Behavior of Polypropylene Under Stress Relaxation and Dynamic Loading Using Molecular Dynamics Simulations

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ABSTRACT

Molecular dynamics simulations of stress relaxation and dynamic loading of isotactic polypropylene have been studied using full atomistic model. Curves of relaxation, used to evaluate the relaxation parameters, show agreement with experimental results. The relaxation time is calculated from the simulated stress relaxation curve. The dynamic loading curves show that stress leads strain as proposed by other theoretical models. Storage modulus, loss modulus and loss factor have been calculated. Despite limitations of smaller simulation time, the results are in comparable range with the experimental values. The length scale limitation of MD simulation is taken care of by the use of periodic boundary conditions. The effect of temperature and the polymeric chain length on the viscoelastic relaxation parameters are investigated.

KEYWORDS: *Polypropylene,Viscoelasticity and Molecular dynamics (MD) simulation*

INTRODUCTION

Amorphous polypropylene (PP) while deforming may behave like a glass, a rubbery substance or a viscous liquid depending on the rate of deformation and temperature. Viscoelastic behavior is a function of both frequency of loading and temperature. A common way of measuring the viscoelastic function is dynamic mechanical testing [1], [8]. Early works of stress relaxation with molecular dynamics (MD) simulations have been performed by Blonski et al. [2], Brostow and Kubat [3].Yashiro et al. [4] and Hossain et al. [5] used MD simulations to study tensile deformation mechanism of pure polyethylene (PE). It was reported that for the polyethylene there are four distinct regimes in

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J. Polym. Mater. Vol. **35,** No. 1, 2018, 1-13

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the stress-strain curve: elastic, yield, strain softening and strain hardening. Due to time and length scale problem with polymers at atomistic level simulations, all the studies have been performed with a high strain rate (from to $1.0\times10^{8}s^{-1}$ to $5.0\times10^{11}s^{-1}$)) using the united atom model. The study of mechanical properties and stress development in amorphous polymeric materials are of complex nature due to a lot of factors, e.g., time-dependent behavior, the processing history and their anisotropic character. A significant advantage of computer simulation is the ability to create a condition that can not be replicated in a controlled experimental environment, also they can be used to determine the effects of one system variable at a time [10]. Atomistic simulations have been used to study structure and mechanical response of glassy polymer and have led to clarification of some important issues, in spite of the limitations in terms of length and time scales. Barrat et al.[17] in their review have shown results from computer simulation studies on chain dynamics around the glass transition temperature (T_g) and mechanical behaviour below T_g. It has been claimed that computer simulations are able to address and give clear answers in the field of glassy polymer.Takahashi et al. [16] examined the gap of length and time scales among models using mapping scheme based on power law. These gaps were estimated by mapping between the atomistic model of polyethylene and the bead spring model. It is the linkage between the vastly different scales of atomistic molecular dynamics (AMD) and high-level coarse grained molecular dynamics (CGMD) which provide useful information for refinement of CGMD model. Most of the simulations in these works have been performed for ideal lattices and also for lattices with defects. The simulated stress relaxation curve exhibited three regions: initial (nearly horizontal); central (descending approximately linearly) and final corresponding to the internal stress. But these simulations have been limited in some aspects. For example: a) they use only the simple Lennard-Jones (LJ) potential, b) they employ united atom model, and c) they consider only simple systems d) they use two-dimensional (2D) analysis schemes. The trade off gained by the simplifications was that the authors were able to simulate the behavior for a long period of time.

In this research work, molecular dynamic simulations of stress relaxation phenomenon and dynamic loading have been performed using the full atom model and realistic potential field with the aim of studying the dynamic deformation behavior of polypropylene. Stress relaxation measurement is one possible method to study the viscoelastic nature of a polymeric material. In this test, specimen is initially strained in tension to a predetermined level, so that the stress anomaly can be neglected. This straining is done at constant temperature. The strain level is then kept constant at this value and the stress necessary to maintain this strain is measured as a function of time with temperature being kept constant. Here strain is made up of two components: elastic strain and creep strain. During the stress relaxation the elastic strain decreases and creep strain increases keeping the total strain constant. As a result, stress is found to decrease with time due to molecular relaxation processes. In the second set of simulations, dynamic loading simulation is performed at an applied harmonic frequency ω. In the case of a linear viscoelastic material, the stress will also alter sinusoidally but out of phase with the strain if sinusoidal strain is applied. From the stress strain graphs obtained, the frequency dependent modulus and loss factor can be generated. The objective of the present paper is to perform stress relaxations of isotactic polypropylene using realistic consistent valence force field (CVFF) potential along with the dynamic loading. This will further our understanding of the service performance as well as service life of the material. The simulations are performed over a range of temperatures around the glass transition temperature of PP.

Simulation details

The simulation of dynamic mechanical phenomena is performed using full atomistic model of isotactic PP (i-PP) chains with different degree of polymerization. Pure isotactic PP chains modelled consist of 60, 200 and 1000 monomers with end of the chains being terminated by Hydrogen atoms. The unit cell is designed as an amorphous polymer block by placing the i-PP chain within simulation box with nano scale dimensions (50×50×153.15Å) using traditional Metropolis and biased sampling [12] of Amorphous Cell applications in Material studio [13]. Four successive stages of equilibrium simulation are performed [5], [14] on initial unit cell to relax it before stress relaxation and dynamic loading simulation. Initially, each system is relaxed by Langevin dynamics at 500 K for 10 ps, which is followed by NPT dynamics at 500 K for 25 ps. The NPT ensemble is adopted for the system to anneal to the desired temperature with a linear decrement of temperature for 25 ps. Upon reaching the desired temperature, this is followed by NPT dynamics at simulation temperature for 50 ps. After these four equilibration stages, polypropylene system reaches an equilibrium state with an equilibrium density of 0.73 g/cm^3. The interatomic interaction is expressed with standard CVFF potential [11]. The potential function is composed of different contributions from bond stretching, bond angle, torsional angle and non-bond interaction.

The basic equation of energy are as under in eqn (1). CVFF potential energy, E, is expressed as a function of internal degrees of freedom and the nonbonded distances.

$$
\begin{aligned}
E = & \sum_{i}\sum_{j>i}\left(K_r * (R_{ij} - R_0)^2\right) + \sum_{i}\sum_{j>i}\sum_{k>j>i}\left(K_\theta * (\theta_{ijk} - \theta_0)^2\right) \\
& + \sum_{i}\sum_{j>i}\sum_{k>j>i}\sum_{l>k>j>i}\left(K_\phi * [1 + \cos(n * \phi_{ijkl} - \phi_0)]\right) + \sum_{i}\sum_{j>i}\left(\frac{A_{ij}}{R^{12}} - \frac{B_{ij}}{R^{6}}\right)
\end{aligned}
\tag{1}
$$

Where K_r ((kcal/mol)/ $\AA^2$) is the bond energy parameter, R_0 is the equilibrium bond length in $\AA$, R_{ij} is the interatomic distance between i th & j th atom in $\AA$ unit, K_θ (kcal/moldeg.^{2}) is related to force constant for angle variation, θ_0 is the equilibrium angle, θ_{ijk} is the angle between i^{th}, j^{th} and k^{th} atom, K_ϕ is the force constant for dihedral angle, ϕ_{ijk} is dihedral angle between i^{th}, j^{th}, k^{th}, and l^{th} atom, ϕ_0 is equilibrium dihedral angle, n is an integer, A_{ij}

& B_{ij} are constant for LJ potential and R is the equilibrium bond length in $Å$.

The different parameters used for eqn (1) for polypropylene are given in Table 1. Parallel molecular dynamic code of Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [9] has been used for the simulation of structures made with amorphous cell module. This initial structure was then equilibrated with Langevin dynamics and NPT dynamics, [4]. Once the equilibrated structure was prepared, then the stress relaxation and dynamic loading simulations were performed in the temperature range of 100 K to 400 K.

Stress Relaxation

Stress relaxation behaviour gives service performance of any material. In a typical stress relaxation experiment on polymeric material at room temperature, the time span is about 10^5–10^7 s. However for MD simulation, that much of real time length is not feasible to simulate with currently available computer resources unless the models are grossly simplified. MD simulation of stress relaxation is done in two stages. First a small stress is applied to the system, within the elastic limit, and the system is relaxed after every few time steps so as to achieve quasi-static conditions. In second phase, strain is held constant and the molecular chains are allowed to relax for sufficient time. Due to relaxation processes, the stress will keep on reducing. The relaxation mechanisms operate at different scales. In these simulations, which are carried out on shorter chain length, the nanoscale relaxation processes are captured in the relaxation curve.

TABLE 1: Potential Parameters for Polypropylene

Parameters[1]	Values	Units
r_{0CH}	1.105	Å
r_{0CC}	1.526	Å
k_{rCH}	340.62	$kJmol^{-1}Å^{-2}$
k_{rCC}	322.72	$kJmol^{-1}Å^{-2}$
$k_{\theta HCH}$	39.50	$kJmol^{-1}$
$k_{\theta HCC}$	44.40	$kJmol^{-1}$
θ_{0HCH}	106.4	deg
θ_{0HCC}	110.0	deg
A_1	0.1581	-
A_2	1	-
A_3	3	-
ε_{rHH}	0.0380	$kcalmol^{-1}$
σ_{HH}	2.449	Å
ε_{rCC}	0.0389	$kcalmol^{-1}$
σ_{CC}	3.875	Å

[1] Where r_{0CH} indicates carbon-hydrogen equilibrium distance, r_{0CC} indicates carbon-carbon equilibrium distance, k_{rCH} indicates bond stretching stiffness for carbon-hydrogen bond, krcc indicates bond stretching stiffness for carbon-carbon bond, $k_{\theta HCC}$ and $k_{\theta HCH}$ indicate angle bending stiffnesses; θ_{0HCH} and θ_{0HCC} indicate equilibrium angles; A_1, A_2 and A_3 are the torsional/dihedral parameters; ε_{rHH}, σ_{HH} non bond parameters of hydrogen bonds and ε_{rCC}, σ_{CC} are the non bond parameters of carbon.

Results of Stress Relaxation

Stress relaxation results for 60 monomeric chains of PP are reported in Fig. 1 and Fig. 2. Fig. 1 shows the initial stressing phase (before relaxation) where the applied stress is plotted. The simulations were performed at different temperature. Apart from the obvious expect results of reduced stiffness with temperature, Fig. 1 also depicts the change in nature of stress strain behaviour with temperature. At 100K the material behaves as if in brittle state with no plateaus obtained during loading. However these plateaus can be seen at 400K and 200K. Similar simulations were also performed at

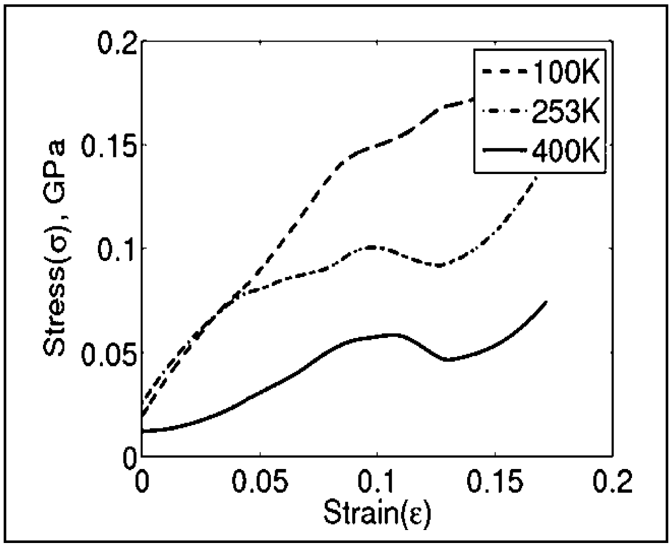


Fig. 1. Applied stress in stress relaxation simulation for 60 monomeric chains of PP

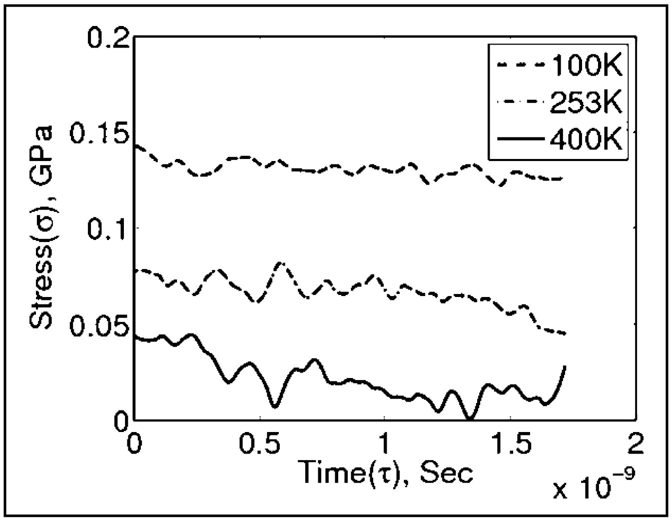


Fig. 2. Stress evaluation in stress relaxation simulation for 60 monomeric chains of PP

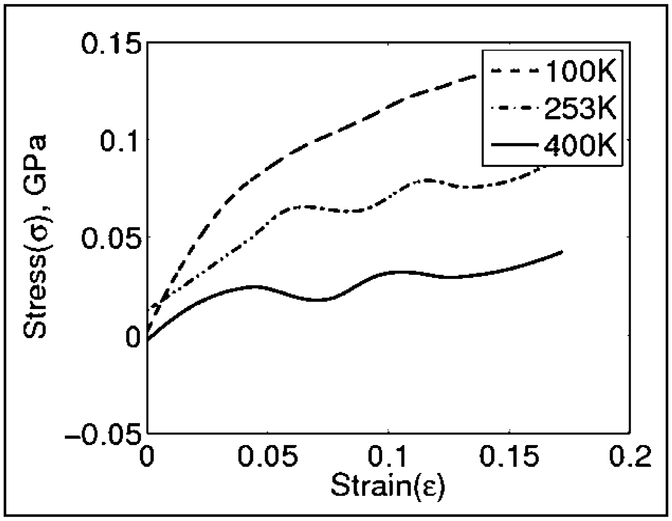


Fig. 3. Applied stress in stress relaxation simulation for 200 monomeric chains of PP

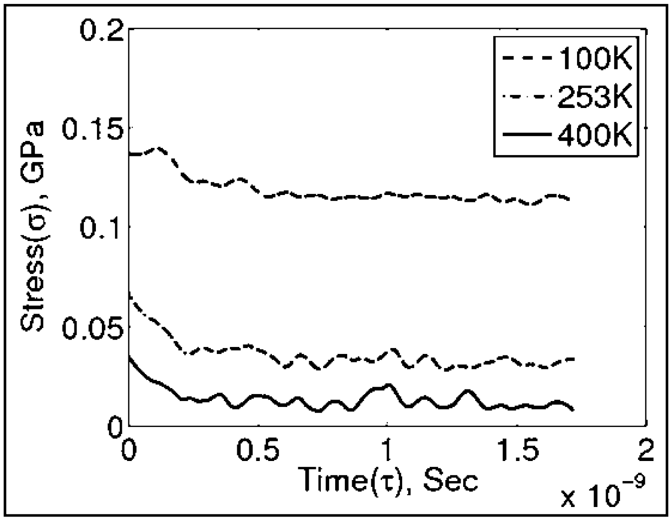


Fig. 4. Stress evaluation in stress relaxation simulation for 200 monomeric chains of PP

polymeric index of 200 (Fig. 3 and Fig. 4) and 1000 (Fig. 5 and Fig. 6). The purpose of preparing these additional simulations was to illustrate the effects of chain length on the relaxation behaviour. Since, during relaxation, it is actually partial movement of chains which constitutes the phenomenon. Thus chain length is expected to show a significant influence on the relaxation time. Fig. 2 indicates the stress relaxation as a function of

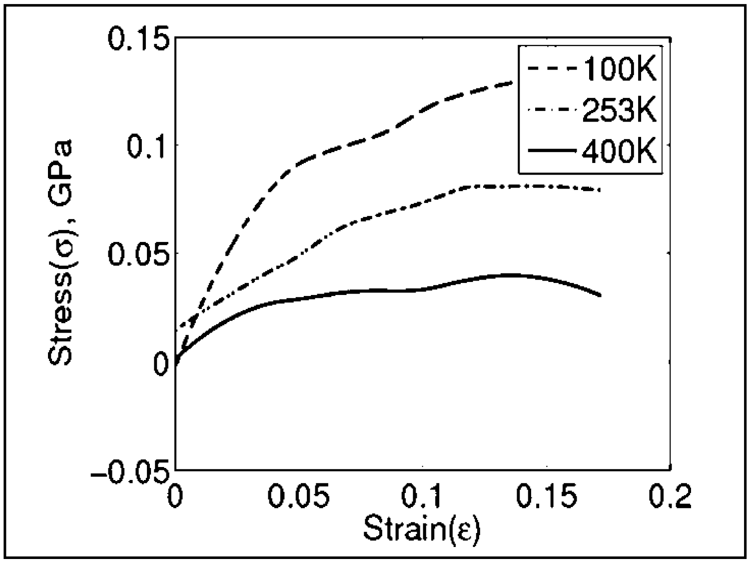


Fig. 5. Applied stress in stress relaxation simulation for 1000 monomeric chains of PP

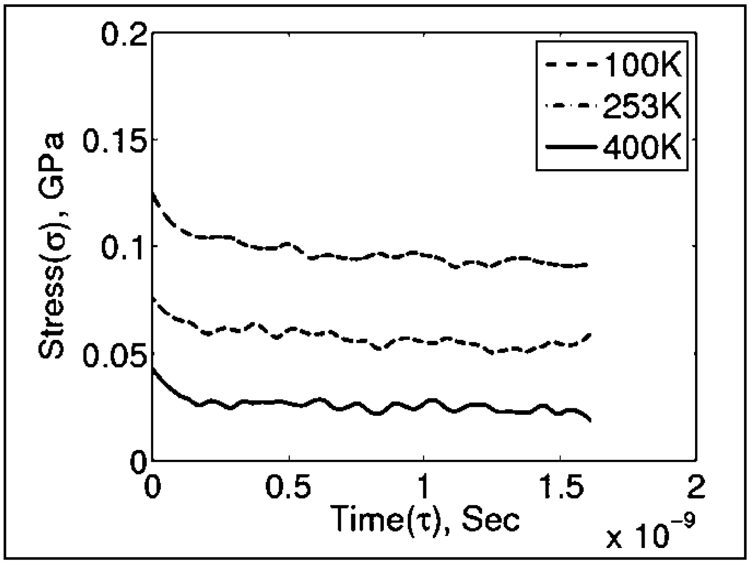


Fig. 6. Stress evaluation in stress relaxation simulation for 1000 monomeric chains of PP

time. Similar relaxation results for 200 and 1000 monomeric chains of PP are shown in Figs. 3 to Fig. 6 respectively.

With small time simulation of stress relaxation with different temperatures the results are fitted with empirical equation given below:

$$\sigma = Ke^{-\frac{t}{\tau}} \tag{2}$$

Where σ is stress along to Z-axis, τ is relaxation time, t is the time for stress relaxation and K is the constant.

Table 2 shows the parameters evaluated from the curve fitting procedure given above and some important phenomena show up in the results. With increase of temperature, the relaxation time reduces sharply as confirmed with fitted data in Table 2. As the temperature is increased, the mobility of atoms is also increased and as results the system attains a state of lower residual stress. It is also noticed from Table 2 that with change in monomeric the relaxation time increases monotonically. The residual stresses are not same for the stress relaxation simulation but dependent on temperature.

The fitted relaxation parameters help to estimate the viscosity of polymer as given in Table 2. The values are less comparable to the experiment values reported by Liang and Peng [7]. The melt shear viscosity of PP is in the range of 2.3 PaS to 3.1 PaS (temperature varying from 463K to 503K and shear rate form $10^{-2}s^{-1}$ to $10^{2}s^{-1}$). In our MD simulation, irrespective of the chain length, the viscosity of PP is varying form 0.46 PaS to 14.55 PaS over the temperature range. The fact is also justified with less degree of polymerization in our simulated system. Experimentally it has been established for several polymers that the flow viscosity increases with increase of molecular mass [1].

One typical sample used for stress relaxation simulation of 200 monomeric PP at 100K temperature is given in Figs. 7 and 8. After initial strain of 0.2, the unit cell was allowed to relax. During relaxation, the individual chain at atomic resolution changes its conformation. In the inset of Fig. 8a is a small portion of the system shown in which a single chain is highlighted against other chains to visualize the chain dynamics at atomistic level. Measurement of dimensions of the loops are with passage of time as shown in Fig. 8b in schematic diagram establishes that the chain is uncoiling during relaxation and its loops dimension changes form 28 Å upto 17 Å in 1.72 nanoseconds.

TABLE 2: Evaluated Relaxation parameters for Polypropylene

Chain	Temp., T (K)	Modulus Y (GPa)	Relax. Time, ζ (sec.)	Viscosity, η (PaS)	Reference
60 mers	100 253 400	1.57 1.4 0.42	0.20e-8 0.14e-8 0.11e-8	3.15 1.96 0.46	Present work
200 mers	100 253 400	1.5 0.84 0.51	0.62e-8 0.25e-8 0.23e-8	9.3 2.1 1.17	
1000 mers	100	2.31	0.63e-8	14.55	
-	453	-	-	10 to 200 (during 0.1 to 1000 Hz)	Karamipour et al. [18]

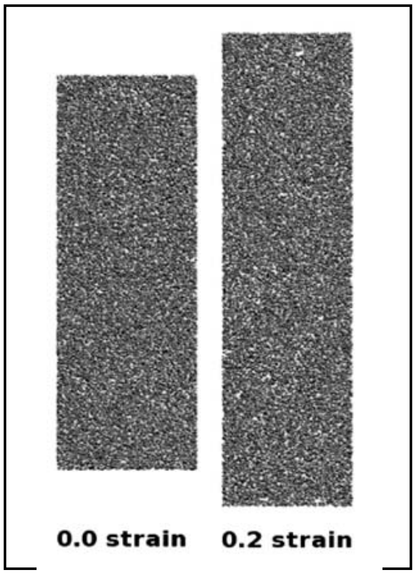
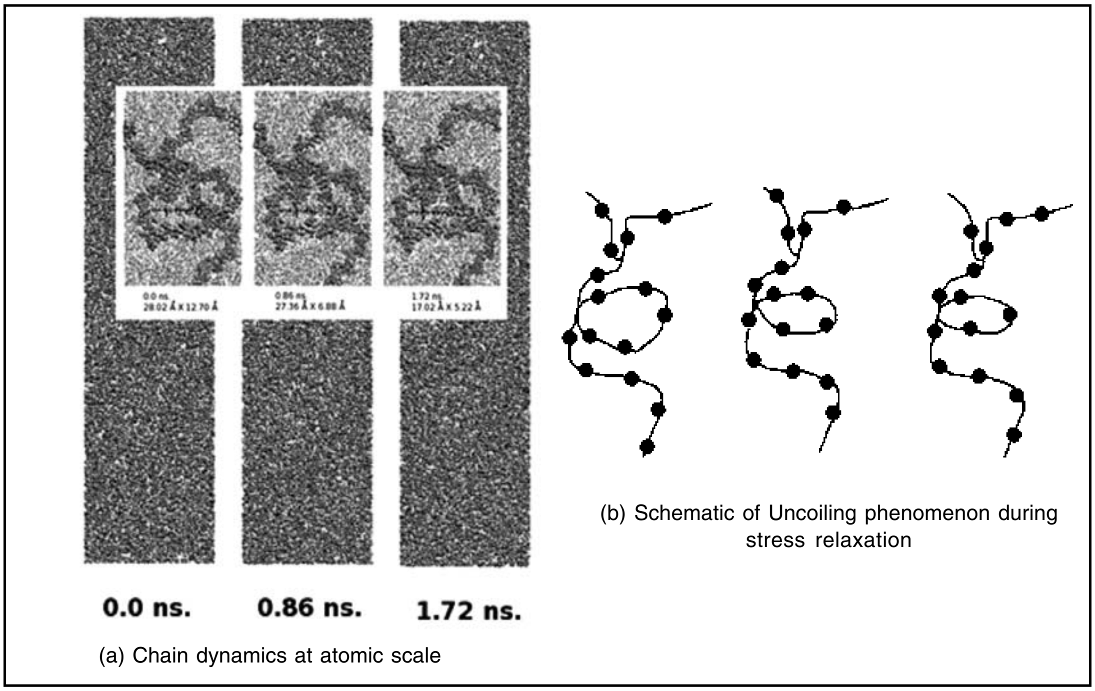


Fig. 7. Initial applied strain of PP.



(a) Chain dynamics at atomic scale

(b) Schematic of Uncoiling phenomenon during stress relaxation

Fig. 8. Atomic resolution of structure during stress relaxation of PP.

Dynamic loading

For dynamic loading, a variable strain is applied along the z-axis as follows:

$$\grave{o} = \grave{o}_0 e^{j\omega t} \tag{3}$$

where the strain amplitude, $\grave{O}_0$ is 0.037 and the time period is 10×10^5 fs. Therefore, the stress response is evaluated from MD simulation also follows the strain pattern (sinusoidal nature) with a phase lead angle ϕ as given below:

$$\sigma = \sigma_{\grave{O}} e^{j(\omega t + \phi)} \tag{4}$$

where σ_0 is the stress amplitude and ϕ is the phase gap between strain and stress. So the dynamic modulus of the system is given as

$$\frac{\sigma}{\grave{o}} = \frac{\sigma_0}{\grave{o}_0} e^{j\phi} = \frac{\sigma_0}{\grave{o}_0} cos\phi + j\frac{\sigma_0}{\grave{o}_0} sin\,\phi \tag{5}$$

so,

$$E_{complex} = E_{storage} + jE_{loss} \tag{6}$$

and

$$loss\ factor,\ \eta = tan(\phi) = \frac{E_{loss}}{E_{storage}} \tag{7}$$

Results of Dynamic Loading

After initial relaxation at desired temperature, the simulations were conducted with a sampling time of 1 fs. Results of PP with 200 monomeric chains are shown in Fig. 9 and 10 for the two frequency values of 10^9 and 10^{10} Hz.

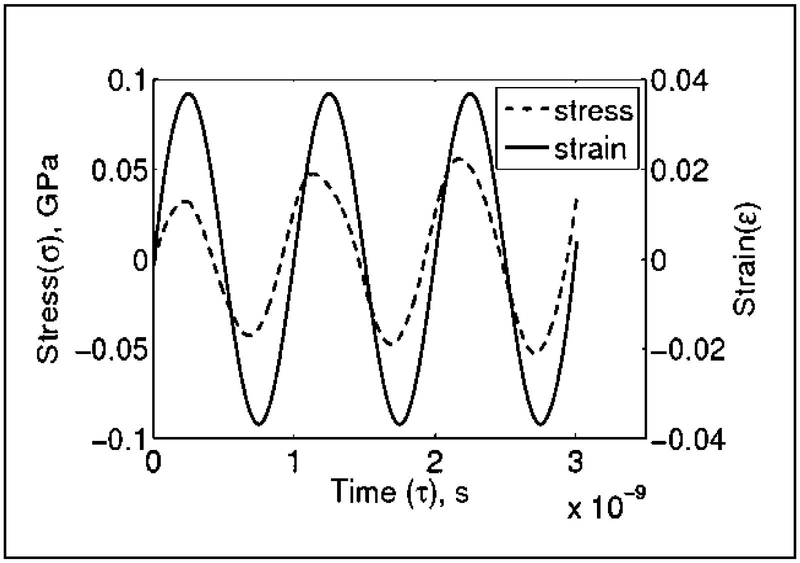


Fig. 9. Dynamic response at frequency of 10^9 (Hz) for 200 monomeric PP with 100K temp.

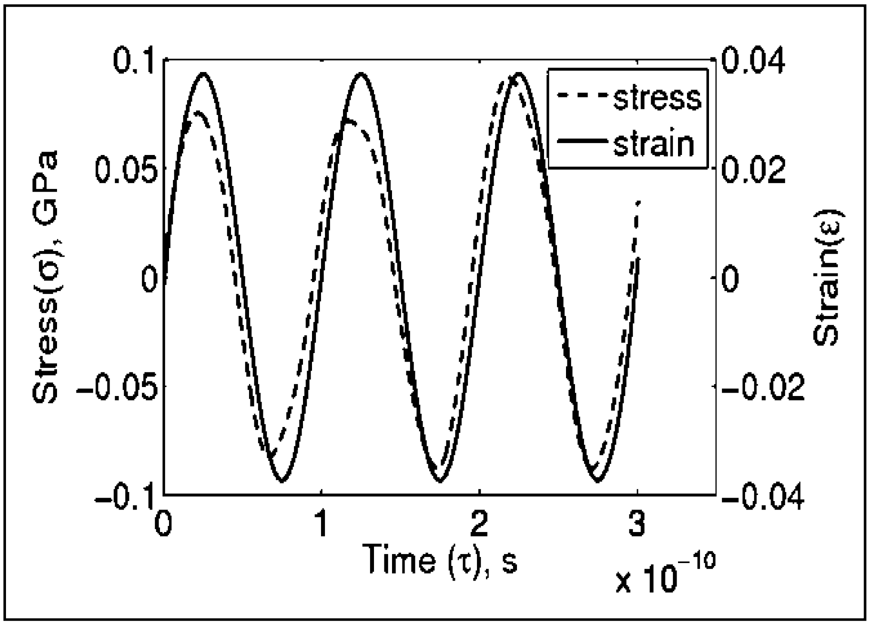


Fig. 10. Dynamic response at frequency of 10^{10} (Hz) for 200 monomeric PP with 100K temp.

TABLE 3: Dynamic test for Polypropylene

Chain	Temp.(K)	Freq.(Hz)	Storage modulus (Gpa)	Loss modulus (Gpa)	Loss factor	Reference
200	100	1.0e^{9}	2.24	0.26	0.12	
	100	1.0e^{10}	2.36	0.44	0.19	
200	253	1.0e^{9}	1.40	0.35	0.25	Present work
	253	1.0e^{10}	1.59	0.30	0.19	
200	300	10e^{10}	1.35	0.39	0.29	
-	293	10	1.31	0.12	0.09	Lazan [6]
-	293	-	1.51	0.19	0.13	
-	293	1000e	1.71	0.28	0.16	
-	-	-	0.75	0.06	0.075	Finegan et al. [15]
-	-173 to 403	120 to 1000	8.3 to 9.9	0.01 to 0.025	0.02 to 0.24	Karamipour et al. [18]

The stress leading phenomenon is clearly shown in both the plots. Similar dynamic simulations were performed with 60 and 1000 monomeric chains of PP. Dynamic loading simulation results evaluated from these graphs are summarized in Tab. 3 also compared with previous findings. Though the simulation is performed with high frequency (e.g. 10^{10},10^{9} Hz) compared to the experimental one, the results are comparable. Comparison of storage modulus values also shows that, with the exception of 60 mer. PP, the storage modulus in general shows slight increase with increase in frequency. The value of loss factor at this high frequency is 0.19-0.33 evaluated. On literature, the loss factor for PP has reported to be around 0.16 as Lazan [6]

CONCLUSIONS

This paper presents the numerical simulation of two dynamic phenomenon viz. stress relaxation and dynamic loading for amorphous isotactic sample by use of molecular dynamic simulation. The effects of increasing temperature and chain length have been demonstrated. The simulations show gradual unwinding of chain during relaxation process. When applied with harmonic loading the strain lagging behind stress is also seen in the averaged out graphs. The dynamic storage modulus as well values calculated from these simulations are realistic. The simulation uses full atom model of Polypropylene chains and a realistic potential field. The simplifications of 2D model, or united atom model or considering on some potential components are not applied. The amorphous PP of 60, 200 and 1000 monomeric chain length at different temperatures is taken for both stress relaxation and dynamic loading to study the effect of molecular mass and temperature. Viscosity increases with increasing chain length and decreasing temperature. The dynamic loading results though limited in time length of scale do give realistic values of loss factor as well as storage modulus. It is believed that the work done would be a useful step forward in understanding and simulating the dynamic mechanical gross properties of polymers.

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Received: 10-06-2017

Accepted: 01-02-2018