

Development of a New Force Field for Property Prediction of Cyclo-Olefin Copolymers

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The applicability of the Dreiding 2.21 and PCFF force fields to the prediction of properties of cyclo-olefin copolymers was evaluated. The initial performance of the force fields was only modest, and reoptimization of the force field parameters was required. The reoptimization was performed for the Dreiding 2.21 force field by fitting the force field to the potential energy curves of B3LYP/6-31G* calculations. The modifications to the force field resulted in a considerable improvement, bringing the calculated mechanical and thermal properties close to the experimental values. Experimental substructures for polymer fragments were obtained from the Cambridge structural database. Theoretical potential energy minima were found to be in good agreement with the experimental structural data.

1. Introduction

Cyclo-olefin copolymer (COC) plastics are widely applied in optical and technical applications, such as optical data storages, medical devices, and shockproof plastics. Among their several useful properties are optical clarity, excellent dielectric strength, moisture barrier properties, high-temperature resistance, and good mechanical properties, such as high modulus of elasticity and tensile strength.¹

The manufacture and physical properties of COC have been studied extensively by experimental techniques, the focus being mainly on the development of manufacturing technologies.^{2–4} Theoretical studies on polynorbornane and COC have focused mostly on polynorbornane polymers^{5–10} rather than COC.^{11,12}

The second-generation polymeric force fields, such as PCFF^{13–20} and COMPASS,²¹ have frequently been applied for studies on polymer properties.^{22–24} However, these force fields are not applicable for all polymers, and new ones have been developed. For example, Cun et al.²² have reoptimized the Dreiding 2.21 force field for polycarbonate and Blomqvist and co-workers^{23,24} developed the PCFF force field for various polyesters. The object of our study was to evaluate the performance of the Dreiding 2.21²⁵ and PCFF force fields for property prediction of COC and, if necessary, to develop a more applicable force field by reoptimizing the force field parameters.

2. Theory and Computational Details

The cyclo-olefin copolymer chain was modeled with two molecular models, each representing a fragment of the polymer chain. Cyclo-olefin copolymers usually consist of norbornane and ethane units, between which the sequence can vary markedly. The applied molecular models were the NEN unit and the EENEE unit (Figure 1).

Experimentally determined crystal structures were utilized as a support for the conformational analyses. The crystal structures containing similar polymer fragments were acquired from the Cambridge structural database. The structures, containing transition metals and the structures, which were part of a rigid ring,

were omitted. The search yielded 246 suitable crystal substructures: 61, 68, 50, 20, and 47 for torsions T1–T5, respectively. The applied structure units are shown in Figure 2.

The applicabilities of the Dreiding 2.21 and PCFF force fields for prediction of polymer properties were tested by geometry optimizations, conformational analyses, and property simulations. The geometry optimizations and conformational analyses were carried out by HF/3-21G and B3LYP/6-31G* methods using the Gaussian 98 program,²⁶ as well as with PCFF and Dreiding 2.21 force-field-based molecular mechanics methods, for which the Cerius² program²⁷ was applied. On the basis of conformational analyses, the parameters of the Dreiding 2.21 force field were modified to obtain the best fit with B3LYP/6-31G* calculations. The focus was on noncorrelating parameters of the force field because the changes in noncorrelating parameters do not affect the other parameters of the force field. The term 1–4 nonbonded interaction is included in the van der Waals term of the force field.

The single-chain Young's modulus studies on COC were carried out with the PCFF and Dreiding 2.21 force fields together with the modified Dreiding 2.21 force field. The ab initio methods that were utilized were HF/3-21G* and B3LYP/6-31G*. The Young's modulus of polymers can be predicted by studying the single-chain behavior of a polymer since it depends mainly on intramolecular interactions. The effect of intermolecular interactions is much less important.^{28–31} The Young's modulus study was performed by fixing the specified atomic distances and optimizing the rest of the molecule. The fixed atomic distances were C1–C2 and C3–C4 in NEN and C7–C16 in EENEE (Figure 1). The monitored magnitudes were the change in the total energy ΔE and the elongation of the atomic distance (C–C) ΔL . The stretching force and Young's modulus were calculated with eqs 1 and 2, respectively,

$$F = \left(\frac{\partial E}{\partial L} \right) = \left(\frac{\Delta E}{\Delta L} \right) \quad (1)$$

$$\frac{\Delta L}{L_0} = \frac{1}{Y A} F \quad (2)$$

where L_0 is the equilibrium length, ΔL is the elongation, A is the cross-sectional area, ΔE is a change in the total energy, and Y is Young's modulus.

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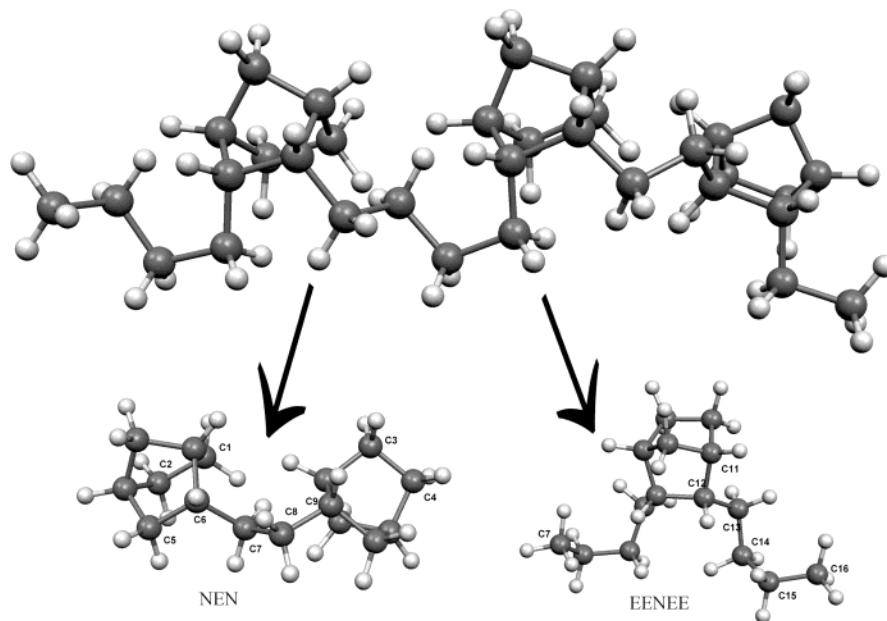


Figure 1. Applied molecular models, NEN and EENEE, representing the cyclo-olefin copolymer chain.

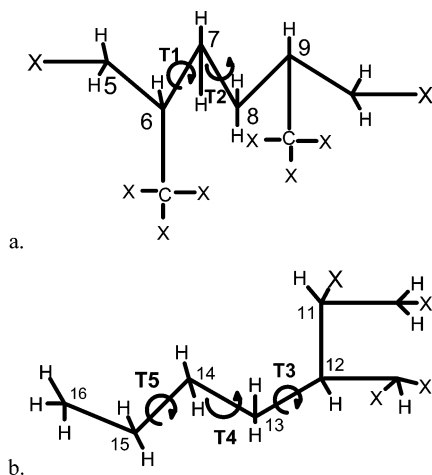


Figure 2. Model molecules of COC in the crystal structure search: (a) represents the NEN unit, (b) represents the EENEE unit.

The molecular dynamics simulations were carried out with Dreiding 2.21 and modified Dreiding 2.21 force fields. The aim of the simulations was to determine the mechanical properties (bulk modulus, Young's modulus, shear modulus, and Poisson's ratio) and thermodynamical properties (glass transition temperature). The mechanical properties were determined by the second-derivative method,²² excluding shear modulus, for which the second-derivation method was not available. The shear modulus was determined instead by the constant stress method.^{22,32} The simulation cube contained five polymer chains, each chain containing 99–132 atoms.

The glass transition temperatures of COC were determined by NPT (constant particle number, pressure, and temperature) molecular dynamics simulation. The temperature range was 200–450 K for EENEE-type COC and 300–650 K for NEN-type COC. The simulation step was 1 fs, and electrostatic interactions were calculated by utilizing the Ewald method with a dielectric constant of 2.35. The simulations were run for 10 ps at all temperatures. The monitoring of the specific volume–temperature (*V*–*T*) curve enables the prediction of the glass transition temperature (*T_g*). A break in the slope of the *V*–*T* curve represents the location of the *T_g*.^{7,33–35} Error limits were derived from standard deviations.

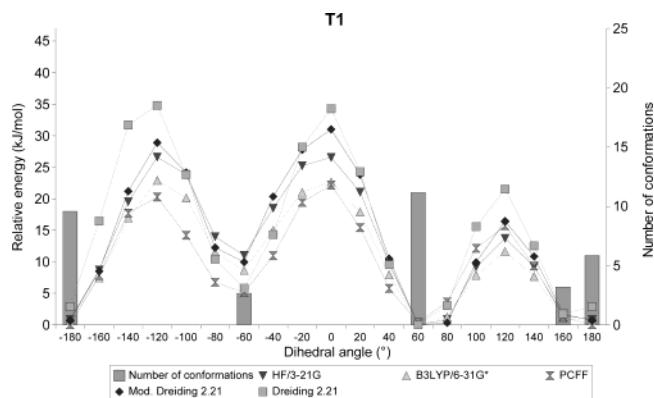


Figure 3. Conformational analysis of the NEN molecule for torsion T1. The bar diagram compares the hits of the crystal structure search with the calculated conformations.

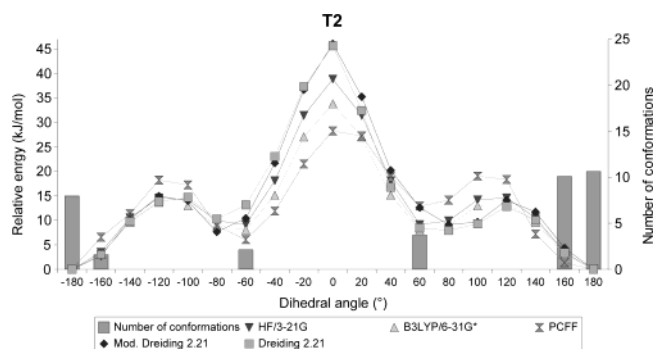


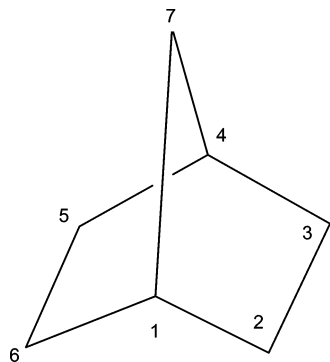
Figure 4. Conformational analysis of the NEN molecule for torsion T2. The bar diagram compares the hits of the crystal structure search with the calculated conformations.

3. Results and Discussion

3.1. Conformational Analyses and Modification of the Force Fields. The NEN model contains two relevant torsions for conformational analysis: T1 (C5–C6–C7–C8) and T2 (C6–C7–C8–C9). The conformational energy curves of torsions T1 and T2 are shown in Figures 3 and 4. In torsion T1, the global minimum appeared at dihedral angle of 60.0° and the local minima at the points of 60.0° and 180.0°. The global maximum appeared at a dihedral angle of 0° and the other

TABLE 1: The Modified and Original Parameters of the Dreiding 2.21 Force Field for COC

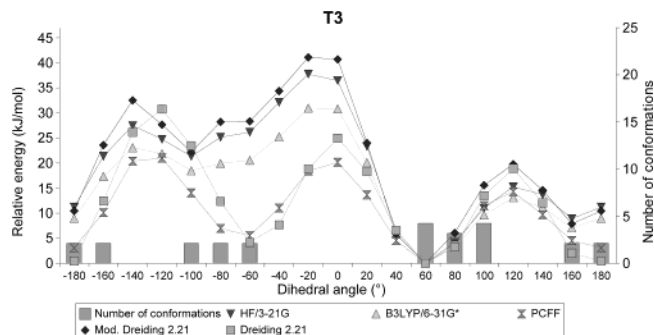
torsion (NEN) {T1 and T2}	modified Dreiding 2.21 (kJ/(mol Å ²))	Dreiding 2.21 (kJ/(mol Å ²))
V ₁	0	0
V ₂	2.34	2.09
V ₃	8.71	0
torsion (EENEE) {T3, T4 and T5}	modified Dreiding 2.21 (kJ/(mol Å ²))	Dreiding 2.21 (kJ/(mol Å ²))
V ₁	0	0
V ₂	5.23	2.09
V ₃	7.66	0

**Figure 5.** Schematic illustration of the norbornane ring with atom labels.

maxima at points -120.0° and 120.0° . The energy barriers are due to the steric repulsion of the norbornane rings. The crystal structures were also found at the global and local minima points in good agreement with the calculations.

The energy curve of torsion T2 (Figure 4) showed the molecule to have a global minimum at dihedral angle of 180.0° , whereas the two other local minima appeared at dihedral angles of $+60.0^\circ$ and -60.0° . The global minimum corresponded to the trans conformation of the NEN molecule. The molecule had an energy barrier at a global maximum point of 0° and local maxima at points 120.0° and -120.0° . The relatively high energy barrier around 0° is due to the strong steric repulsion of the norbornane rings. The experimental observations suggest that the deepest minima should be located at a dihedral angle of about 180.0° , and the calculations were in agreement with this. Crystal structures were found at dihedral angles of approximately $+60.0^\circ$ and -60.0° , which according to the calculations were local minima.

As can be seen in Figure 3, locations of the potential energy minima and maxima produced by the force field and ab initio methods were similar but the energy differences at the global and local maxima were notable. For example, the energy difference between the original Dreiding 2.21 and B3LYP potential energy curves was 11.6 kJ/mol at the global maximum point 0° of torsion T1. To improve the performance of the Dreiding 2.21 force field, the force field parameters were reoptimized (modified Dreiding 2.21 force field). The bond stretching parameters and bond bending parameters were obtained from the work of Ahmed et al.¹⁰, and the torsion terms were reoptimized by reproducing the new parameters from B3LYP/6-31G* torsional behavior (Table 1). Because the PCFF force field had a strong correlation between the force field terms, it was not utilized. The atom labels are shown in Figure 5, and the Dreiding 2.21 force field is presented in Equation 3.

**Figure 6.** Conformational analysis of the EENEE molecule for torsion T3. The bar diagram compares the hits of the crystal structure search with the calculated conformations.

$$E_{\text{pot}} = E_{\text{Bond stretching}} + E_{\text{Bond bending}} + E_{\text{Torsion}} + E_{\text{Inversion}} + E_{\text{Vdw}} + E_{\text{Coulombs}}$$

$$E_{\text{Bond stretching}} = \sum_R \frac{1}{2} k_e (R - R_e)^2$$

$$E_{\text{Bond bending}} = \sum_\theta \frac{1}{2} K (\theta - \theta_0)^2 \quad (3)$$

$$E_{\text{Torsion}} = \sum_\varphi \frac{1}{2} V \{1 - \cos[n(\varphi - \varphi_0)]\}$$

$$E_{\text{Inversion}} = \sum_\psi \frac{1}{2} K_{\text{inv}} (\psi - \psi_0)^2$$

$$E_{\text{Vdw}} = D_0 \left\{ \left(\frac{R_0}{R} \right)^{12} - 2 \left(\frac{R_0}{R} \right)^6 \right\}$$

Although the PCFF and Dreiding force fields describe the torsional behavior well, they clearly fail to describe the geometry of the norbornane ring of COC. In the case of the PCFF force field the deviations from experimental values were 0.090–0.200 Å in the C–C bonds and 5.8–59.7° in the bond angles. The Dreiding 2.21 force field performed slightly better, the deviations being 0.090–0.160 in the C–C bonds and 5.8–45.0° in the bond angles. The modifications to the Dreiding 2.21 force field resulted in a considerable improvement, bringing the bond lengths and angles close to the experimental values. The deviations between the modified Dreiding 2.21 force field and experimental values were 0.007–0.040 Å in the C–C bonds and 0.1–3.2° in the bond angles. The bond angles and lengths predicted by the ab initio method were also in agreement with experimental values. Relative to the experimental values, the bond length deviations were 0.007–0.010 Å and the deviations in the bond angles were 0.3–0.8°.

The EENEE fragment contained three relevant torsions, which were studied in conformational analysis. These are labeled T3, T4, and T5 in Figure 2. The torsion behavior of the Dreiding 2.21 and PCFF force fields was incorrect in the conformational analysis of torsion T3. This is clearly seen in the torsion energy profile between -180.0° and 0.0° (Figure 6) where three local minima are found.

The global minimum of torsion T3 appeared at a dihedral angle of 60.0° , and the local minima appeared at dihedral angles of -100.0° and $+160.0^\circ$. The largest energy barrier was located at the point 0° where the repulsion between the norbornane ring and the carbon chain (C13–C14–C15–C16) was strongest. Two local maxima were located at dihedral angles of 120.0° and -140.0° . The ab initio calculations were in line with each

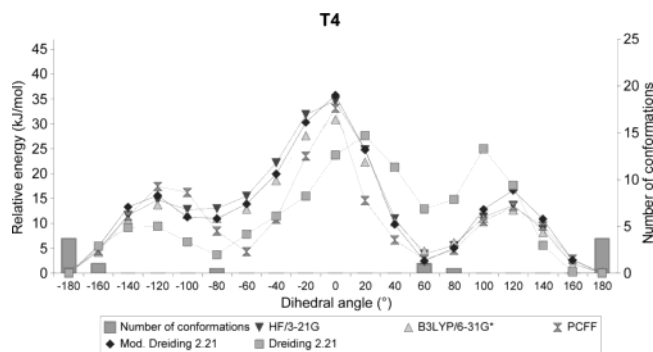


Figure 7. Conformational analysis of the EENEE molecule for torsion T4. The bar diagram compares the hits of the crystal structure search with the calculated conformations.

TABLE 2: Parameters Applied in the Determination of the Single-Chain Young's Modulus

NEN (modified Dreiding 2.21)				
ΔE (kJ) $\times 10^{-21}$	F (N) $\times 10^{-10}$	ΔL (pm)	$\Delta L/L_0$ $\times 10^{-2}$	F/A (N/m ²) $\times 10^7$
1.33	1.36	0.98	1.62	5.07
1.63	1.51	1.08	1.77	5.61
1.95	1.66	1.18	1.94	6.16
2.30	1.80	1.28	2.10	6.69
2.67	1.93	1.38	2.26	7.20
3.06	2.07	1.48	2.42	7.69

other and were also in reasonable agreement with the crystal structure findings. Most crystal structures appeared around the global minimum point of $+60.0^\circ$ and the local minima.

The conformational analysis for the torsion T4 is presented in Figure 7. The global minimum appeared at a dihedral angle of 180.0° and the local minima points at dihedral angles of -80.0° and $+60.0^\circ$. The global maximum was at the point 0° , whereas the local maxima appeared at dihedral angles of -120.0° and 120.0° . The steric repulsion between the norbornane unit and the carbon chain (C13–C14–C15–C16) was the strongest at point 0° . The energy barrier of torsion T4 was 3.9 kJ/mol lower than the corresponding energy barrier of torsion T3 at the point 0° . This difference was due to the steric effect of the norbornane ring, which was weaker in torsion T4 than in torsion T3.

Excluding the PCFF and the original Dreiding 2.21 force fields, the calculations were found to agree well with the experimental observations. The main difference in torsion behavior was observed at local minimum point -80.0° . The PCFF method indicated that this minimum was located at the point -60.0° . The maxima of the potential energy curve of the Dreiding 2.21 force field were shifted, and the sizes of the energy barriers were incorrect.

The conformational analysis for the torsion T5 is presented in Figure 8. The global minimum appeared at a dihedral angle of 180.0° in agreement with the experimental findings. Two local minima were located at dihedral angles of -60.0° and 60.0° . The local maxima appeared at dihedral angles of -120.0° and 120.0° and a high-energy barrier at the global maximum point 0° . The energy barrier was clearly lower than the corresponding energy barriers of torsions T3 and T4 at the point

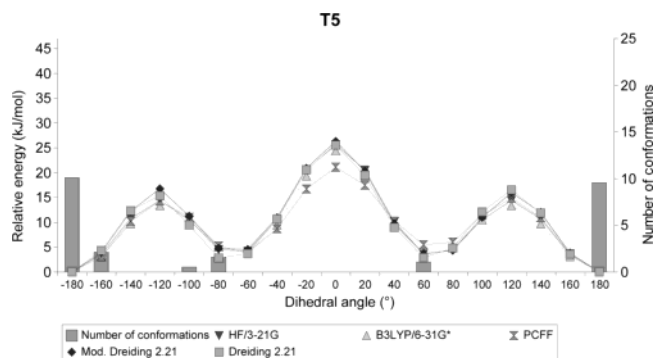


Figure 8. Conformational analysis of the EENEE molecule for torsion T5. The bar diagram compares the hits of the crystal structure search with the calculated conformations.

0° . The energy differences were 14.4 kJ/mol for torsions T3 and T5 and 9.4 kJ/mol for torsions T4 and T5. The steric repulsion between the norbornane ring and the carbon chain (C13–C14–C15–C16) was significantly weaker than in torsions T3 and T4. It was also notable that the PCFF force field and original Dreiding 2.21 force field were successful in the case of torsion T5 since the steric effect of the norbornane ring was weak at that point. The calculations at both local minima, 60.0° and -60.0° , were in agreement with the experimental findings.

3.2. Testing of the Force Fields. **3.2.1. Single-Chain Young's Modulus.** The applicability of the utilized force fields for prediction of polymer properties was tested by a single-chain Young's modulus study and molecular dynamics simulations. The single-chain Young's modulus of polymers has been studied earlier by Zhang et al.²⁸ for polyethylene and by other groups for polymers such as PVC,³¹ PMMA,³¹ and PTFE.³⁶ In the single-chain Young's modulus studies, the accuracy of the results was verified by performing an ab initio based single-chain Young's modulus study utilizing HF/3-21G* and B3LYP/6-31G* methods. The measured cross-sectional area A was $1.23 \times 10^{-18} \text{ m}^2$ for the NEN model and $2.69 \times 10^{-18} \text{ m}^2$ for the EENEE model. The results of the calculation are listed in Tables 2 and 3.

In general, the calculations were in agreement with the experimental data. The Young's moduli determined by the HF/3-21G* method were higher than the experimental values, whereas the values obtained by B3LYP/6-31G* were within the range of the experimental ones. The modification of the Dreiding 2.21 force field improved the calculated Young's moduli of COC significantly. The PCFF and original Dreiding 2.21 force fields clearly overestimated the Young's moduli of NEN-type COC, while underestimating the Young's moduli of EENEE-type COC. The significant failure in the case of NEN is clearly due to the nonproper description of norbornane units by the force fields. The values obtained by the modified Dreiding 2.21 force field were in agreement with the ab initio results.

3.2.2. Molecular Dynamics. The molecular dynamics results for COC are listed in Table 4 together with the experimental values. The original Dreiding 2.21 force field overestimated the calculated Young's (Y) and shear moduli (S). The bulk moduli (B) and Poisson's ratios (ν) were underestimated. The modifica-

TABLE 3: Calculated Single-Chain Young's Moduli (GPa) of COC

molecule	PCFF	Dreiding 2.21	modified Dreiding 2.21	HF/3-21G*	B3LYP/6-31G*	exptl ¹
EENEE	1.20	2.34	2.99	3.29	2.82	2.6–3.2
NEN	5.52	6.73	3.27	3.62	2.87	2.6–3.2

TABLE 4: Calculated Glass Transition Temperatures and Mechanical Properties of COC

property	COC type	Dreiding 2.21	modified Dreiding 2.21	exptl ^{1,27}
<i>B</i> (GPa)	NEN	4.07	4.78	4.1–5.9
<i>B</i> (GPa)	EENEE	4.23	4.30	4.1–5.9
<i>Y</i> (GPa)	NEN	4.41	3.45	2.6–3.2
<i>Y</i> (GPa)	EENEE	4.62	3.24	2.6–3.2
<i>S</i> (GPa)	NEN	2.08	1.25	1.00
<i>S</i> (GPa)	EENEE	1.66	1.26	1.00
ν	NEN	0.32	0.38	0.37–0.41
ν	EENEE	0.31	0.38	0.37–0.41
T_g (°C)	NEN	275.5 ± 14.5	238.2 ± 12.9	180–200
T_g (°C)	EENEE	144.5 ± 9.9	130.1 ± 4.3	80–100

tions to the force field improved the property predictions, bringing the properties close to the experimental ones. The simulation of the mechanical properties did not bring the Young's modulus of COC any closer to the experimental value than did a single-chain method (Table 3), providing further evidence of the significance of intramolecular interactions for Young's modulus.

The glass transition temperatures (T_g) determined by the original Dreiding 2.21 force field were clearly higher than the experimental glass transition temperatures, whereas the values obtained by the modified Dreiding 2.21 force field were in reasonable agreement with the experimental ones. The T_g value of NEN-type COC was clearly higher than the T_g value of EENEE-type COC because a larger number of norbornane units in the polymer chain increases the glass transition temperature.³⁷ The calculated T_g values with error limits are listed in the Table 4.

4. Conclusions

The applicability of the PCFF and Dreiding 2.21 force fields for COC was evaluated. The performances were only modest, and the force field parameters were reoptimized for the Dreiding 2.21 force field. The parameters for the modified Dreiding 2.21 force field were produced as the result of a conformational analysis searching for the best match with the B3LYP/6-31G* potential energy curves. A crystal structure search in the Cambridge structural database provided useful support for the calculations, verifying the correctness of the observed potential energy minima. The modified Dreiding 2.21 force field significantly improved the prediction of the mechanical and thermal properties of COC, bringing them close to the experimental values.

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