Green Characterization of Advanced Sustainable Materials for Engineering Applications: Determination of Material Thermal Properties using Molecular Dynamics

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ABSTRACT

The concept of holistic sustainability offers novel approaches to minimize the impact of laboratory experiments in the field of engineering polymer materials by utilizing digital smart tools. One of the main tools is the advanced simulation which is a sustainable approach to predict characteristics of systems and materials with minimal environmental impact. Molecular dynamics (MD) has recently become a powerful tool to predict properties of standard materials such as commercial plastics and thermosets. The aim of this study is to determine the minimum model size required to accurately estimate thermal properties of new materials. In this work, two novel vitrimer variants are introduced. The vitrimers are based on triketone monomers which cross-link following the reversible dynamic covalent bonding exchange mechanism and created both experimentally and numerically. The average glass transition temperature was numerically estimated using MD simulations and verified with experimental data. In the MD model, the cut-off distance was tuned to control the reaction kinetics and consequently reduce the computational time. The results show that a minimum model size of 5000 atoms should be maintained to ensure accuracy. This highlights that thermal properties of new complex vitrimer systems can be numerically estimated at high accuracy using reduced size models and hence save both experimental and computational hours and contribute to the materials green development and testing plans.

Keywords: Green characterization, Sustainability, Simulation, Modelling, Polymers, Vitrimers, Molecular Dynamics.

1. INTRODUCTION

The interest in the use of polymers as substitutes for other materials such as metals, wood, and ceramics has greatly grown over the last few decades [1,2]. Polymers have traditionally been categorized into two major groups: thermoplastics and thermosets [3,4, 5]. Nevertheless, as the use of thermoset systems grows, the limitations and drawbacks, such as the lack of reparability, re-processability and recyclability, need to be tackled as a matter of urgency in the interests of sustainable growth. Materials which can automatically repair internal and external damage during service life, as well as thermosets which enable re-processing and recycling while retaining their functional properties, are aggressively sought in the wake of the dynamism displayed by living nature. Recently, the implementation of reversible chemical bonds in polymer networks tackled this issue where a new family of thermosets known as "Vitrimers" was invented [6,7]. Vitrimers behave at service temperatures like permanently cross-linked materials, are insoluble at all temperatures, but when heated, they can still flow and hence resemble thermoplastic behavior. Vitrimers consist of a polymer network capable of modifying its topology without reducing its connectivity due to exchange reactions, which hold the number of chemical bonds and cross-links constant [8,9]. The transmission of these dynamic covalent bonds (DCBs) usually happens by either associative or dissociative pathways. Bond breaking and reformation occur concurrently in an associative direction (Figure 1b), while in a dissociative direction the bond dissociates first and then after some time a new bond forms (Figure 1a). [10,11,12]
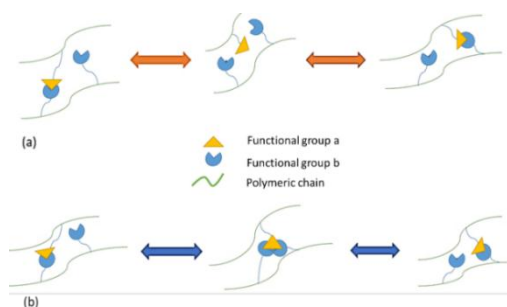

Figure 1*: Dissociative (a) bond exchange and Associative (b) bond exchange
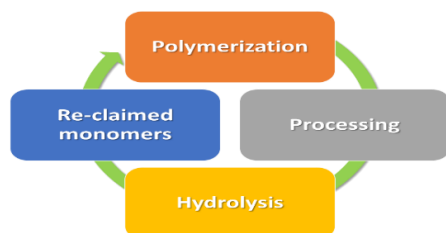

Figure 2: PDK closed loop cycle

One of the recently developed vitrimers is the polydiketoneamine based vitrimers which is explained in the next section 1.1.

1.1 Poly (diketoneamine) Vitrimer

The next generation of vitrimers was reported by Christensen et.al. [6] which polymerizes with dynamic covalent diketoneamine bonds. Poly-(diketoneamine)s (PDK) 'click' from a wide array of triketones and aromatic or aliphatic amines together, leaving only water as a by-product. Recovered monomers can be recycled into the same formulation of polymer without loss of performance, as well as other polymer formulations with distinct properties which promotes a closed recycling of this type of polymers as shown in (Figure 2).

1.2 Molecular Dynamics simulations (MD)

MD simulations provide estimates over system's dynamic properties such as coefficients of transport, time-dependent responses to stimuli, rheological properties, and spectra. This provides an insight into molecular interactions and consequently reliable predictions of bulk properties can be simulated also at temperature or pressure extremes that are difficult to maintain in the laboratory [11]. MD simulations usually depend on large system sizes for results accuracy, Dai et. al. [13], used a model size of around 92K atoms to predict the subsurface damage mechanism during Nano-scratching of single crystal silicon. In an epoxy system with a reduced model size, Qu et.al. [14] simulated thermomechanical properties using a model size of 2766 atoms with cell length of 30 Å. For a 90% cross-linked system a deviation of 30 K between the simulated and experimental values was reported. In another study by Yan et.al. [15], the cure behavior in Epoxy was studied with a system size of 1817 molecules and the effect of varying the cut-off distances from 1.5 – 2.5 Å on the cross-linking density was investigated. A 90% cross-linking density was achieved at 1.8 Å cut-off distance. The cut-off distance here means that two reactive atoms lying within this defined cut-off distance will react by forming covalent bonds with the nearest reactive pairs. Schichtel et.al. also proposed a novel methodology of simulating the reaction kinetics of thermosetting polymers by selective minimization of high potential energy groups for model size of 50K atoms with higher cut-off distances of 3.25 and 4.5 Å [12]. The numerical results showed realistic variations of the thermoset density in relation to the cross-linking density. On the other hand, Ciarella et.al. [16] constructed a model demonstrating the stress-relaxation behaviour of vitrimers with molecular dynamics using 1500-star polymers. It was proven that the distinguished bond-swapping mechanism of vitrimers could be successfully simulated using coarse grain approach.

In another research by Koo et.al. [17] used MD to determine the Tg of a new developed stress-sensitive material and validated the results with DSC experimental values. The model size was 4235 atoms with a cut-off distance of 4 Å. The results showed good agreement between numerical and experimental values with error range 1.2 – 1.3%. Bermejo et.al.[18] also studied the Tg of cross linked PVA using MD at different cross-linking densities. Tg was determined by simulating V/T (V: specific volume, T: temperature) curves and proved to produce the experimental trend observed on the polymeric systems.

In this work, two novel variants of poly-(diketoneamine) vitrimers based on the PDK vitrimer reported by Christensen et.al. were chemically synthesized then modelled using reduced model size and increased cut-off distance to simulate their glass transition temperature (Tg). To validate the model, a standard reference material namely Poly(ethylene terephthalate) (PET) which is the most popular thermoplastic polymer resin of the polyester family[20] modelled and its melting temperature (Tm) was simulated. Differential scanning calorimetry (DSC) was also performed to determine the Tg for the two variants (PDK-G) and (PDK-A) in addition to the Tm for the standard Polyethylene-terephthalate (PET) to validate the numerical results. The numerical modelling and simulation were based on molecular dynamics simulations using LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator, Sandia National Laboratories, USA) [12].

Hence, The aim of this study is to determine the minimum model size required to accurately estimate thermal properties of new materials. In this work, two novel vitrimer variants are introduced.

2. METHODOLOGY

First, the chemical synthesis process for the two poly (diketoneamine) variants namely
PDK-G and PDK-A were performed and the determination of the Tg was conducted experimentally.
Secondly, the MD model was constructed for the reported PDK in [6] to determine the suitable cut-off distance for the system since the two new variants are also based on poly-(diketoneamine). Standard PET (polyethylene terephthalate) which represents a polymer from another family (thermoplastics), was modelled and the Tm (its processing temperature) was simulated using LAMMPS using the same parameters. Afterwards, PDK-G and PDK-A are modelled different model sizes to determine their Tg.

The last step was the validation of the numerical results with the experimental results.

1.3 Materials

In this section, the materials used in this study are presented. The laboratory prepared PDK variants are thoroughly discussed explaining their preparation and characterization methods. Regarding the PET which is a commercial material, only the chemical structure will be presented since it will be used in building the molecular model.

1.3.1   Synthesis and characterization of PDK vitrimer variants

For chemical synthesis of PDK-G and PDK-A, the following main chemicals were used;
5,5-dimethyl-1,3-cyclohexanedione (dimedone), N,N'-dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (DMAP), tris(2-aminoethyl)amine (TREN), Dichloromethane (DCM) were purchased from Sigma-Aldrich. Azelaic acid and Glutaric purchased from Loba Chemie PVT.LTD. Figure 3(a) & (b) show the preparation of Azelaic based triketoneamine (TK-A) and Glutaric based triketoneamine (TK-G) monomers from the starting acids Azelaic and Glutaric acid respectively. TK-A and TK-G are then polymerized in the presence of TREN to produce PDK-A and PDK-G reaction shown in (Figure 4 & Figure 5) following the procedure presented by Christensen et.al.in [6]. The calculated molecular mass for the TK-A is 432.25 and for TK-G is 376.19.
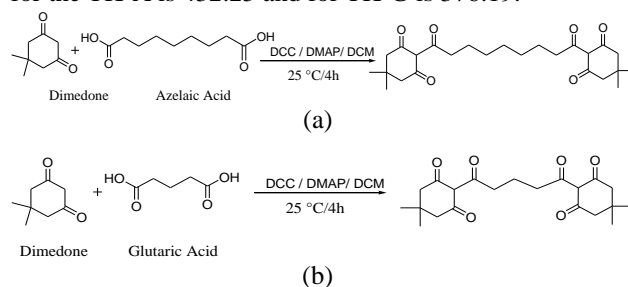

(a)

(b)

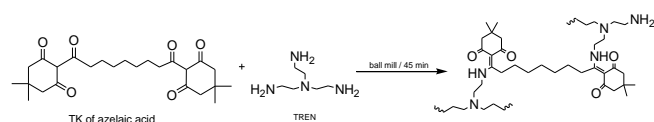**Figure 3: Synthesis of (a) TK-A from Azelaic acid and (b) TK-G from Glutaric acid**

Figure 4: Polymerization of Triketone Dimer of Azelaic acid with TREN
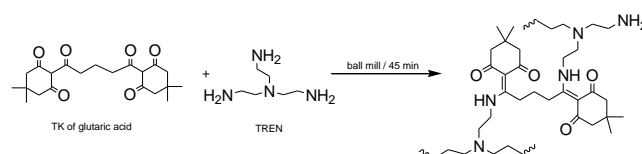

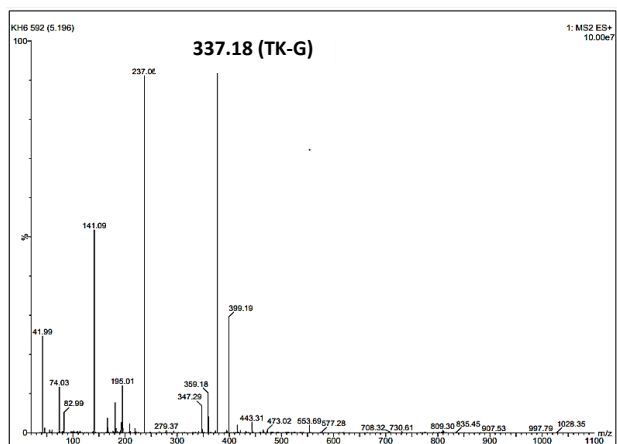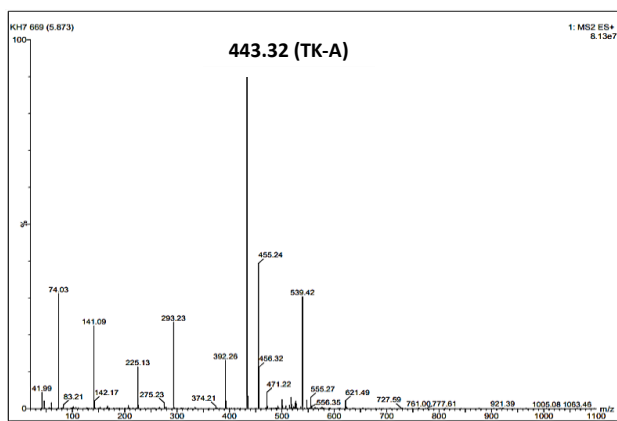**Figure 5: Polymerization of Triketone Dimer of Glutaric acid with TREN**

Figure 6: Mass spectroscopy results of TK dimers

Structural elucidation of the synthesized compounds was performed using LC-MS, FT-IR & 1H-NMR. LC-MS (Figure 6) showed the exact molecular mass of the prepared compounds as (M+H)+.

FT-IR revealed the presence of the carbonyl functional groups (C=O) with their characteristic absorption bands around 1600 cm-1 in addition to absorptions due to the C-H bonds in the range from 2962 -2853 cm-1.

1H-NMR (Figure 7) showed sets of equivalent protons accommodated in the synthesized compounds with the methyl protons being the most up field while the cyclohexadione methine protons appearing as the most down field protons.
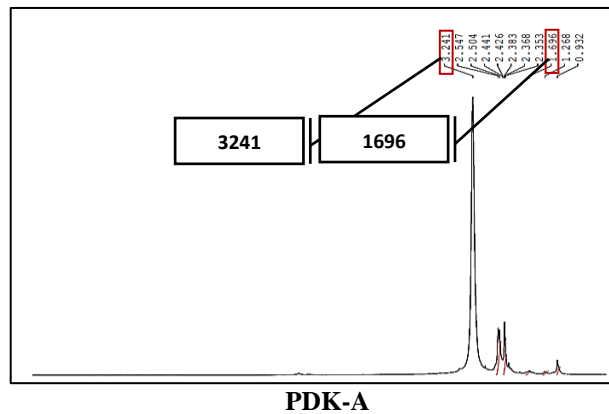
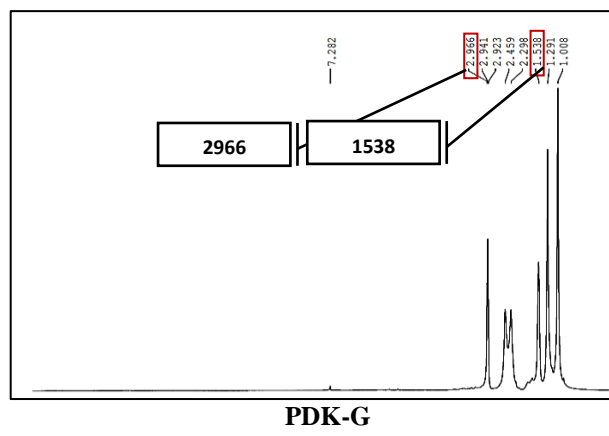Polymerization products were tested using FT-IR (Figure 8) where N–H stretch bands appeared in the range from 3400-3250 cm^{-1}.
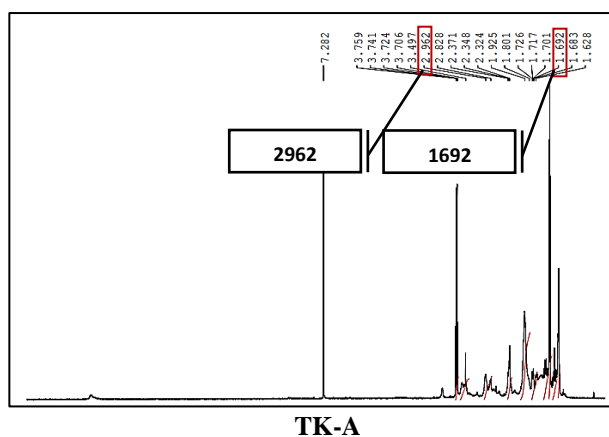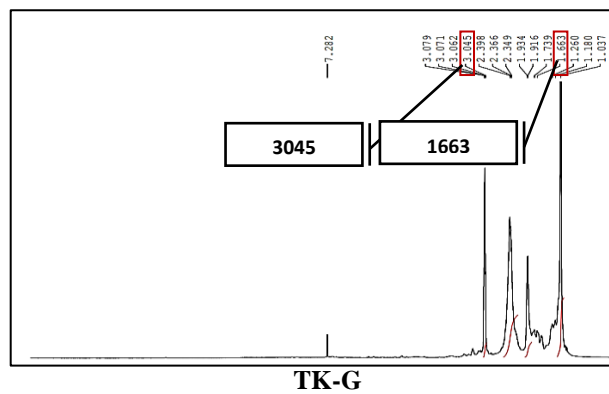
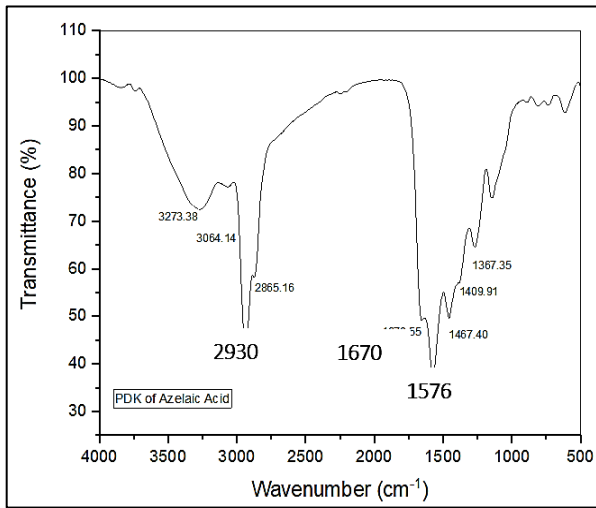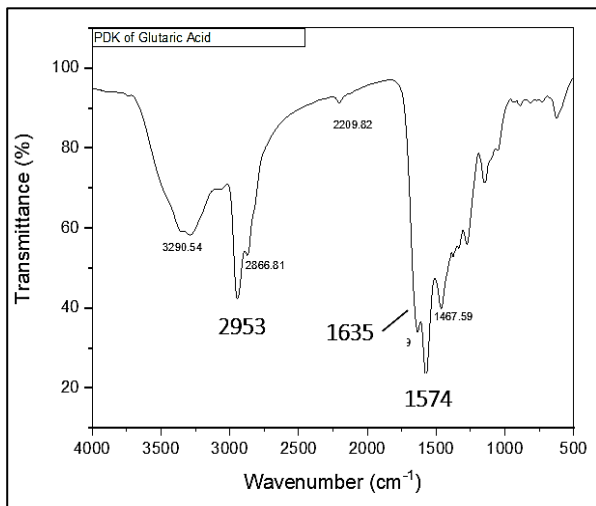**Figure 7: NMR results for the TK monomers and the PDK variants**

PDK-A

PDK-G

Figure 8: FT-IR spectroscopy of PDK-A and PDK-G

1.3.2 Commercial Polyethylene-terephthalate

The standard PET is recycled QPET 80, provided by BariQ for techno and advanced industries, Egypt. PET is synthesized by polycondensation process, terephthalic acid and ethylene glycol are esterified directly at moderate pressure (2.7–5.5 bar) and high temperature (220–260 °C). Water is eliminated in the reaction, and it is also continuously removed by distillation as shown in (

Figure 9). Although the PET was not chemically synthesized in this study, but the condensation reaction has to be presented since in MD it is very important to understand the steps of synthesis of each material under study in order to be able to build the model and choose the reactive sites correctly [19]
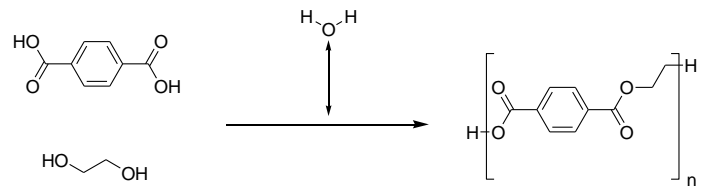

Figure 9: Synthesis of PET

1.4 Experimental Determination of Glass Transition Temperature (Tg)

The calorimetric characterization was performed according to ASTM D3418 on a differential Scanning Calorimeter - TA Instruments DSC Q2000 at a heat/cool/heat cycle under nitrogen gas atmosphere from 25°C till 300°C at a rate of 10°C/min. The weight of the reference pan was 20 milligrams (mg) and the average samples weights were between 5 – 7 mg for PDK-A and PDK-G respectively and 17 mg for PET. In the results, only the heating cycle is displayed as it is the relevant cycle for the determination of T_g & T_m. (Figure 10 & Figure 11) represent the T_g values of the PDK-A and PDK-G. For the while for the azelaic based PDK polymer (PDK-A), the experimental T_g 96.32 °C while for the glutaric based PDK (PDK-G), the experimental T_g was 97.4°C.

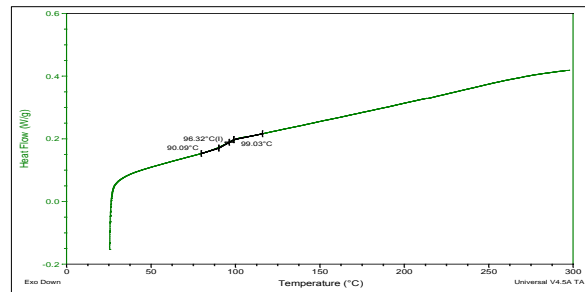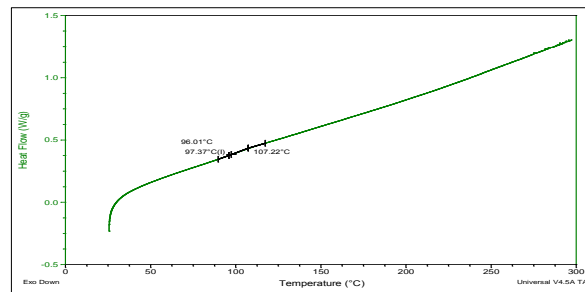**Figure 10: T_g value from DSC curve for the Azelaic based PDK (PDK-A)**

Figure 11: T_g value from DSC curve for the Glutaric based PDK (PDK-G)

The DSC Curve for PET is shown in Figure 12 represents both T_g and T_m for PET. The measured T_g value was 80.78 °C and the melting peak was distinguished at 250.15 °C which is also in good agreement with literature values [20].
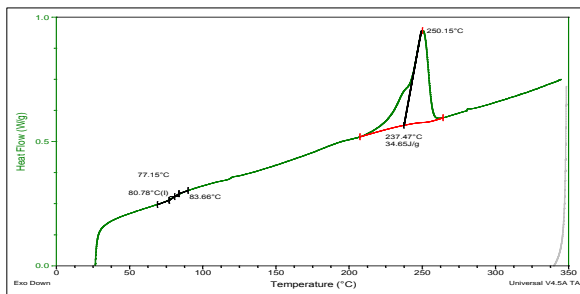
Figure 12: DSC curve for PET

3. CONSTRUCTION OF THE MOLECULAR DYNAMICS MODEL

The initial step in conducting MD simulations is determining the appropriate inter-atomic potential. The PCFF (polymer consistent force field) potential was used with cut-off of 9.5 Å in all simulations[16]. The concept of determining the best cut-off distance was tested on the PDK vitrimers reported by Christensen et.al. [6]based on the highest reaction rate. Afterwards, the models for PET, PDK-G and PDK-A were constructed and the simulations were made using the selected best cut-off distance. The standard PET was simulated using a relatively large model size of 15000 atoms. A reduction of the model size to around 5000 atoms was performed for the PDK-G. After verifying the results with the experimental values, a further reduction for the model to around 3000 atoms was tried to determine the suitable model size for simulating the PDK vitrimers thermal properties.

3.1 Determination of the best cut-off distance

To model the time dependency of the reaction and to obtain the physical cut-off distance and its corresponding reaction rate constant (k), an equation was formulated accordingly using the general rate equation [21].

$$\frac{da}{dt} = k(T)[1 - a]^n \qquad (1)$$

Where da/dt = reaction rate (1/sec), a = fractional conversion, k(T) = specific rate constant at temperature T, n = reaction order. By introducing the maximum number of reactions (nmax), this can be evaluated to:

$$a\,(t) = nmax - \ nmax * \sqrt[1-n]{(1-n)(c1-kt)} \qquad (2)$$

nmax = 91, n = 0.923, k = 0.000022305, c_1 = 12.99334
First, a system that consists of ~17000 atoms was constructed at the target density of 0.75 g/cm^3 using Enhanced Monte Carlo algorithm (EMC) [22] .It contained the two monomers which are triketone-6 (TK6) and tris (2-aminoethyl) amine (TREN) alongside a defined PDK partial chain and a water molecule.

The structure was equilibrated with an NPT ensemble at 300 K and 1 atm factor equal to 100 and 1 atm with a pressure damping factor equal to 1000 with time step 0.25 fs for 125 ps.
After the equilibration, a parametric study with 3 cross-linking simulations was constructed with 3 different cut-off distances to determine the best cut-off / reaction rate relation to be used for the following simulations. The chosen cut-offs to be investigated were 3, 4, and 5 Å. Simulations were kept at 300 K and 1 atm with a temperature and pressure damping coefficients of 150 and 1500 respectively. The crosslinking was done using the fix bond/react command [23] in LAMMPS [12].

$$a\,(t) = nmax - \ nmax * \sqrt[1-n]{(1-n)\left(c_1 - \left(\frac{r_0}{r_{max}}\right)^m * k\,t\right)} \qquad (3)$$

As shown in (Figure 13) curves were plotted from each cut-off distance simulation for data fitting. The fitting was done using a genetic algorithm written in MATLAB using (Equation 3) which is a modified version of (Equation 2)) where the (r_0/r_{max})m factor was added to predict the physical reaction cut-off r0 and to get the corresponding reaction rate constants for all the used cut-offs r_{max}.
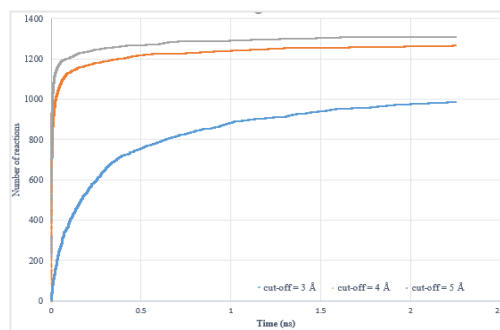

Figure 13: Numbers of reactions simulations of PDK using cut-offs of 3, 4 and 5 Å

It was obvious from the curve that the increase in the cut-off distance leads to the increase in the reaction kinetics i.e. reaction rate. Since the simulation is run in a limited timeframe, it was decided to use the highest reaction rate which is realized at 5 Å to ensure that all reactions had occurred and hence the targeted cross-linking density is achieved.

3.2 Construction and preparation of the PET molecular model

First, two molecular systems were constructed using Enhanced Monte Carlo algorithm (EMC) [22].The first system contained both terephthalic acid (TPA) and ethylene glycol (EG) monomers (Figure 14) alongside a water a molecule and a sample of a PET chain which exist for the purpose of making reaction templates only. The system had approximately 15000 atoms (Figure 15). The number of TPA monomers was equal to the number of EG monomers, i.e. ratio 1:1.
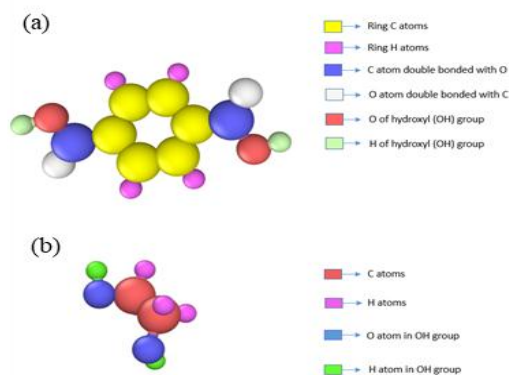
Figure 14: TPA monomers (a) and EG monomers (b) with their respective colour map
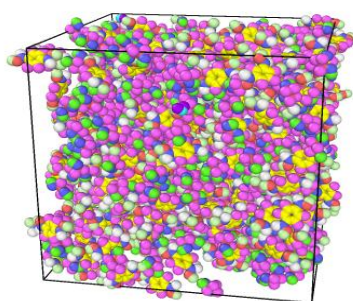

Figure 15: Constructed molecular system of PET monomers

Afterwards, the monomer system was equilibrated using an NPT ensemble at 300 K and 1 atm for 125 ps. The outer time step used for all simulations was 1 fs using the rRESPA integration scheme [24]. Then, the system underwent condensation reaction for 200 ps using a cut-off distance of 5 Å to obtain the high molecular weight of PET. Following the reaction, the PET systems was equilibrated at 300 K and 1 atm using an NPT ensemble with a temperature damping factor equal to 100 and a pressure damping factor equal to 1000 for another 500 ps

3.3 Construction and preparation of the PDK variants molecular model

The two poly (diketoneamine) variants systems were constructed using Enhanced Monte Carlo algorithm (EMC) [22].The first one contained triketone monomers synthesized from Glutaric acid (TK-G) (Figure 16a), while the second system contained triketone monomers synthesized from Azelaic acid (TK-A) (Figure 16b) each cross-linked with TREN (Figure 16c). Both systems also contained a water molecule and a partial polymeric PDK [6]chain to be used for the reaction templates. The TK-G system had 5871 atoms while the TK-A system had 3943 atoms. The number of atoms is dependent on the mole ratio TREN/TK- A & TREN/TK-G. The ratio of the number of TREN monomers to the TK-G monomers (TREN/TK-G) was equal to 1, while the ratio of the

number of TREN monomers to the TK-A (TREN/TK-A) was equal to 0.38 for the Azelaic system. This ratio was set according to the chemical synthesis of both TK monomers previously explained in 2.1.1. The reactive sites in both systems were kept constant at 1 equiv. NH_2.
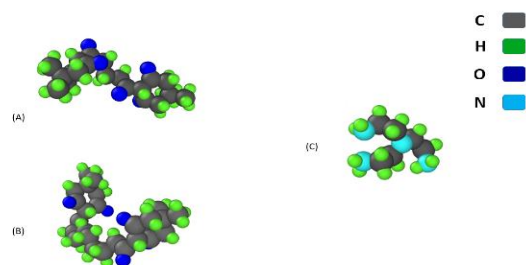

Figure 16: (a) Triketone monomer synthesized from glutaric acid, (b) from azelaic acid, and (c) the TREN monomer
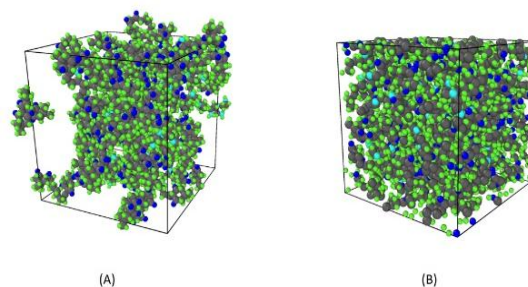
Figure 17: Graphical illustration example for: (a) monomer system before cross-linking, and (b) post cross-linking polymeric system.

Afterwards, both PDK monomer systems were equilibrated using the same settings used for the PET monomer system. The cross-linking reaction of both systems was also carried out similarly to the PET system. A summary of the decisive simulation parameters is listed in (Table 1).

Table 1. Simulation Parameters

Polymer	System Size	Equilib-ration temp.	Equilib-ration pressure	Ensemble	Equilib-ration run time	Reaction time
Units	atom	K	atm		Time step	ps
PDK	17000	300	1	NPT	500 000	500
PET	15000	300	1	NPT	500 000	200
PDK-G	5871	300	1	NPT	500 000	200
PDK-A	3943	300	1	NPT	500 000	200

3.4 Computation of glass transition temperature

The annealing protocol applied to all systems in this work was similar to the one in [18] to obtain the glass transition temperature and melting temperatures from the temperature vs free volume plot. The polymer systems were heated up and equilibrated at 500 K using an NPT ensemble at 1 atm pressure for a duration of 500 ps each. Then, the temperature was dropped by 20 K until reaching a minimum temperature of 200 K. At each temperature drop, the system was equilibrated at said temperature for 200 ps under 1 atm. The free volume data was collected for each temperature and averaged over its whole duration using Excel's average function. Finally, the temperature and average free volume data were plotted against each other using Excel.

To calculate the glass transition (T_g) or melting temperature (T_m), the simulated change in free volume versus temperature data was plotted. Segmental linear regression was performed as in [25], with the temperature range chosen for fitting determining the T_g which is the intersection point of the two fits. According to [18], during cooling, the density of material increases i.e. the free volume decreases when approaching the T_g. Passing by a phase change will cause change in slope and hence the transition could be determined, either T_m or T_g. The plot results for the simulated T_g and T_m for PET are shown in (Figure 18).
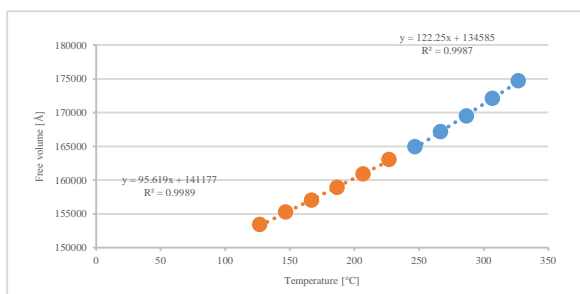

Figure 18: Segmental linear regression for the PET data for T_m calculation

The simulation result for the melting temperature of PET was 247.708°C. The simulated estimate of the glass transition temperature range for PDK-G was from 89.23 – 128.63 °C as shown in (Figure 19). The T_g calculated at the intersection point was 97.4 °C.
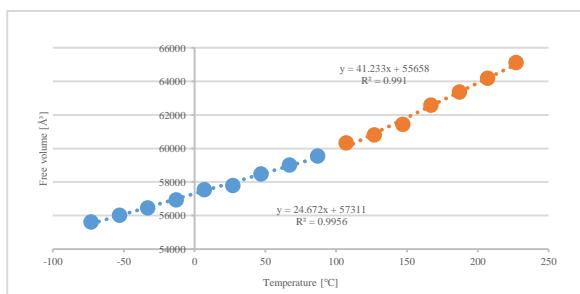

Figure 19: Simulated T_g value for the Glutaric based PDK (PDK-G)

For PDK-A, glass transition temperature simulation range was from 85.79 – 117.31°C **(Figure 20)** resulted in T_g of 96.32 °C at the point of intersection.
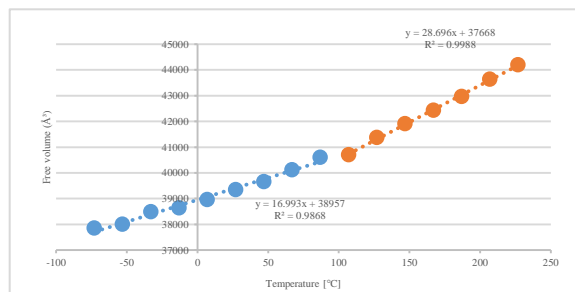

Figure 20: Simulated T_g value for the Azelaic based PDK (PDK-A)

4. RESULTS AND DISCUSSION

The PET simulated system results showed good conformity with experimental results where the simulation result for the melting temperature of PET showed only 2.6°C deviation from experimental values.

For PDK-G, only 1.87 °C deviation between simulation and DSC results was observed. On the other hand, the smaller model size of the PDK-A has led to more deviations in the results where a deviation of 13.82 °C was observed between simulation and experimental results.

It is important to note that many factors play decisive roles in the determination of the glass transition temperature (T_g) among which are the cooling/heating rates during the DSC measurements, the degree of cross linking and impurities in the compound. As a general comment regarding the deviation of simulated average T_g and experimental T_g, it was observed from the findings that the simulated T_g is always higher than the experimental T_g which agrees with polymers thermal properties as discussed in [18]. Hence, here it is worth mentioning that the difference between the simulated heating rate which was less than 1 fs and the DSC heating rate (10 k/min) could be a major factor affecting the results and leading to the reported deviations. This is due to the computational capacity limitations since as described in 3.4 the system had to be equilibrated at each temperature drop.

The other factor is the cross linking, the cross-linking density in the model is set to 91%, the cross-linking density of the PDK-G and PDK-A vitrimers apparently vary from this percent which is obvious from their lower T_g which reflect their increased chain mobility and consequently their cross-linking density.

The last factor is the impurities, which is the most common factor usually affecting the accuracy of the simulation models as they are constructed according to the theoretical ideal status of the material since the determination of the impurities and their chemical

compositions and considering them in the simulations cannot be realized.

5. CONCLUSION

This works presented the modelling and simulation of two novel vitrimers and proved that MD is a powerful tool able to simulate the thermal properties of genuine vitrimer variants for PDK. The two variants were synthesized and characterized namely PDK-G and PDK-A and the glass transition temperatures were determined using DSC for the variants and the PET which was used as a standard material in this study. Molecular dynamics (MD) simulation technique using LAMMPS was used to estimate the glass transition temperature for PDK-G and PDK-A and the melting temperature of PET with different model sizes at a constant cut-off distance and cross-linking density.

The results concluded the following:

- For PET, 0.4% deviation between simulation and DSC results for Tm was obtained which is a remarkable result of small sized model in comparison to what found in the literature.
- Similar findings for the genuine PDK-G were less than 1% deviation in the Tg for numerical and experimental results was confirmed which is not yet reported in literature.
- PDK-A showed less reliable results with a deviation exceeding 10% which is attributed to the decreased model size.
- The results proved that a model size below 5000 atoms for simulating the thermal properties of vitrimers is not recommended.

This concludes that material computation is a powerful "green sustainable tool" able of accurately simulating material properties and saving the use of environmentally harmful chemicals from one side and from the other the use of energy for promoting the chemical reactions.

Abbreviations

A	Azelaic Acid based compounds
DCB	Dynamic covalent bond
DCC	N,N'-dicyclohexylcarbodiimide
DCM	Dichloromethane
Dimedone	5,5-dimethyl-1,3-cyclohexanedione
DMAP	4-dimethylaminopyridine
EG	Ethylene glycol
EMC	Enhanced Monte Carlo algorithm
FT-IR	Fourier-transform infrared spectroscopy
G	Glutaric Acid based compounds
^{1}H-NMR	Proton nuclear magnetic resonance
TK	Triketoneamine
LAMMPS	Molecular dynamics simulator
LC-MS	Liquid chromatography–mass spectrometry
MatLAB	Programming and numeric computing platform
MD	Molecular dynamics
NPT	Isothermal–isobaric ensemble
PCFF	Polymer consistent force field
PDK	Polydiketoneamine
PET	Polyethyleneterephthalate
rRESPA	multi-timescale integrator
T_g	Glass transition temperature
T_m	Melting temperature
TREN	Tris(2-aminoethyl)amine
TPA	Terephthalic acid

Symbols

Å	Angstrom
K	Degree Kelvin
V	Specific volume
T	Temperature
h	Hours
min	Minutes
°C	Degree Celsius
da/dt	reaction rate
a	fractional conversion
k(T)	specific rate constant at temperature T
n	reaction order
n_{max}	Maximum number of reactions
ps	picoseconds

Declaration of Competing Interests
The authors state that they have no known competing financial interests or personal relationships that could appear to have influenced the work described in this study.

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