Supplementary data

Revealing thermophysical and mechanical responses of graphene-reinforced polyvinyl alcohol nanocomposites using molecular dynamics simulations

*Pabitra Narayan Samanta, Devashis Majumdar, and Jerzy Leszczynski**

Center for Computational Chemistry, Department of Chemistry, Physics and Atmospheric Sciences, Jackson State University, Jackson, MS 39217, USA

***Corresponding Author.**

E-mail: jerzy@icnanotox.org

Table S1: Statistical analysis of the simulation cells of pristine PVA polymer and graphene-reinforced polymer nanocomposites obtained from the ensemble averages of the MD trajectory. The error estimate was conducted over 1000001 points, accumulated from the 200 ns NPT production MD trajectory, using block averaging size of 5 and full-precision averages as implemented in the GROMACS code.

Composite	Temperat-ure (K)	Box Dimension (nm^3)			Error Estimate
		Initial	After Equilibration	After Production MD	
PVA	300	13.0 x 13.0 x 13.0	5.59 x 5.59 x 5.59	5.59 x 5.59 x 5.59	0.00029
PVA	400	13.0 x 13.0 x 13.0	5.65 x 5.65 x 5.65	5.65 x 5.65 x 5.65	0.00034
PVA + 0.8% Graphene Filler	300	13.7 x 13.7 x 13.7	5.61 x 5.61 x 5.61	5.61 x 5.61 x 5.61	0.00029
PVA + 2% Graphene Filler	300	13.7 x 13.7 x 13.7	5.62 x 5.62 x 5.62	5.62 x 5.62 x 5.62	9.4e-05
PVA + 5% Graphene Filler	300	13.7 x 13.7 x 13.7	5.67 x 5.67 x 5.67	5.67 x 5.67 x 5.67	0.00053
PVA + 10% Graphene Filler	200	13.7 x 13.7 x 13.7	5.72 x 5.72 x 5.72	5.72 x 5.72 x 5.72	4.6e-05
PVA + 10% Graphene Filler	300	13.7 x 13.7 x 13.7	5.74 x 5.74 x 5.74	5.74 x 5.74 x 5.74	0.00039
PVA + 10% Graphene Filler	400	13.7 x 13.7 x 13.7	5.80 x 5.80 x 5.80	5.80 x 5.80 x 5.80	0.00035

Table S2. Statistical analysis of the volume, density, pressure, temperature, and total energy of the simulated system of pristine polymer obtained from the ensemble averages of the production MD trajectory. The error estimate was conducted over 1000001 points, accumulated from the 200 ns NPT production MD trajectory at 300 K, using block averaging and full-precision averages as implemented in the GROMACS code.

Composite	Observables (Units)	Ensemble Averages	Block Averaging Size [nbmin x nbmax]	Error Estimate
PVA	Volume (nm^3)	175.0	5 x 5	0.027
			6 x 6	0.024
			8 x 8	0.023
			10 x 10	0.020
	Density (kg/m^3)	1254.29	5 x 5	0.19
			6 x 6	0.17
			8 x 8	0.17
			10 x 10	0.14
	Pressure (bar)	0.94	5 x 5	0.14
			6 x 6	0.093
			8 x 8	0.17
			10 x 10	0.25
	Temperature (K)	300.6	5 x 5	0.0048
			6 x 6	0.0041
			8 x 8	0.0046
			10 x 10	0.006
	Total Energy (kJ/mol)	-197259.0	5 x 5	12
			6 x 6	15
			8 x 8	18
			10 x 10	19

Table S3. Statistical analysis of the volume, density, pressure, temperature, and total energy of the simulated system of pristine polymer obtained from the ensemble averages of the production MD trajectory. The error estimate was conducted over 1000001 points, accumulated from the 200 ns NPT production MD trajectory at 400 K, using block averaging and full-precision averages as implemented in the GROMACS code.

Composite	Observables (Units)	Ensemble Averages	Block Averaging Size [nbmin x nbmax]	Error Estimate
PVA	Volume (nm^3)	180.2	5 x 5	0.032
			6 x 6	0.038
			8 x 8	0.030
			10 x 10	0.036
	Density (kg/m^3)	1218.4	5 x 5	0.22
			6 x 6	0.26
			8 x 8	0.20
			10 x 10	0.24
	Pressure (bar)	1.1	5 x 5	0.21
			6 x 6	0.13
			8 x 8	0.17
			10 x 10	0.31
	Temperature (K)	400.8	5 x 5	0.012
			6 x 6	0.012
			8 x 8	0.011
			10 x 10	0.0096
	Total Energy (kJ/mol)	-147258.0	5 x 5	23
			6 x 6	22
			8 x 8	25
			10 x 10	40

Table S4. Statistical analysis of the volume, density, pressure, temperature, and total energy of the simulated system of graphene-reinforced polymer nanocomposite obtained from the ensemble averages of the production MD trajectory. The error estimate was conducted over 1000001 points, accumulated from the 200 ns NPT production MD trajectory at 200 K, using block averaging and full-precision averages as implemented in the GROMACS code.

Composite	Observables (Units)	Ensemble Averages	Block Averaging Size [nbmin x nbmax]	Error Estimate
PVA + 10% Graphene Filler	Volume (nm^3)	187.09	5 x 5	0.0045
			6 x 6	0.0042
			8 x 8	0.0052
			10 x 10	0.0053
	Density (kg/m^3)	1302.0	5 x 5	0.032
			6 x 6	0.029
			8 x 8	0.036
			10 x 10	0.037
	Pressure (bar)	1.2	5 x 5	0.16
			6 x 6	0.19
			8 x 8	0.19
			10 x 10	0.17
	Temperature (K)	201.0	5 x 5	0.0071
			6 x 6	0.0050
			8 x 8	0.0067
			10 x 10	0.0067
	Total Energy (kJ/mol)	-217407.0	5 x 5	3.4
			6 x 6	4.4
			8 x 8	4.2
			10 x 10	4.2

Table S5. Statistical analysis of the volume, density, pressure, temperature, and total energy of the simulated system of graphene-reinforced polymer nanocomposite obtained from the ensemble averages of the production MD trajectory. The error estimate was conducted over 1000001 points, accumulated from the 200 ns NPT production MD trajectory at 300 K, using block averaging and full-precision averages as implemented in the GROMACS code.

Composite	Observables (Units)	Ensemble Averages	Block Averaging Size [nbmin x nbmax]	Error Estimate
PVA + 10% Graphene Filler	Volume (nm^3)	189.36	5 x 5	0.038
			6 x 6	0.034
			8 x 8	0.031
			10 x 10	0.030
	Density (kg/m^3)	1286.28	5 x 5	0.26
			6 x 6	0.23
			8 x 8	0.21
			10 x 10	0.21
	Pressure (bar)	1.2	5 x 5	0.16
			6 x 6	0.29
			8 x 8	0.24
			10 x 10	0.29
	Temperature (K)	301.3	5 x 5	0.0057
			6 x 6	0.0090
			8 x 8	0.0091
			10 x 10	0.0069
	Total Energy (kJ/mol)	-170306.0	5 x 5	40
			6 x 6	36
			8 x 8	32
			10 x 10	28

Table S6. Statistical analysis of the volume, density, pressure, temperature, and total energy of the simulated system of graphene-reinforced polymer nanocomposite obtained from the ensemble averages of the production MD trajectory. The error estimate was conducted over 1000001 points, accumulated from the 200 ns NPT production MD trajectory at 400 K, using block averaging and full-precision averages as implemented in the GROMACS code.

Composite	Observables (Units)	Ensemble Averages	Block Averaging Size [nbmin x nbmax]	Error Estimate
PVA + 10% Graphene Filler	Volume (nm^3)	194.70	5 x 5	0.035
			6 x 6	0.032
			8 x 8	0.028
			10 x 10	0.030
	Density (kg/m^3)	1251.0	5 x 5	0.22
			6 x 6	0.21
			8 x 8	0.18
			10 x 10	0.19
	Pressure (bar)	0.8	5 x 5	0.29
			6 x 6	0.42
			8 x 8	0.27
			10 x 10	0.26
	Temperature (K)	401.3	5 x 5	0.013
			6 x 6	0.0073
			8 x 8	0.009
			10 x 10	0.013
	Total Energy (kJ/mol)	-117215.0	5 x 5	45
			6 x 6	41
			8 x 8	40
			10 x 10	37

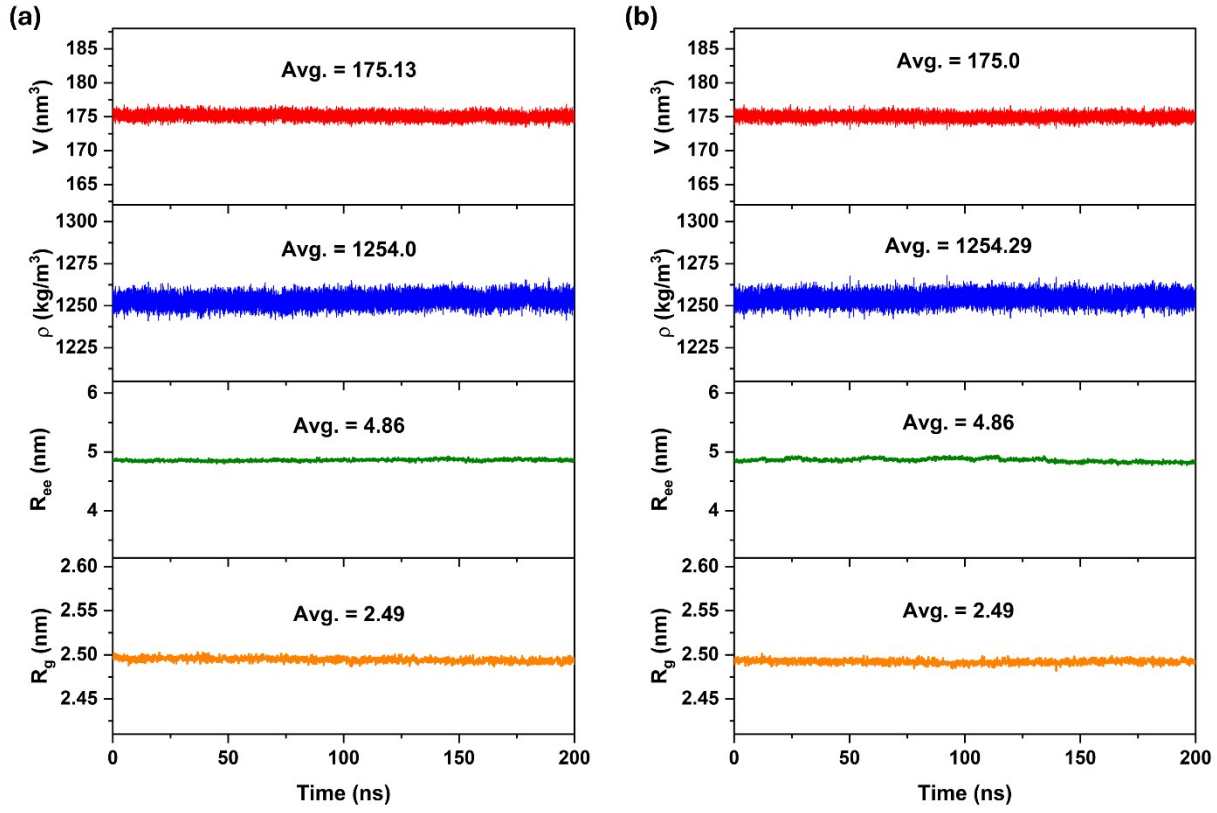

Fig. S1. Comparison of temporal evolution of the calculated volume (V) and density (ρ) of the PVA composite and the computed end-to-end distance (R_{ee}) and radii of gyration (R_g) of the PVA polymer chains, as acquired from the **(a)** NPT **equilibration** and **(b)** NPT **production** MD runs at **300 K**. The calculated ensembled-averaged quantities are also depicted for each quantitative estimation of the structural properties of the PVA composite.

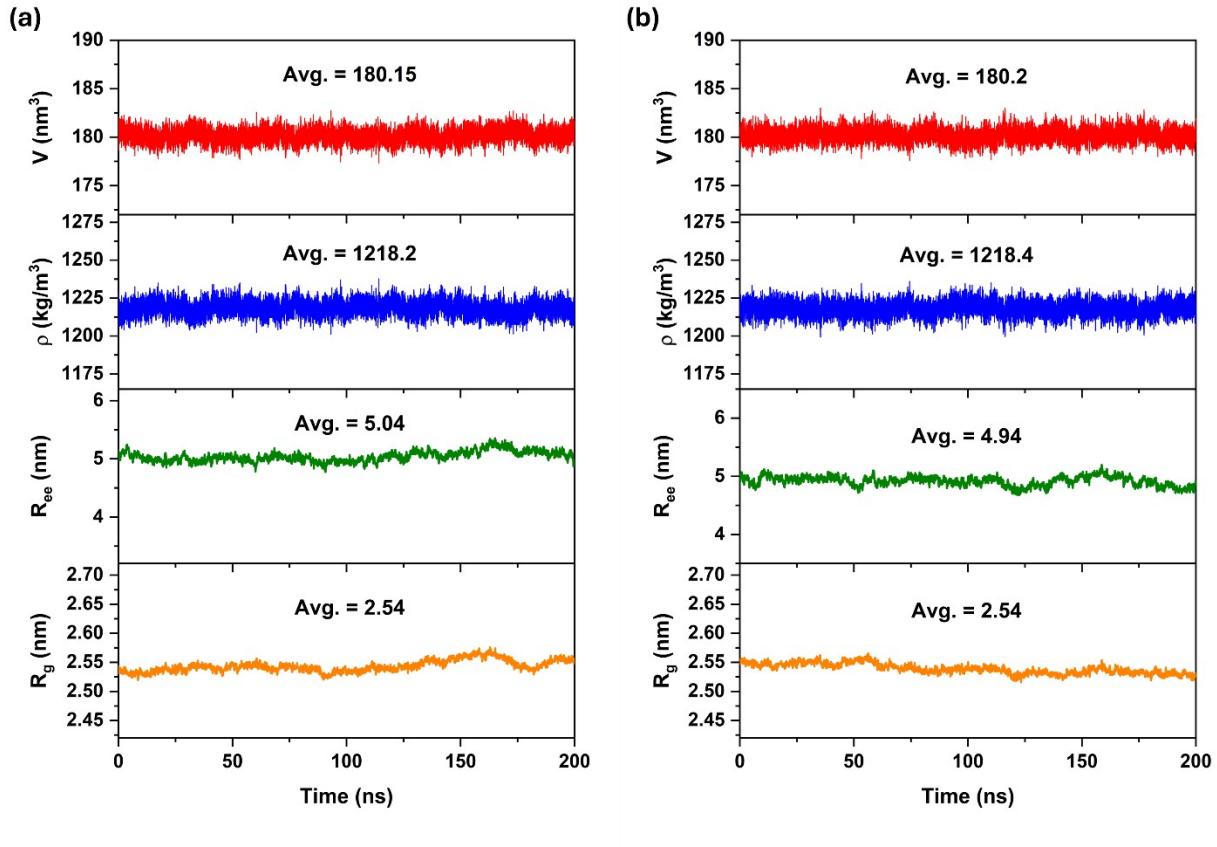

Fig. S2. Comparison of temporal evolution of the calculated volume (V) and density (ρ) of the PVA composite and the computed end-to-end distance (R_{ee}) and radii of gyration (R_g) of the PVA polymer chains, as acquired from the **(a)** NPT **equilibration** and **(b)** NPT **production** MD runs at **400 K**. The calculated ensembled-averaged quantities are also depicted for each quantitative estimation of the structural properties of the PVA composite.

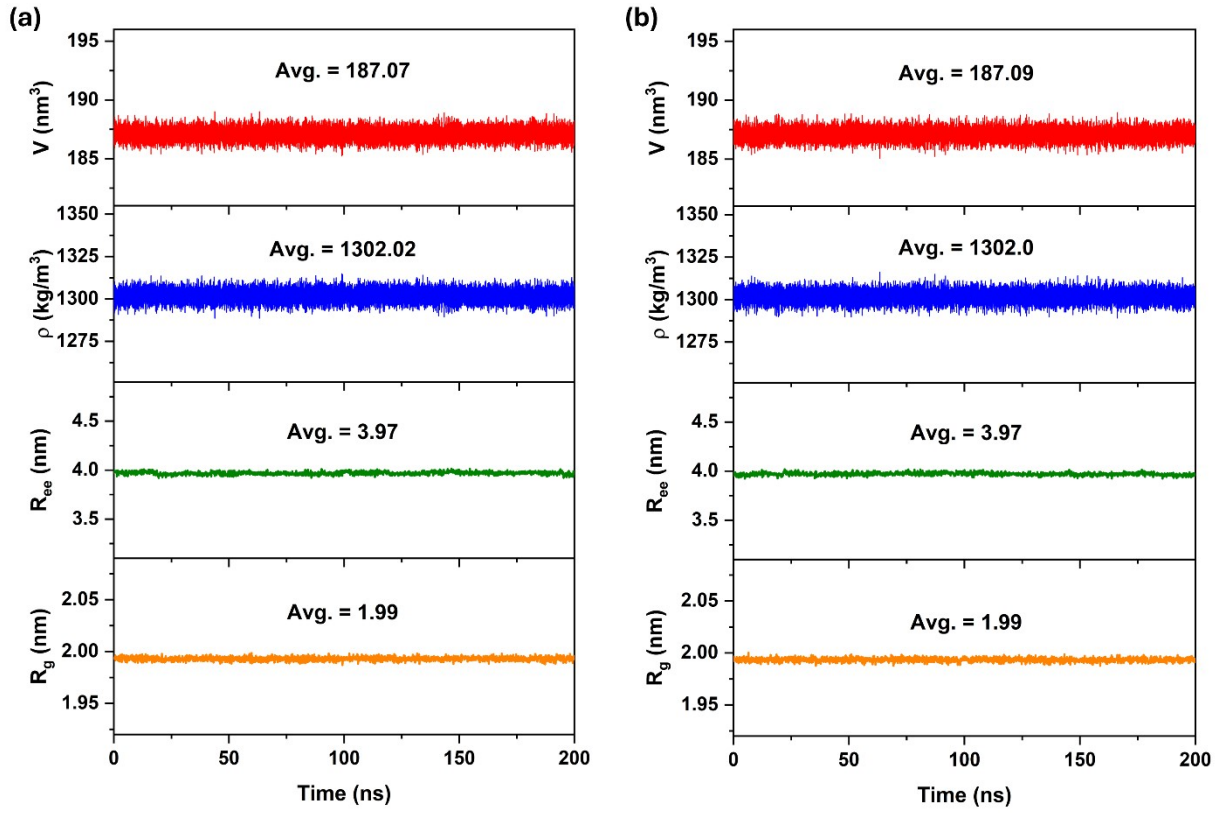

Fig. S3. Comparison of temporal evolution of the calculated volume (V) and density (ρ) of the PVA composite with 10% graphene nanofiller and the computed end-to-end distance (R_{ee}) and radii of gyration (R_g) of the PVA polymer chains, as acquired from the **(a)** NPT **equilibration** and **(b)** NPT **production** MD runs at **200 K**. The calculated ensembled-averaged quantities are also depicted for each quantitative estimation of the structural properties of the G-PVA nanocomposite.

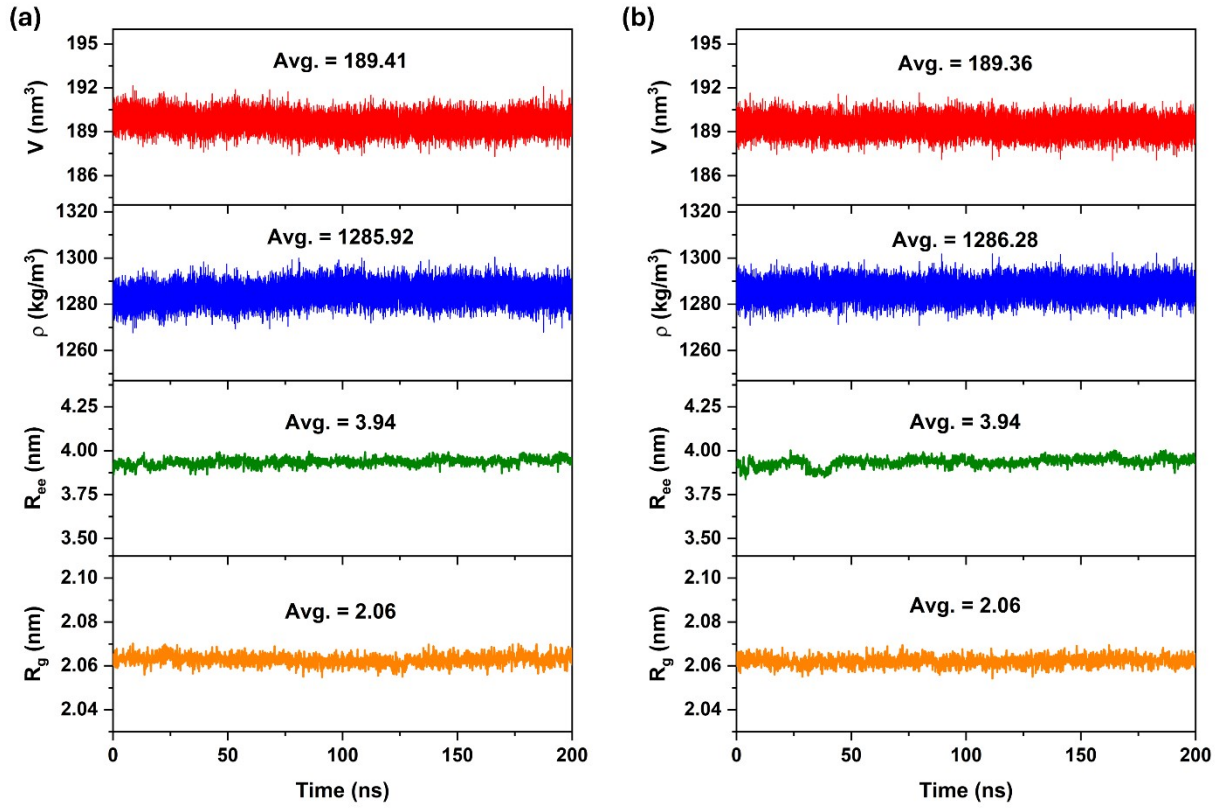

Fig. S4. Comparison of temporal evolution of the calculated volume (V) and density (ρ) of the PVA composite with 10% graphene nanofiller and the computed end-to-end distance (R_{ee}) and radii of gyration (R_g) of the PVA polymer chains, as acquired from the **(a)** NPT **equilibration** and **(b)** NPT **production** MD runs at **300 K**. The calculated ensembled-averaged quantities are also depicted for each quantitative estimation of the structural properties of the G-PVA nanocomposite.

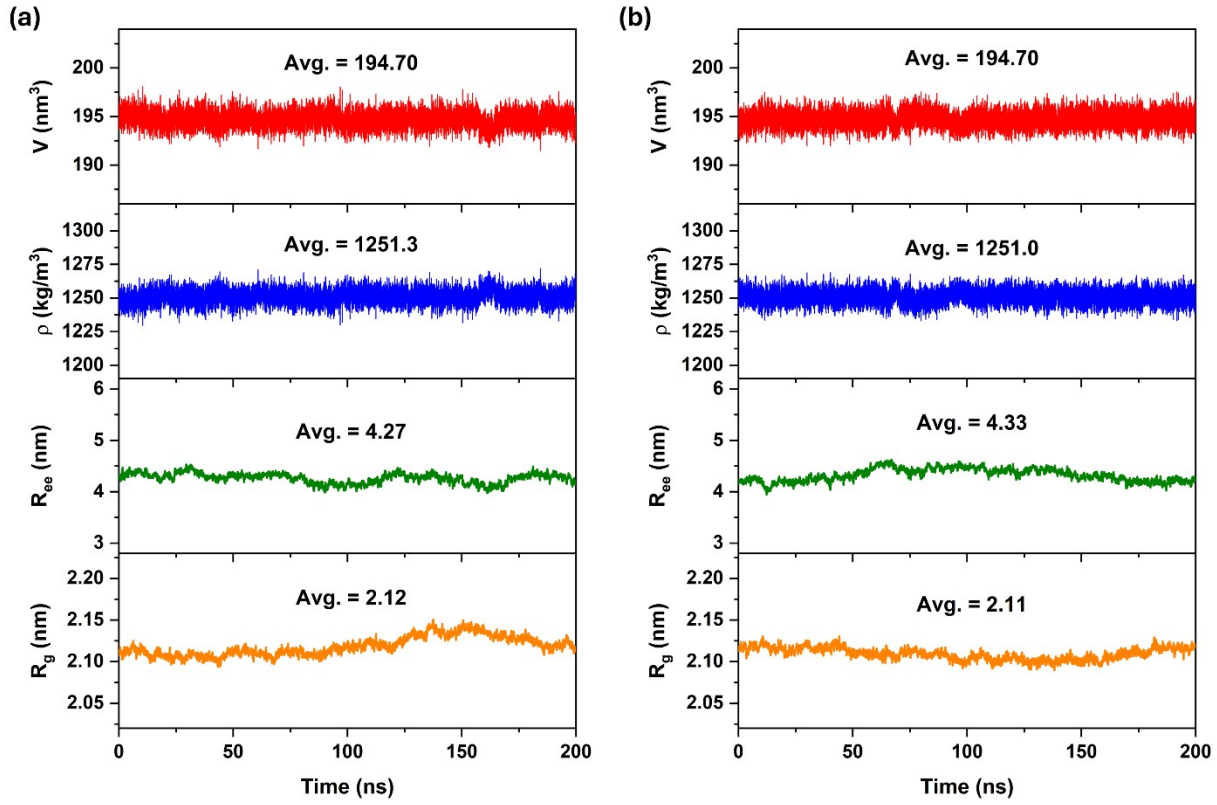

Fig. S5. Comparison of temporal evolution of the calculated volume (V) and density (ρ) of the PVA composite with 10% graphene nanofiller and the computed end-to-end distance (R_{ee}) and radii of gyration (R_g) of the PVA polymer chains, as acquired from the **(a)** NPT **equilibration** and **(b)** NPT **production** MD runs at **400 K**. The calculated ensembled-averaged quantities are also depicted for each quantitative estimation of the structural properties of the G-PVA nanocomposite.

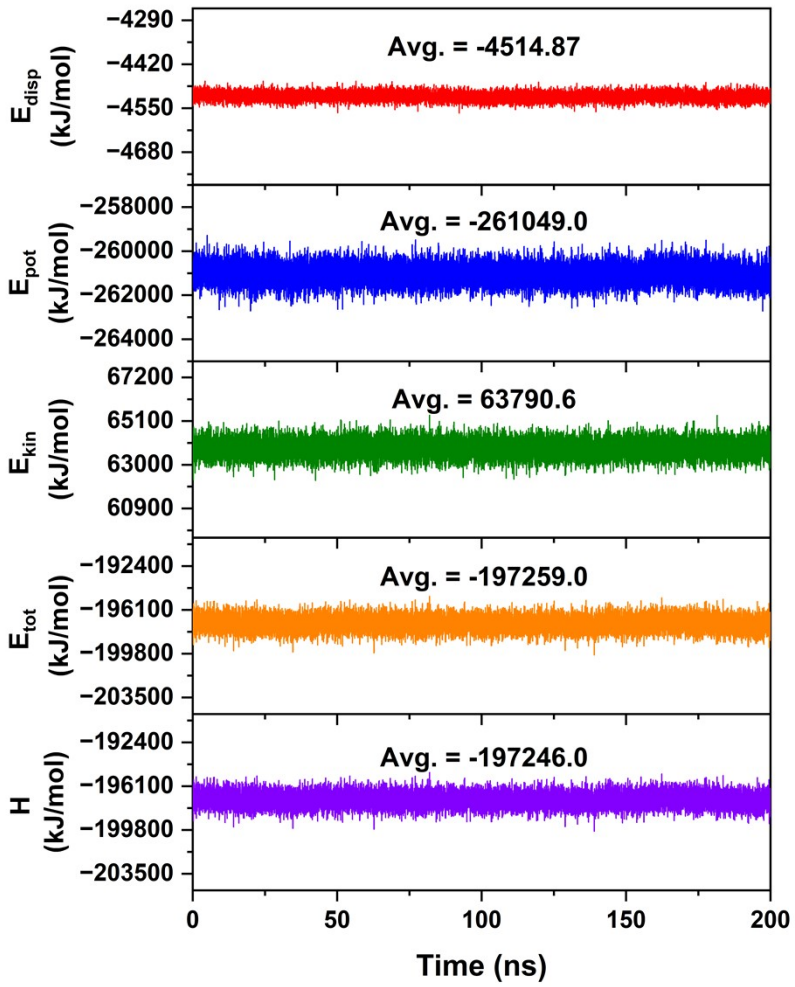

Fig. S6. Manifestation of the temporal evolution of calculated dispersion energy (E_{disp}), potential energy (E_{pot}), kinetic energy (E_{kin}), total energy (E_{tot}), and enthalpy (H) of the simulated PVA composite, as accumulated from the 200 ns production MD runs under NPT ensemble at 300 K.

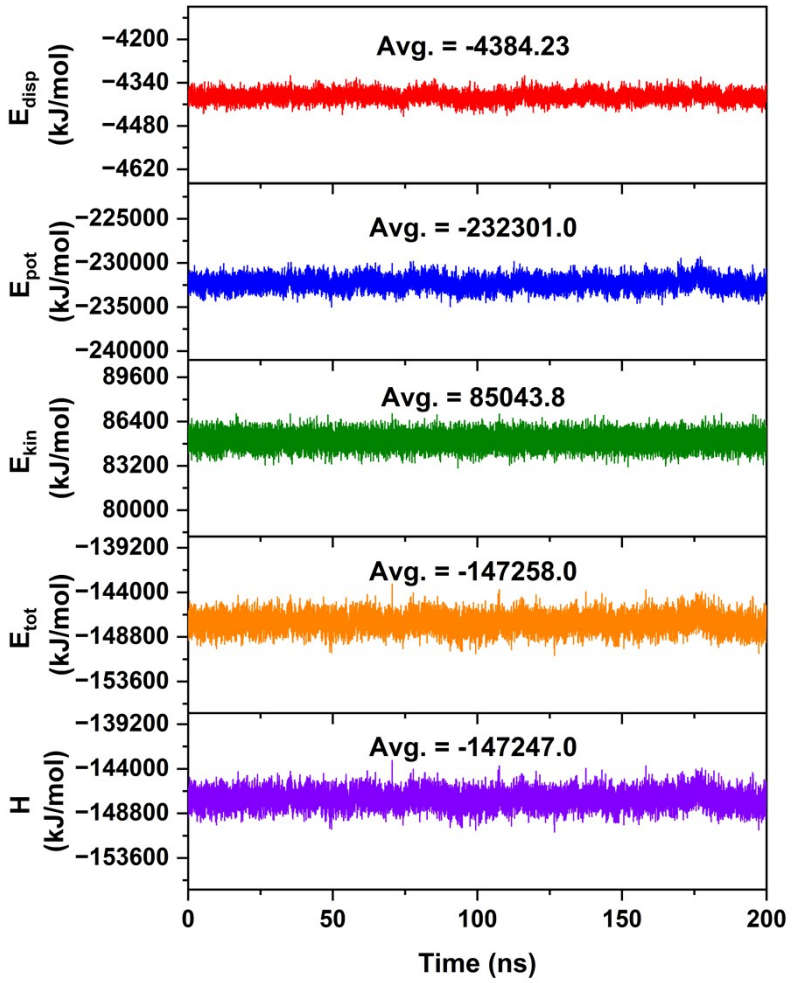

Fig. S7. Manifestation of the temporal evolution of calculated dispersion energy (E_{disp}), potential energy (E_{pot}), kinetic energy (E_{kin}), total energy (E_{tot}), and enthalpy (H) of the simulated PVA composite, as accumulated from the 200 ns production MD runs under NPT ensemble at 400 K.

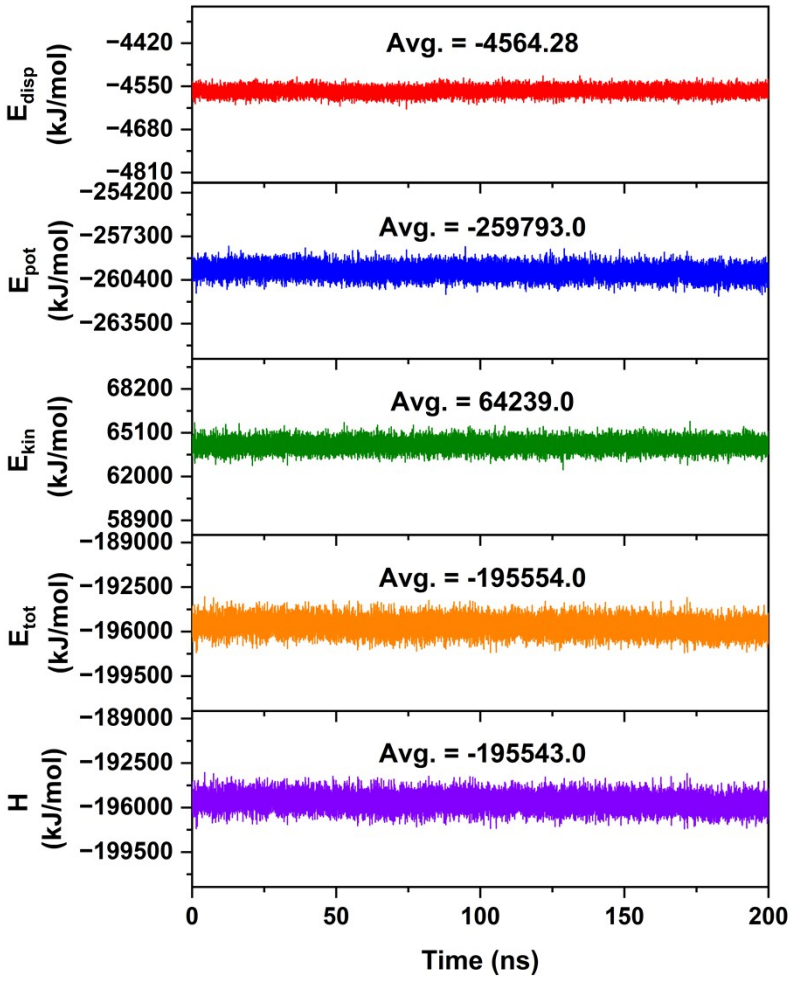

Fig. S8. Demonstration of relative changes of calculated dispersion energy (E_{disp}), potential energy (E_{pot}), kinetic energy (E_{kin}), total energy (E_{tot}), and enthalpy (H) of the simulated PVA composite with ~0.8% graphene nanofiller, as accumulated from the 200 ns production MD runs under NPT ensemble at 300 K.

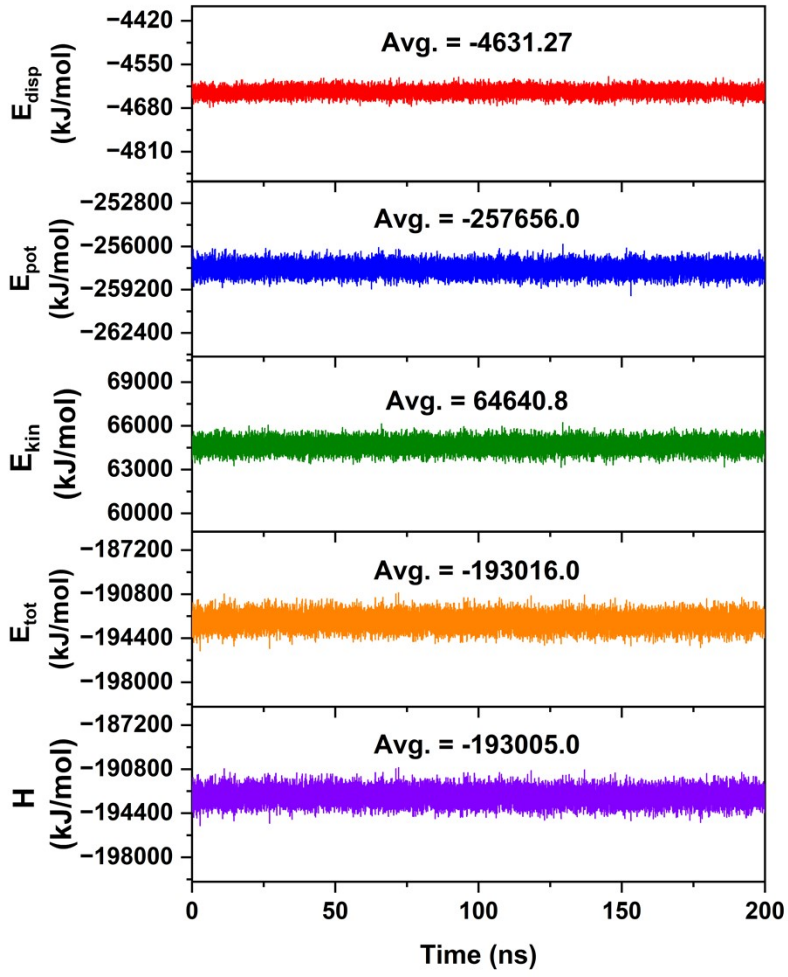

Fig. S9. Demonstration of relative changes of calculated dispersion energy (E_{disp}), potential energy (E_{pot}), kinetic energy (E_{kin}), total energy (E_{tot}), and enthalpy (H) of the simulated PVA composite with ~2.0% graphene nanofiller, as accumulated from the 200 ns production MD runs under NPT ensemble at 300 K.

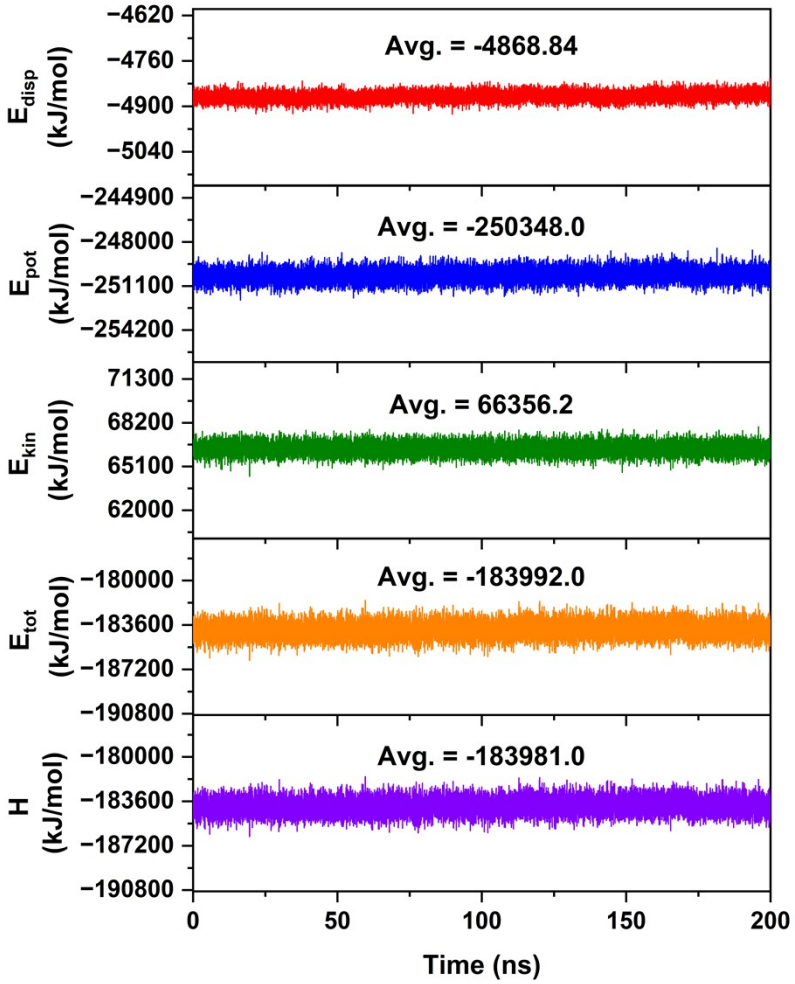

Fig. S10. Demonstration of relative changes of calculated dispersion energy (E_{disp}), potential energy (E_{pot}), kinetic energy (E_{kin}), total energy (E_{tot}), and enthalpy (H) of the simulated PVA composite with ~5.0% graphene nanofiller, as accumulated from the 200 ns production MD runs under NPT ensemble at 300 K.

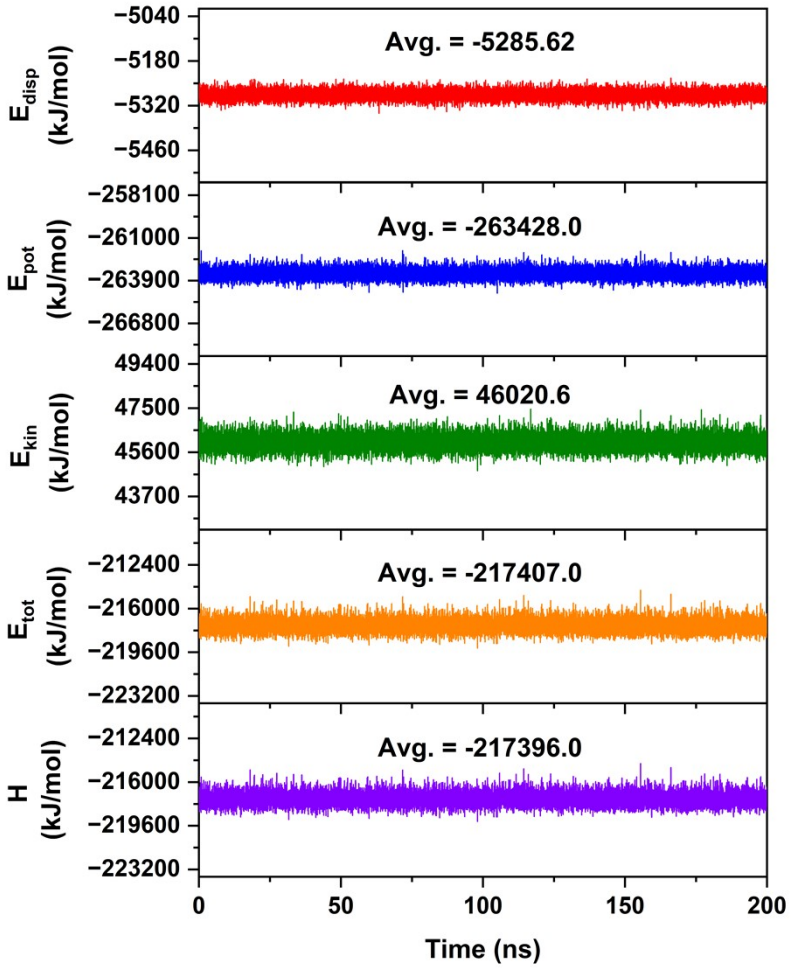

Fig. S11. Demonstration of relative changes of calculated dispersion energy (E_{disp}), potential energy (E_{pot}), kinetic energy (E_{kin}), total energy (E_{tot}), and enthalpy (H) of the simulated PVA composite with ~10.0% graphene nanofiller, as accumulated from the 200 ns production MD runs under NPT ensemble at 200 K.

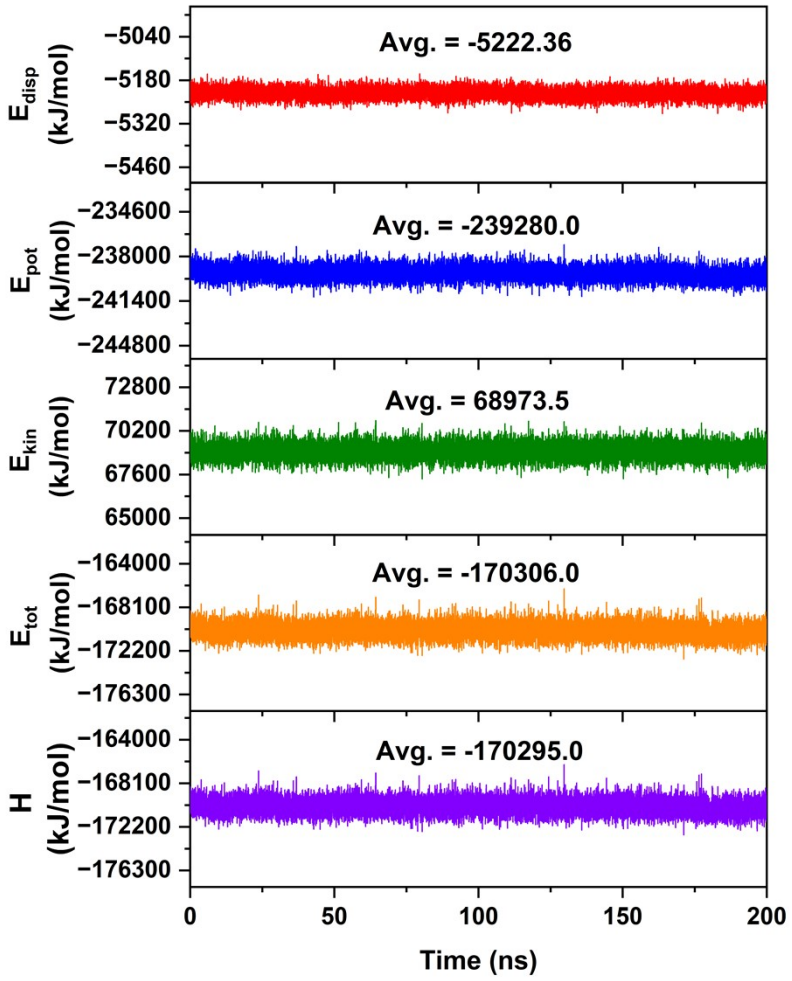

Fig. S12. Demonstration of relative changes of calculated dispersion energy (E_{disp}), potential energy (E_{pot}), kinetic energy (E_{kin}), total energy (E_{tot}), and enthalpy (H) of the simulated PVA composite with ~10.0% graphene nanofiller, as accumulated from the 200 ns production MD runs under NPT ensemble at 300 K.

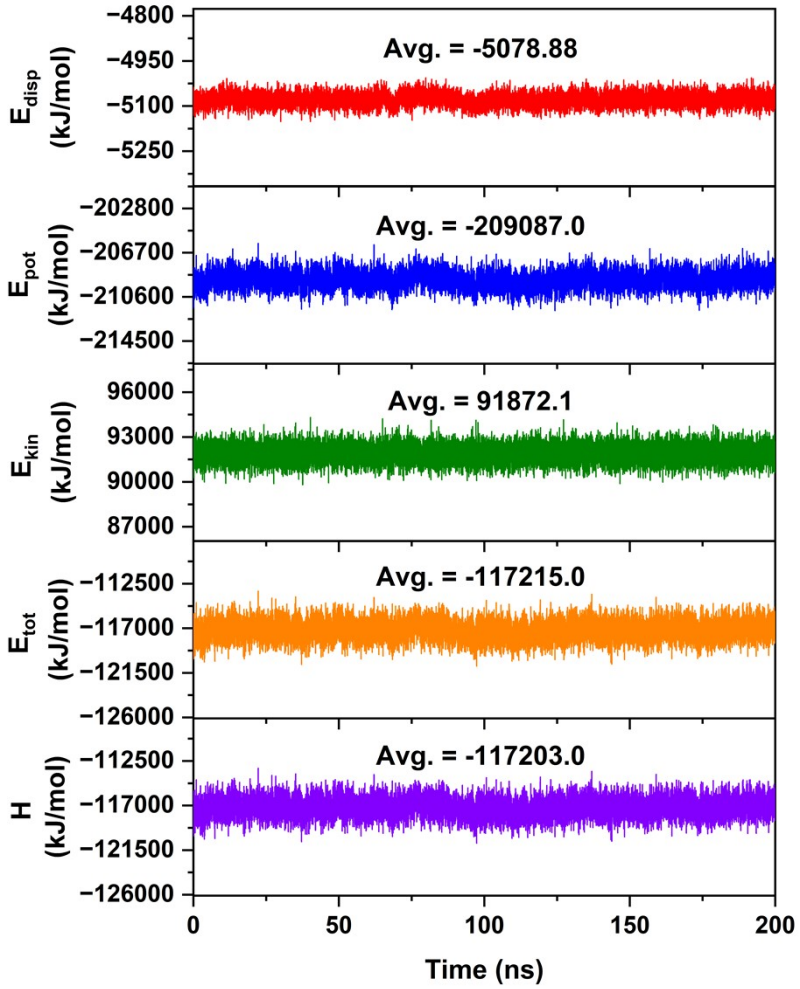

Fig. S13. Demonstration of relative changes of calculated dispersion energy (E_{disp}), potential energy (E_{pot}), kinetic energy (E_{kin}), total energy (E_{tot}), and enthalpy (H) of the simulated PVA composite with ~10.0% graphene nanofiller, as accumulated from the 200 ns production MD runs under NPT ensemble at 400 K.

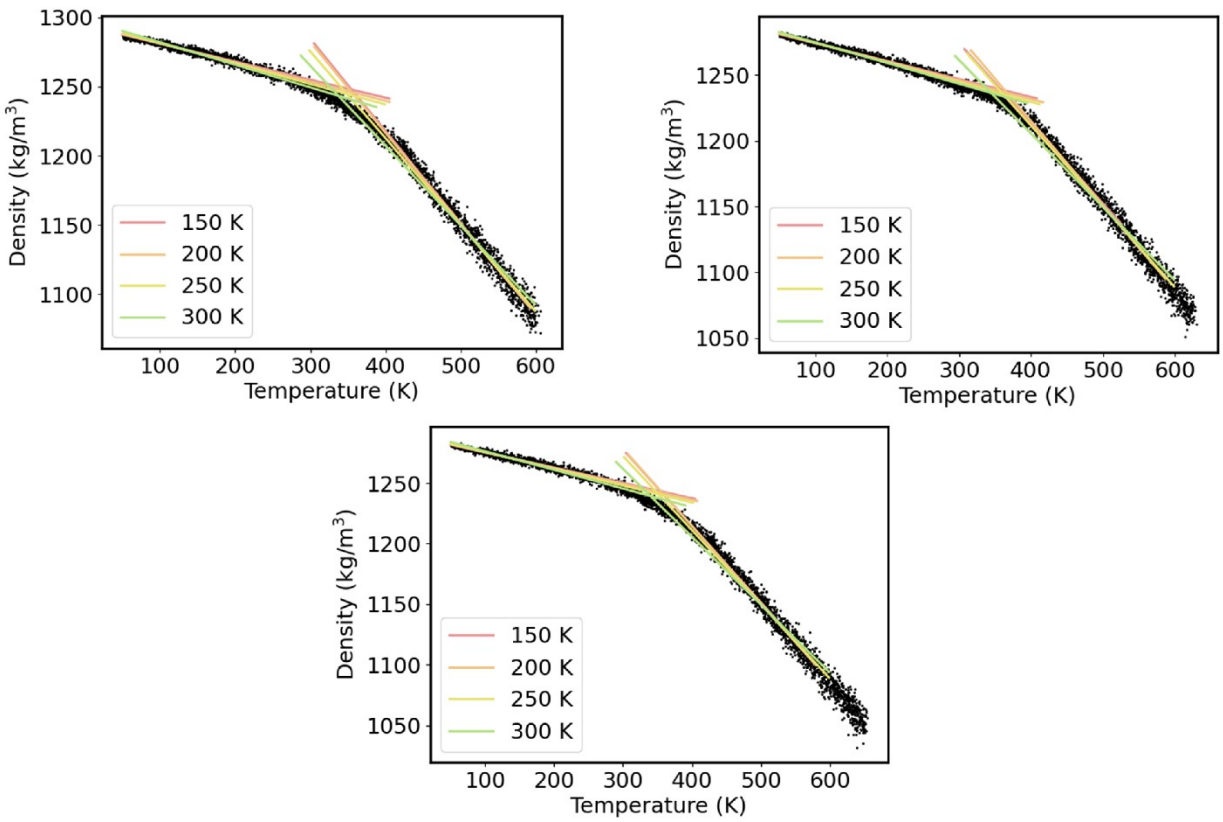

Fig. S14. Representation of the bilinear fit of the glassy and rubbery states on the density vs. temperature curve with four different fitting ranges for three independent thermally equilibrated starting configurations of the pristine PVA composite.

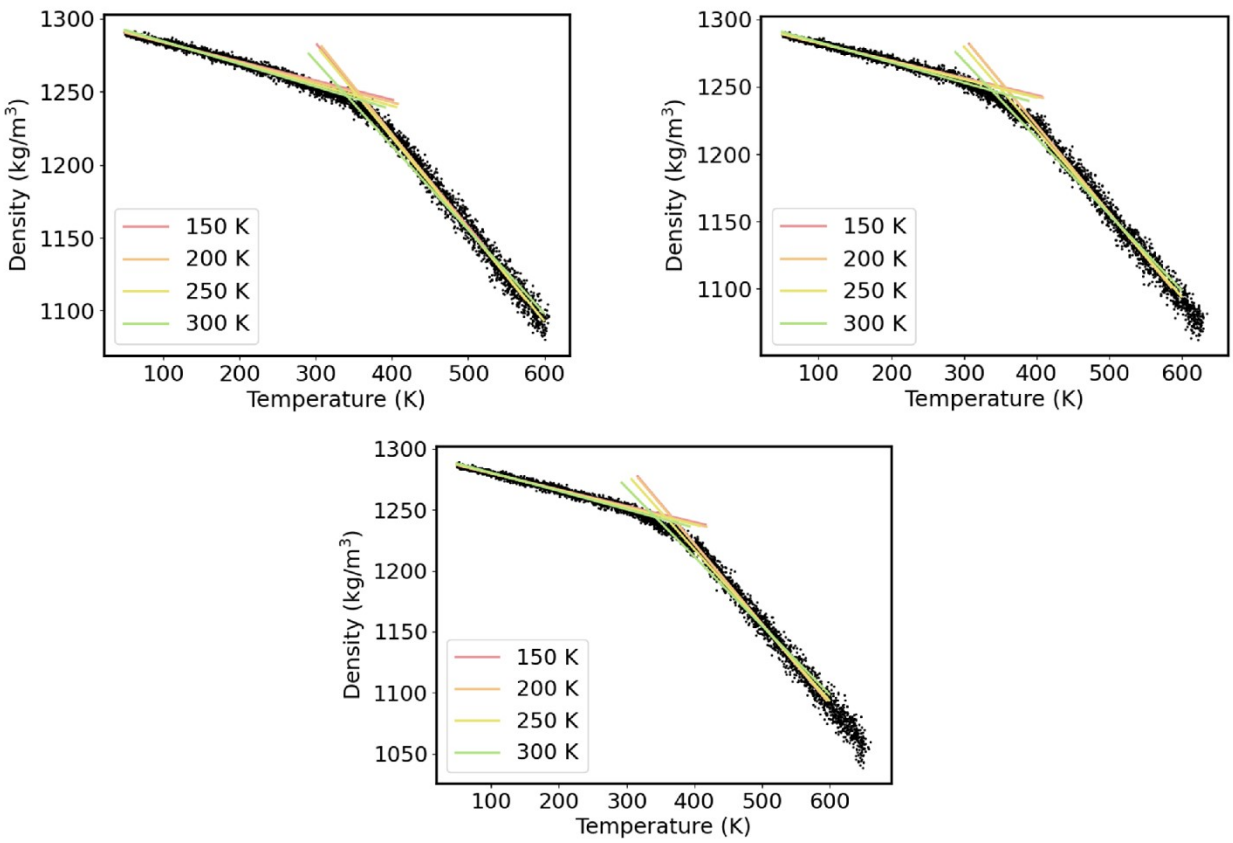

Fig. S15. Representation of the bilinear fit of the glassy and rubbery states on the density vs. temperature curve with four different fitting ranges for three independent thermally equilibrated starting configurations of the 2% graphene-filled PVA composite.

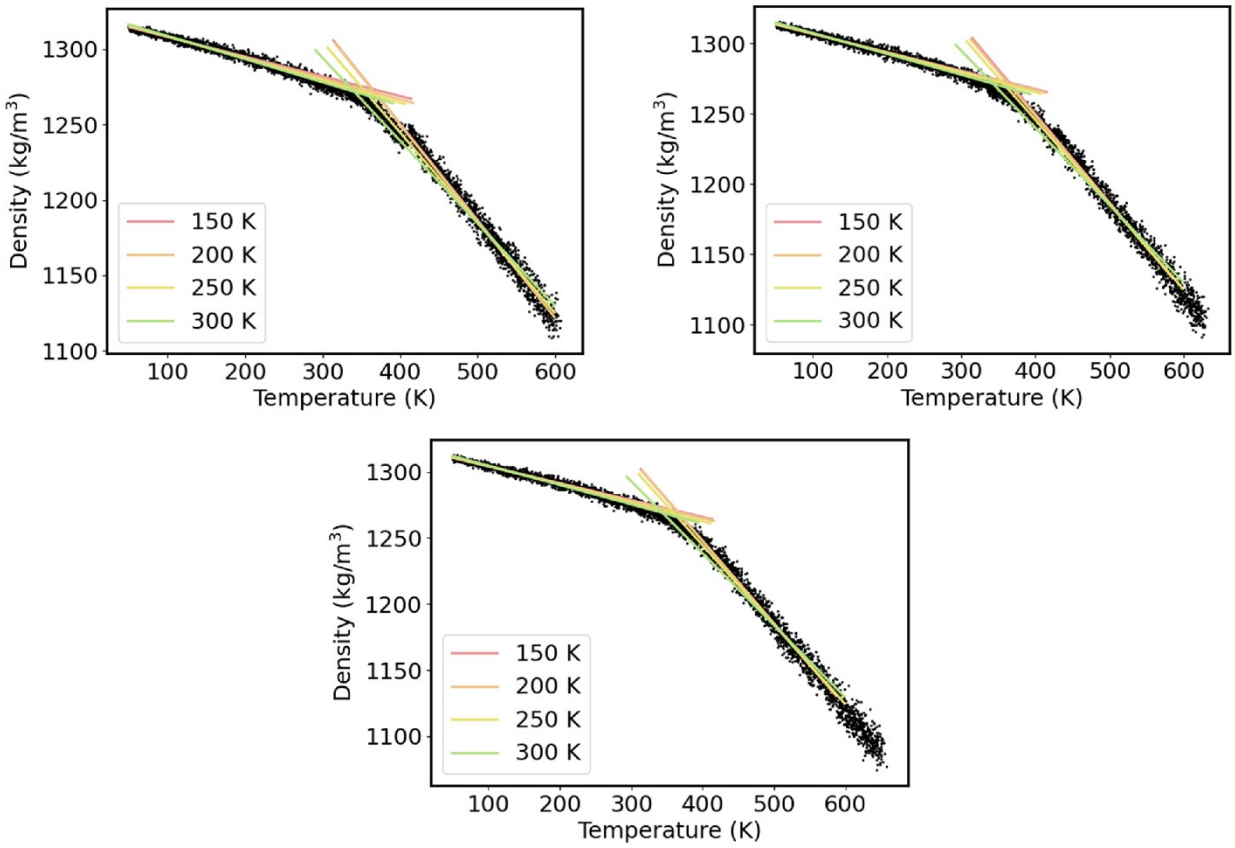

Fig. S16. Representation of the bilinear fit of the glassy and rubbery states on the density vs. temperature curve with four different fitting ranges for three independent thermally equilibrated starting configurations of the 10% graphene-filled PVA composite.