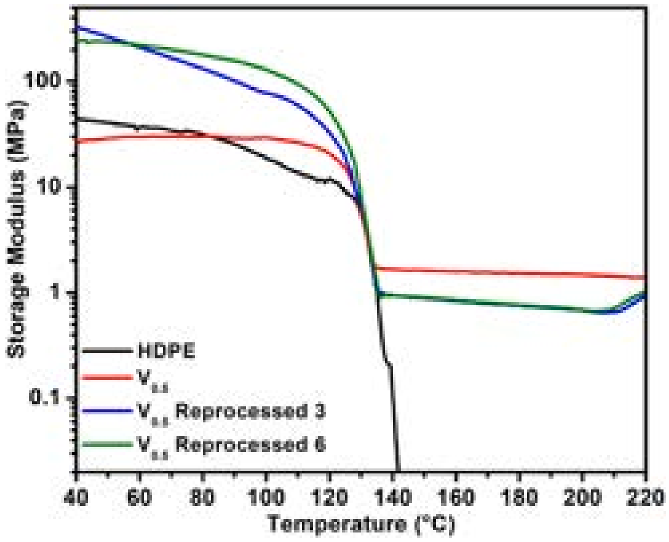

Fig. 10. Storage moduli for $V_{0.5}$ reprocessed samples. Six reprocessing cycles were performed, but only $V_{0.5}$ Reprocessed 3, and $V_{0.5}$ Reprocessed 6 (which were reprocessed 3 and 6 times, respectively) are shown for simplicity.

for systems with 0.25, 0.5, and 1 mol% T are 1.11, 0.67, and 0.83 MPa, respectively. Why does it matter? The storage moduli for these vitrimers increased to 1 MPa, showing a very enhanced crosslinked structure, nearly 10 times higher than that recently reported for silyl polyethylene vitrimers by Zych et al. [5] A possible explanation for this phenomenon is that the aminoxyl radical bonds reversibly with HDPE macroradical [39] and prevents permanent crosslinking from taking place but subsequently regenerates the HDPE macroradical at higher temperatures, which is then available to undergo grafting with VTMS and crosslinking with BTMSPA. We also explored the impact of diethyl maleate **(D)** on the PE silyl ether vitrimers, and the systems were labeled as V-D systems. The surface energy of the polymeric system is maintained by D enabling more VTMS to participate in grafting and enhance the crosslinking density, as observed in the V-D system (Fig. 4). For the V-D system, the storage moduli at 180 °C for 0.25, 0.5, and 1 mol% are 0.82, 1.07, and 1.40 MPa, respectively.

Table 2 shows crosslinking densities for silyl ether vitrimers from DMA data at 180 °C. The crosslinking densities of all the vitrimeric systems were calculated at 180 °C by using **equation (1):**

$$\nu = \frac{\boldsymbol{E'}}{\boldsymbol{3RT}} \qquad \text{(equation 1)}$$

where $\boldsymbol{E'}$ is the storage modulus obtained from DMA, $\boldsymbol{R}$ denotes the universal gas constant, and $\boldsymbol{T}$ is the temperature.

Overall, it can be seen that $V_{0.5}$, the HDPE vitrimer with 0.5 mol% VTMS loading, showed the highest crosslinking density among all the samples, without the use of **T** and **D** as compared to 0.25 and 1 mol% VTMS-loaded samples. This is evident from the crosslinking density of $V_{0.5}$, which is 13 times higher than that of $V_{0.25}$ and V_1 (Table 2). To show the effect of the addition of the radical scavenger **T** and the surface energy mediator **D**, $V_{0.25}$ and V_1 systems were compared with their counterparts having both T and D added (i.e., they were compared with the V-T and V-D systems). Both T and D had an enhanced effect on the storage modulus. This indicates that the radical scavenger T enhances crosslinking by regenerating HDPE macroradicals at higher temperature, initially preventing the self-crosslinking that would have made the polymers unprocessable. On the other hand, D maintains the surface energy thereby enabling more VTMS to crosslink with the crosslinker BTMSPA [36]. To demonstrate the importance of BTMSPA crosslinker, an experiment was conducted with the $V_{0.5}$ system without BTMSPA. This resulted in highly crosslinked HDPE with torque going past 42 Nm, a situation where melt-reprocessing becomes impossible. The role of BTMSPA is, in fact, due to the neighboring group effect of the amino nitrogen, has an enhanced effect on the exchange reaction that makes the polymer malleable for reprocessing.

The vitrimers and their precursors were characterized via DSC to investigate their melting and crystallization behavior. An initial heating cycle was used to remove any thermal history, which was followed by cooling and then another heating cycle. The degree of crystallinity was calculated based on the enthalpy of melting (ΔH_m) and theoretical value of enthalpy of melting of 100 % crystalline polyethylene (293.6 J g^{-1}) [40] using **equation (2):**

$$\textit{Percentage crystallinity}\ \chi_c = \frac{\Delta H_m}{\Delta H_{m0}} \times 100 \qquad \text{(equation 2)}$$

Overall, the crystallinity of vitrimeric samples decreased to approximately 53 % relative to the crystallinity of 66 % for HDPE, representing an almost 20 % reduction in crystallinity (Table 3). This decrease was observed across all vitrimeric samples with VTMS grafting densities ranging from 0.25 to 1 mol%. The reduction in crystallinity corresponds to crosslinking due to their vitrimeric nature and the grafting of dimethyl maleate. As a side note, one potential application of this work will be for 3D printing, where such a decrease in crystallinity will suppress warping, and silyl ether exchange will enhance inter-layer adhesion and structural integrity [6].

Importantly, the heating and cooling curves are primarily broadened as compared to those of HDPE, which exhibits sharp melting and cooling curves (Fig. 5). This behavior indicates the crosslinks are spread throughout the polymer and are not restricted to a particular region. These vitrimers maintained a similar melting temperature to that of HDPE, except for $V_{0.25}$ and V_1, where it increased by 6 °C. The reason for this increase is unclear, as other samples melted at approximately 134 °C despite having higher crosslinking densities than samples $V_{0.25}$ and V_1. Conversely, the crystallization temperature for all HDPE vitrimers decreased by 2 °C. Overall, the thermal properties are largely retained, except for the reduced crystallinity in the system.

The mechanical properties of these vitrimers are attributable to the cumulative effect of increasing crosslinking densities and decreasing crystallinity in these systems. Studies have shown that a lower degree of crystallinity leads to a weaker tensile strength due to a lower degree of intermolecular bonding. Similarly, increasing crosslinking in the system will enhance the tensile strength due to the formation of a more extensive network structure, so that more force is required to create a small strain. These are reflected in the tensile stress at yield and break, which remained similar to that of HDPE (Figs. 6 and 7).

Young's modulus decreased almost 50 %, mainly due to a reduction in crystallinity by enhanced crosslinking. In a crystalline polymer, the intermolecular bonding is very high as opposed to the crosslinked system in which networks are all randomized. This creates more strain as the chains become oriented in a crystalline system. Therefore, these vitrimers tend to have lower Young's moduli than their pristine polymer. The formation of a networked structure due to crosslinking causes

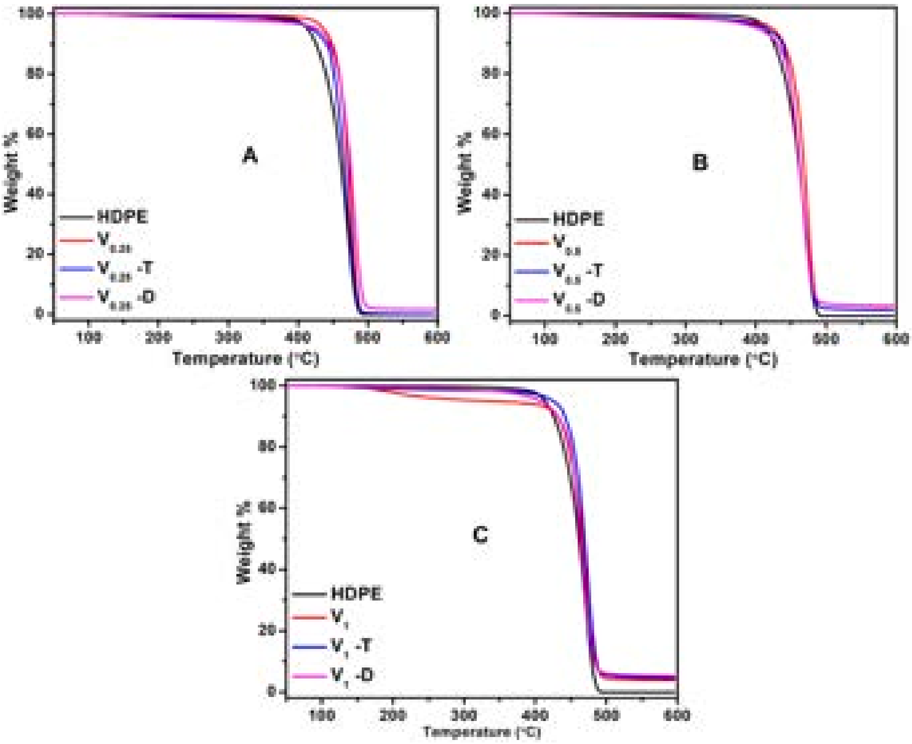

Fig. 11. TGA plots for vitrimeric samples showing a similar degradation trend with respect to control HDPE for PE vitrimers containing 0.25 mol% (A), 0.5 mol% (B), and 1 mol% (C) VTMS respectively.

the polymer to become more stiff and rigid with decrease in elongation. For instance, $V_{0.5}$, having the highest crosslinking density of 13.49 × 10^{-5} mol cm^{-3}, has the lowest elongation at break % of 76.8 %, which is 11 times lower than that of conventional HDPE (Table S1). In contrast, the stiffness/impact strength of this material has increased to 33 kJ m^{-2} as opposed to 6.4 kJ m^{-2} (Fig. 8). Therefore, these vitrimers have 5 times greater fracture resistance in comparison with that of unmodified HDPE. This high toughness will be very desirable for high-performance applications requiring the ability to endure sudden impacts.

Reprocessing of these HDPE vitrimers is a very important aspect of this study. In all vitrimer studies reported in the literature, reprocessing is achieved by employing hot press or compression molding [2–12]. Injection molding is an industrially relevant technique for processing polyolefins that offers numerous advantages over compression molding such as rapid processing, high production volume and absence of waste/scrap. Moreover, polyolefins form 48 % of the total plastics generated worldwide [13]. Therefore, the use of injection molding to reprocess these vitrimers will truly test the recyclability of these emerging high-performance materials as opposed to the heat press used in all conventional vitrimeric studies. To test the recyclability of these vitrimers, reprocessing was performed with $V_{0.5}$, the sample having the highest crosslinking density amongst all the polymers investigated in this study. Firstly, $V_{0.5}$ macrofilaments were generated. These macrofilaments were then ground in an EBERBACH Single Speed Mini Cutting Mill E3300.00 and fed into a DSM micro extruder at 190 °C for 4 min to extrude a sample which was denoted as $V_{0.5}$ Reprocessed 1 depicting vitrimer reprocessed one time. Similarly, $V_{0.5}$ Reprocessed 1 macrofilament was grinded and reprocessed in the DSM micro extruder to generate $V_{0.5}$ Reprocessed 2 samples. This process was continued for six recycling cycles (with the corresponding samples being denoted as $V_{0.5}$ Reprocessed *n*, where is n = 1–6 corresponds to the number of reprocessing cycles) and the mechanical properties of these samples were evaluated. The photographs of the reprocessed samples are shown in Fig. 9. During melt-reprocessing, the torque did not change significantly and remained in the range of 18–20 Nm.

Looking at the photographs in Fig. 9, it is evident that the reprocessed samples start to degrade to some extent over the reprocessing cycles as the color becomes darker. Dynamic mechanical analysis of reprocessed samples indicate that these vitrimers retain the storage energy for the stain applied thereby maintaining constant crosslinking density. Over the reprocessing, some of the crosslinks do degrade, as observed in the storage modulus of $V_{0.5}$ Reprocessed 6 in comparison with that of $V_{0.5}$ **(Fig. 10)**.

By analyzing the mechanical properties of these reprocessed samples, it can be inferred that the tensile strength is retained and comparable to virgin HDPE. Moreover, Youngs's modulus and elongation at break % do not change significantly over the six processing cycles, thus indicating that the crosslinked system possessed a robust network structure. This data is tabulated in Table S2 in the SI. Since reprocessing by injection molding was successfully demonstrated at least six times in the most crosslinked system, all other systems are expected to follow the same trend. Silyl ether systems having a thermally stable Si–O linkage are expected to show good stability when transformed to vitrimeric systems. This is evident from the thermogravimetric analysis for all the samples (Fig. 11). Overall, no real degradation is observed below 220 °C. Also, the V-T and V-D samples are thermally more stable than the V samples. In fact, all vitrimer samples with 0.25 and 0.5 mol% of VTMS such as $V_{0.25}$, $V_{0.25}$-D, $V_{0.25}$-T and $V_{0.5}$, $V_{0.5}$-D, $V_{0.5}$-T are thermally stable at temperatures reaching up to 350 °C or more indicating very robust system.

4. Conclusion

We have successfully demonstrated high storage modulus vitrimers by grafting vinyltrimethoxysilane onto HDPE, with a silyl ether crosslinker, bis[3-(trimethoxysilyl)propyl]amine. Both 2,2,6,6-tetramethyl-4-piperidinol and diethyl maleate play important roles in the storage moduli of vitrimers. This study is the first of its kind to offer a solvent-free, single-step approach to prepare vitrimers from HDPE, demonstrating an impact strength that is 5 times higher relative to that of conventional HDPE, a very high storage modulus (>1.5 MPa), and full melt-reprocessability. We have also demonstrated the successful melt-processing of selected vitrimers six times. Considering the commercially viable extrusion method used here, and the high storage modulus achieved, this method offers considerable benefits and enhancements over the compression molding approaches that have been reported in previous studies.

CRediT authorship contribution statement

Subhaprad Ash: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation. **Rishi Sharma:** Data curation. **Mohamed Shaker:** Data curation. **Shalin Patil:** Data curation. **Shiwang Cheng:** Investigation. **Muhammad Rabnawaz:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

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.

Data availability

Data will be made available on request.

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Mohamed Shaker has a permanent affiliation with the Department of Chemistry, Faculty of Science, Tanta University, Tanta, 31527, Egypt.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.polymer.2024.127374.

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