

Quantum-Chemical Estimating Interaction of sp^2 -Carbon Nanoclusters with PE and PP Oligomers

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Abstract

The purpose of this work was to examine the interaction of graphene-like nanoclusters with fragments of polymers of the same nature, but somewhat different structure, for example, polyethylene (PE) and polypropylene (PP) by means of quantum chemistry. By method of density functional theory with the exchange-correlation functional B3LYP, the basis set 6 - 31 G (d, p) and the Grimme's dispersion correction, the energy values have been calculated of interaction between nanocarbon fragments and oligomers of PE and PP, the most probable structures of their intermolecular complexes being optimized. A graphene-like plane of 40 carbon atoms and 16 atoms of hydrogen was chosen as a model for the surface of the graphene and carbon nanotubes (CNT). In order to take into account the dimensional effect of the surface of the nanotube fragment model on the interaction energy, in addition to the above described, two larger models were used, with the general formula $C_{54}H_{18}$ and $C_{96}N_{24}$. It has been found that the interaction energy of nanocarbon fragment with an oligomer of PP is greater, compared with PE, which is consistent with the experimental data on melting temperatures of pure polymers and nanotube-polymer composites. The polymer with a surface of nanocarbon fragment forms an intermolecular complex not bound covalently and retained by intermolecular dispersion forces. Oligomers of polymeric matters and carbon surfaces in formed nanocomplex are placed closer to each other than separate polymeric links between them.

Keywords

Nanocomposite, Carbon Nanotube, Polyethylene, Polypropylene, Density Functional Theory Method, Cluster Approximation, Dispersion Forces of Interaction

1. Introduction

One of the most promising directions for the development of modern science is nanotechnology [1]. Development of the principles of obtaining polymer nanocomposites is actual [2], the creation of which is based on fundamental research of physico-chemical processes of formation of materials and their structure at the atomic-molecular level, which ensures the possibility of obtaining nanocomposites with predicted functional properties.

In recent time CNT are often used as fillers, which are cylinders having graphene-like surface with distorted sp^2 -hybridized orbitals of carbon atoms. They are considered as ideal reinforcement material for polymers [3].

Thus, it has been found that the addition of 1 to 5 wt% of CNT to thermoplastic polymers increases their elasticity and strength by 36% - 42% [4]. However, the inclusion of CNT in the PE matrix in small amounts (up to 5 wt%) leads to a nonmonotonic change in both the degree of crystallinity of the polymer matrix and the electrophysical and thermodynamic properties [5]. It is also found that the leakage threshold in PE-CNT systems, determined by experimental data on electrical conductivity, is within 0.15 - 0.2 vol%. In this case, the content of CNT up to 2 wt% increases the temperature of thermo-oxidative degradation of the polymer by almost 60°C.

PP-CNT composites were described in paper [6], and features were examined of their structure, melting and crystallization processes, mechanical, electro- and thermophysical characteristics. It is shown that the presence of CNT in PP for insignificant content (up to 2 wt%) leads to a nonmonotonic change in the degree of crystallinity of the composite, which is most clearly reflected in the thermophysical properties. It has been found that the content of 0.5 - 5.0 wt% CNT results in the formation of a continuous grid, which leads to a significant increase in the compression strength, reduction of the deformation rate, increase in electrical conductivity to five orders of magnitude with a slight increase in the thermal conductivity.

CNT in polymer matrices significantly affect the electrical and thermal conductivity, viscosity when moving and other transport properties [7] [8] [9]. The results of the study on the properties of polymer-CNT nanocomposites have shown that the use of nanotubes to fill the polymer matrices of different species significantly alter their physical properties compared to the original polymers. However, the influence of CNT on the properties of nanocomposites obtained at the molecular level has not yet been completely ascertained.

The interaction and properties of composites of organic polymers with nanotubes are successfully investigated by methods of computer simulation [10] [11]. It has been found that the interaction energy of the molecule-off-piecemeal complex is dependent on the dispersion forces between the molecules and carbon nanostructures, and also, in some cases, on Coulomb interactions due to charge transfer and intermolecular H-bonds. In our previous paper [12] it is shown that when molecules adsorb physically on a carbon nanotube, a substan-

tial redistribution of electron density between them occurs in contrast to chemisorption in the case of the formation of covalent bonds between a molecule and a nanotube. Consequently, the above considerations suggest the successful use of quantum chemistry to study the interaction of fragments of polymers with carbon nanostructures.

Therefore, the purpose of this work was to examine the interaction of CNT with fragments of polymers of the same nature, but somewhat different structure, for example, PE and PP by means of quantum chemistry. On the basis of the calculated data, it was possible to estimate the parameters of elementary interaction clusters that ensure the minimization of the energy state of the forming polymer-CNT nanocomposites.

2. Materials and Method

Within the framework of the density functional theory (DFT) with the functional B3LYP [13] [14] and the basis set 6-31G (d, p), the modeling of “fragment of the outer surface of a multilayer carbon nanotube with oligomers” containing one, two, and three elementary units (further monomers, dimers, and trimers) of polymers such as PE and PP, for which there are available experimental physical properties [5] [6]. To simplify the calculations, oligomers as elementary units of PE ($-\text{CH}_2-\text{CH}_2-$)_n and PP ($-\text{CHCH}_3-\text{CH}_2-$)_n, where n = 1, 2, 3, were represented by the corresponding saturated hydrocarbons, namely ethane, *n*-butane and *n*-hexane (for PE) and propane, 2-methylpentane and 2,4-methylheptane (for PP). The calculations used the GAMESS program (US) [15].

In order to take into account the dispersion effects of binding [16] [17] that arise in the formation of non-covalent intermolecular complexes, the dispersion correction of Grimme D3 [18] [19] was taken into account in the intermolecular interaction energy calculations. When creating nanocomposites based on PE and PP, multilayer CNT were used that had an outer diameter of 10 to 20 nm [5] [6]. As shown by the results of the simulation of a cross section of a nanotube with the diameter of 20 nm, it turned out that when the fragments of a small size, for example less 1 nm (trimers) of selected polymers interact, the outer surface of the nanotube looks almost without a positive curvature of the cylinder. It allows us to consider as a result of the interaction of small size oligomers of these polymers with the outer surface of CNT as intermolecular complexes of oligomers of selected polymers with a graphene-like plane.

Therefore, a graphene-like plane of 40 carbon atoms was chosen as a model for the outer surface of the CNT, as was done in [10]. In this case, the distance between the most remote carbon atoms in this graphene-like cluster is 1.2 nm. Therefore, to equalize uncompensated valences and to preserve sp^2 -hybridization at carbon atoms, 16 atoms of hydrogen, one to each carbon atom were added to peripheral atoms (see **Figure 1(a)**). In addition, in order to take into account the dimensional effect of the surface of the nanotube fragment model on the interaction energy, in addition to the above described, two larger models were used, the general formula $\text{C}_{54}\text{H}_{18}$ and $\text{C}_{96}\text{N}_{24}$ (**Figure 1(b)** and **Figure 1(c)**).

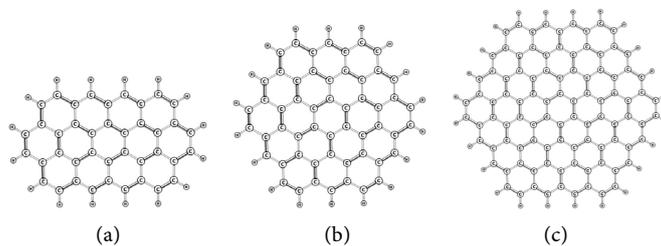


Figure 1. Models for the fragment of the outer surface of CNT by the general composition: (a) $C_{40}H_{16}$; (b) $C_{54}H_{18}$; (c) $C_{96}H_{24}$.

Equilibrium spatial structures of reagent molecules and reaction products were found by minimizing the gradient norm to 0.0001 Hartree. The stationary power minima of relative structures are proved by the absence of negative eigenvalues of Hesse' matrices (matrices of force constants) [20].

3. Results and Discussion

3.1. Interaction between Elementary Units in PE and PP

It is known [21] that for thermoplastic polymers, the intermolecular binding energy between their structural units correlates with the melting temperature of the corresponding matter. In the study of intermolecular interactions of the fragments of polymers with the outer surface of carbon nanotubes, magnitudes of the energy of intermolecular interaction of the fragment of polymers of different sizes for PE and PP were estimated (**Figure 2**). It shows the most probable intermolecular complexes, the total energies of which were minimal. In addition, we have shown that, regardless of the size of the fragment of polymers of PE and PP, the average distance between the carbon atoms is about 0.390 nm, which indicates the absence of chemical bonding between different oligomers [21].

The results of the analysis of calculations (see **Table 1**) demonstrate that the energies of interaction between two identical monomers are -8.0 kJ/mol and -14.4 kJ/mol, respectively for PE and PP. With an increase in the size of the oligomeric units to two ($n = 2$) for each of the polymers, the energy of their interaction is also almost twice as high, while the energy is -20.3 and -25.9 kJ/mol, respectively. By further increasing the size of studied oligomers ($n = 3$), the energy of the intermolecular interaction also increases: -32.9 kJ/mol for PE and -40.6 kJ/mol for PP. In this case, for a linear chain of polyethylene, an increase in the length of the fragments that interact with each other results in a monotonic decrease in the distance between the oligomers ($0.390 \rightarrow 0.378$ nm). This is also consistent with the energy of interaction per number of elemental links of the polymer. In particular, for the complex consisting two double-polymer units to find out this value, it is necessary to divide -20.3 kJ/mol into two and we so obtain the value of -10.2 kJ/mol, which is 2 kJ/mol less than the similar value for a complex of double monomer parts of PE (-8.0 kJ/mol). For the complex consisting of two trimers (**Figure 2(c)**), this value is even larger and is divided into three ($-33.0/3 = -11.0$ kJ/mol).

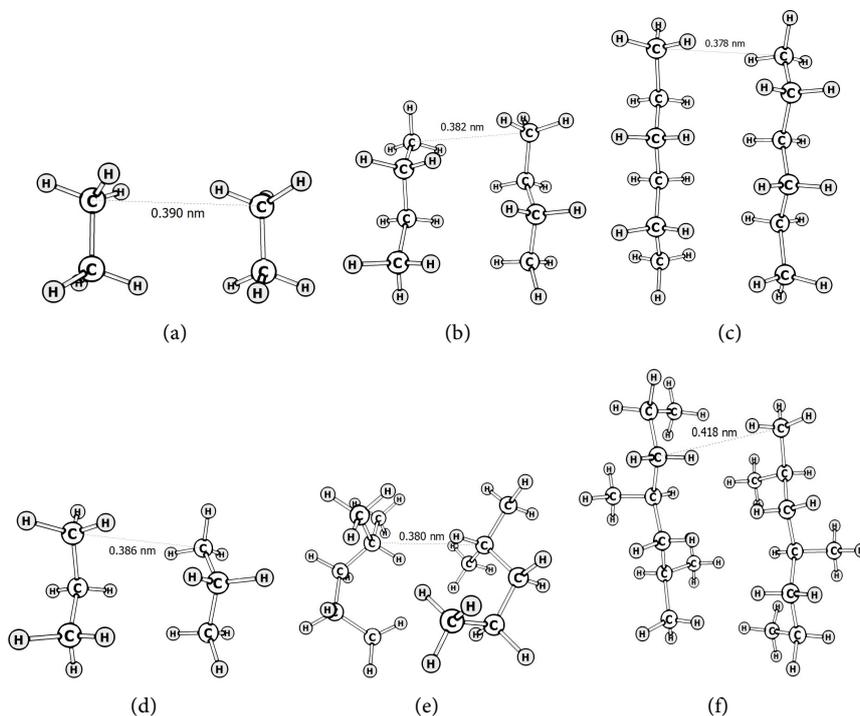


Figure 2. The most probable intermolecular complexes of PE ((a)-(c)) and PP ((d)-(f)) oligomers.

Table 1. Intermolecular binding energy values for pure polymers and nanocomposites (kJ/mol).

Number of links in the oligomer	Pure polymers		Nanocomposites					
	PE	PP	PE			PP		
			C ₄₀ H ₁₆	C ₅₄ H ₁₈	C ₉₆ H ₂₄	C ₄₀ H ₁₆	C ₅₄ H ₁₈	C ₉₆ H ₂₄
1	-8.0	-14.4	-31.5	-30.0	-33.0	-41.3	-45.1	-46.3
2	-20.3	-25.9	-54.6	-56.4	-57.4	-66.4	-69.3	-71.0
3	-33.0	-40.6	-80.5	-80.6	-81.3	-87.6	-89.2	-92.1

For PP, a similar trend of change in distance is not observed. The energy of intermolecular interaction per one elementary PP link also does not increase with an increase in the number of elementary units: compared to the complex consisting of PP monomers and having the intermolecular interaction energy value of -14.4 kJ/mol. For a link consisting of two elementary units, this value is $-25.9/2 = -13.0$ kJ/mol and for the trimeric PP fragment $-40.6/3 = -13.5$ kJ/mol, respectively. This can be explained by the fact that PP has a more complex structure (the presence of a methyl group in each elementary chain), in comparison with PE. Thus, with an increase in the number of elemental units in PP oligomer, the energy per PP unit does not differ significantly; it equals not more 3 kJ/mol. Therefore, for the study of intermolecular interaction between individual groups of polymeric units, it is enough to use oligomers consisting of two or three elementary units.

Consequently, based on the analysis of the calculation results, it can be argued that, regardless of the size of the fragments of these polymers, comparing the value of intermolecular energy for the same number of elementary units of these two polymers, the PP fragments are more tightly bound than those of PE, which means that in order to disconnect the PP links, which are connected by non-covalent bonds, more energy is needed than for PE. The calculation results obtained are consistent with experimental data on the melting temperature of polymers, since the melting temperature of PE is 120°C - 140°C, and for PP this value is higher (130°C to 170°C as dependent on the polymer grade [22] [23]).

3.2. Interaction of Fragments of CNT with PE Oligomers

In connection with the choice of a graphene-like plane as a fragment of the outer surface of CNT interacting with PE oligomers, it is crucially important to confirm the reliability of the calculated energy values of intermolecular interaction. Therefore, intermolecular complexes with different amounts of polymeric units (1, 2, 3) and graphene-shaped planes of various sizes ($C_{40}H_{16}$, $C_{54}H_{18}$, and $C_{96}H_{24}$) were modeled (**Figure 3**).

For complexes where the fragment of the outer surface of CNT has the smallest graphene cluster $C_{40}H_{16}$, the intermolecular distance between of the fragment of polymers and the graphene-shaped plane increases slightly from 0.329 to 0.345 nm with an increase in the size of the fragment of polymers from monomer to dimer, and for the trimer this value is slightly reduced to 0.342 nm. The energy of the intermolecular interaction of the PE monomer with the graphene plane is -31.5 kJ/mol, for dimer this value is -54.6 kJ/mol, and for the trimer -80.4 kJ/mol (**Table 1**). For intermolecular complexes with the graphene-like cluster $C_{54}H_{18}$ a tendency arises to shortening intermolecular distance due to an increase in the size of the PE fragments (0.346 → 0.339 nm).

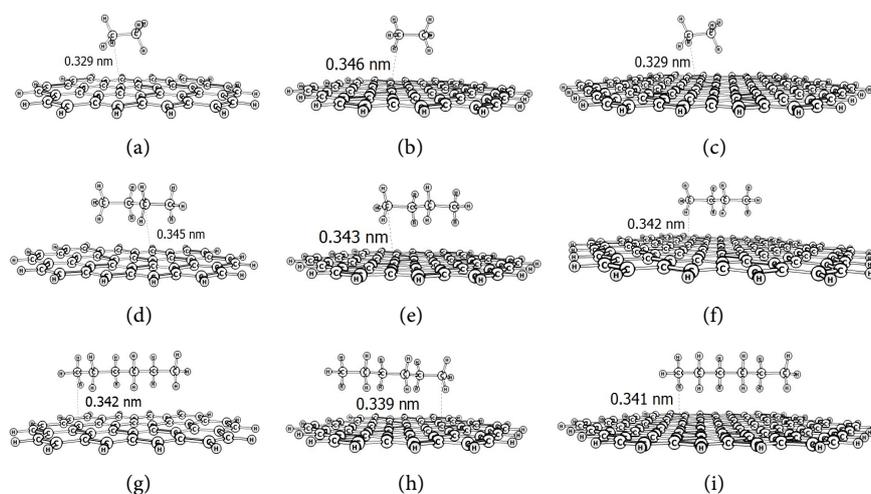


Figure 3. The structure of different length of PE fragments in intermolecular complexes with graphene-like clusters of different sizes, modeling a fragment of the outer surface of CNT.

The energy of the intermolecular interaction between the PE monomer and the $C_{54}H_{18}$ cluster is 30.0 kJ/mol, which is 1.5 kJ/mol less than the value for the complex with the $C_{40}H_{16}$ cluster. For dimer, this value is -56.4 kJ/mol, that is, the energy per polymeric link is slightly smaller than the value for the monomer (-28.2 kJ/mol).

When using as a fragment of the outer surface of CNT as a graphene-like cluster of $C_{96}H_{24}$ composition, there is no similar tendency in shortening the distance compared to the length of the oligomeric chain in previous case with the $C_{54}H_{18}$ cluster. For PE monomer complex the intermolecular distance is the smallest (0.329 nm), and is similar to that in the complex monomer of PE with $C_{40}H_{16}$, unlike that for the complex with dimer. The energies of intermolecular interaction are 33.0, 57.4 and 81.3 kJ/mol, correspondingly for monomer, dimer and trimer (**Table 1**).

Comparing the distances between the carbon atoms for the complexes between two identical oligomers (**Figure 2**) and the distance between the graphene planes and the carbon atoms of PE fragments (**Figure 3**), it is seen that, regardless of the size of the graphene cluster, this distance is approximately 0.05 nm smaller than similar value for the complexes consisting of two fragments of PE.

3.3. Interaction of the Fragments of CNT with PP Oligomers

In the study of the interaction of PP oligomers with fragments of the outer surface of CNT, the same three graphene-like clusters were used, as for oligomers of PE with CNT. These intermolecular complexes are depicted in **Figure 4**.

For complexes of PP monomer with graphene-like clusters of different sizes the distance between the carbon atoms of the monomer and the graphene-like plane almost does not change, in contrast to the similar value for the complex with PE, and make up 0.340 nm. This is probably due to the larger size of the

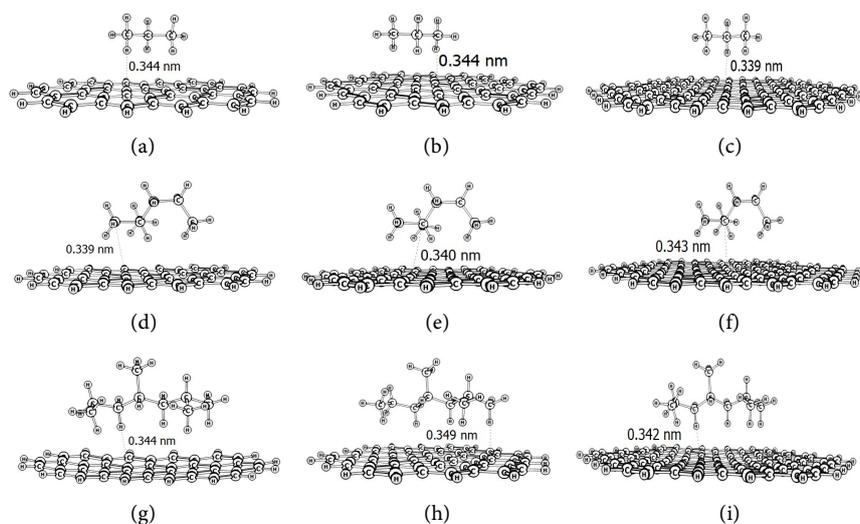


Figure 4. The structure of different length PP fragments in intermolecular complexes with graphene-like clusters of different sizes, which simulate a fragment of the outer surface of CNT.

monomer of PP compared with PE. The energy of the intermolecular interaction for the monomer with the smallest carbon cluster ($C_{40}H_{16}$) is -41.3 kJ/mol. Increasing the size of the cluster to $C_{54}H_{18}$ results in an increase in the energy of the interaction, which in this case has a value of -45.0 kJ/mol, and a further increase in the size of the graphene-like plane to $C_{96}H_{24}$ increases to -46.3 kJ/mol.

Considering the interaction of graphene-like clusters of different sizes with a two-link PP oligomer, it can be seen that increasing the size of the carbon cluster increases the intermolecular distance from 0.339 nm for the $C_{40}H_{16}$ cluster, 0.340 nm for $C_{54}H_{18}$ and 0.343 nm for $C_{96}H_{24}$. This distance is almost the same as for a complex with a monomer.

The energy of intermolecular interaction for a complex with the smallest graphene-like cluster and dimer is -66.4 kJ/mol, and for the dimer oligomer of PP with a larger cluster ($C_{54}H_{18}$), the interaction energy is -69.3 kJ/mol. The energy of the interaction of dimer with a graphene-like cluster of maximum size $C_{96}H_{24}$ has an even greater absolute value of -71.0 kJ/mol.

With an increase in the size of the graphene-like cluster up to $C_{54}H_{18}$ for a complex with a trimer, the binding energy of 1.6 kJ/mol is greater than that for trimer and $C_{40}H_{16}$ (-89.2 kJ/mol), which is not consistent with the fact of increasing the intermolecular distance in these complexes (see **Figure 4(g)** and **Figure 4(h)**).

Using the maximum size of the $C_{96}H_{24}$ cluster in the intermolecular complex with the trimer slightly increases the energy of the intermolecular interaction (-92.1 kJ/mol) compared with those for smaller clusters ($C_{40}H_{16}$ and $C_{54}H_{18}$).

The summary **Table 1** shows the numerical values of intermolecular binding energy between two identical oligomers for PE and PP, as well as for their complexes with graphene-like clusters of different sizes.

To illustrate the dependence of the binding energy on the size of the graphene-like cluster and on the number of polymeric units for PE and PP, graphic dependences were constructed shown in **Figure 5**. It can be seen that average energies of interaction attributable to single C-atom in nanocomposites are maximal for monomer fragments of polymers and cluster $C_{40}H_{16}$, which simulates the outer surface of CNT.

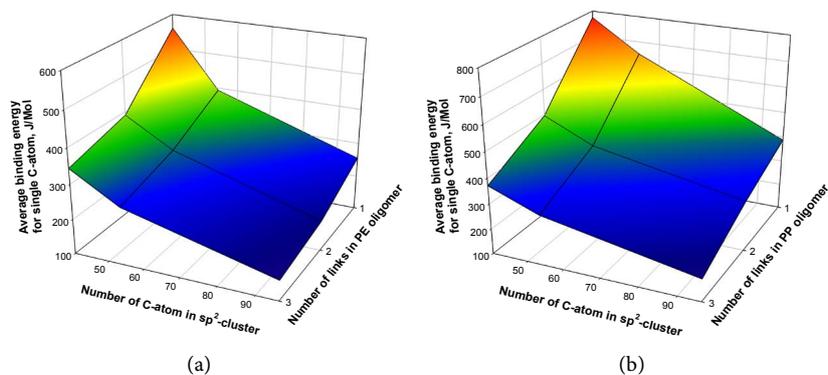


Figure 5. The dependence of average binding energy attributable to one atom of nanocomposite with various sp^2 -cluster of CNT and PE (a) and PP (b) oligomer fragments.

Comparing obtained data it can be seen that irrespective of the size of the graphene-like clusters, the intermolecular interaction between the graphene-like cluster and the fragments of PE and PP is greater than those for the pair of these fragments with each other. Consequently, it can be argued that the introduction of CNT into PE or PP has to increase the strength and melting point of the resulting nanocomposites compared to pure polymers, which is confirmed by experimental data [5] [6].

It can be also seen that for pure polymers and for their nanocomposites (polymer-CNT), the energy of intermolecular interaction is greater for PP than for PE.

4. Conclusions

1) According to the results of simulation, due to addition of CNT to PE and PP, the energy of intermolecular polymer-CNT interaction increases, what is consistent with the increase in the melting temperature of obtained nanocomposites. The energy of intermolecular interaction for polymer-CNT complexes is greater by 18.9 kJ/mol for PE, and by 22.5 kJ/mol for PP, as compared to those of pure polymers.

2) The fragment of polymer with an outer surface of CNT forms an intermolecular complex not bound covalently and retained by intermolecular dispersion forces. Oligomers of polymeric matters and nanotube surfaces in nanocomposites formed are placed closer to each other than separate polymeric links between them.

3) The magnitude of the energy of interaction between CNT fragment and PP oligomers is much greater than that of PE, which is consistent with experimental data on greater strength and thermal stability of PP-based nanocomposite than on PE-based ones.

Conflicts of Interest

The authors declare no conflict of interest.

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