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COMPUTATIONAL MODELLING OF POLYMERS

by

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Polymeric materials and polymer/graphite composites show a very diverse range of material properties, many of which make them attractive candidates for a variety of high-performance engineering applications. Their properties are ultimately determined largely by their chemical structure, and the conditions under which they are processed. There are a great many variables involved.

It would be desirable to start with engineering specifications of material performance, and determine which of an infinite number of possible polymers would be best suited, and what processing methods should be employed. Unfortunately, the state of the art is not yet up to this point. Instead, polymer design is guided in large part by the intuitions of chemists and materials engineers, who must then synthesize candidate polymers, process them into material samples, and test the samples to see if they indeed have the desired properties. This method has some severe drawbacks: It is time-consuming, it is expensive, and it produces a great amount of chemical material that must somehow be disposed of.

It is the aim of computational chemistry to be able to simulate candidate polymers on a computer, and determine what their likely material properties will be. Generally, this involves simulations conducted at the level of atoms and molecules, from which one expects to obtain the properties of a macroscopic sample of the material. Some progress has been made toward this end over the last 15 years, and has been focussed on polymers and proteins, or biopolymers. However, there are a great many difficulties that have been encountered, and wildly inaccurate results are often the subtle consequences of assumptions that are made in order to cut a given problem down to a computable size. Thus, given a polymer system one is interested in, one must examine such factors to ensure that one's computed material properties are not dominated by artifact of the modelling process, by making a critical evaluation of the suitability of a chosen modelling method to the particular problem in hand.

A number of commercially available software packages purport to predict the material properties of samples, given the chemical structures of their constituent molecules. One such system, *Cerius*, produced by Cambridge Molecular Design, of Cambridge, England, has been in use at Langley Research Center. It is comprised of a number of modules, each of which performs a different kind of calculation on a molecule in the program's "workspace" We were particularly interested to evaluate the suitability of this program to aid in the study of microcrystalline polymeric materials.

One of the first model systems we examined was benzophenone (**1**), for which excellent crystallographic data on the molecular geometry in the crystalline state are available. We turned out to be up against the following difficulty: One module of *Cerius* performs a semiempirical quantum calculation, to determine the energy-optimized geometry of a *single* molecule (often referred to as a gas-state geometry, since there is no influence from other molecules). The optimized geometry was fairly close to the crystallographic geometry, and the small difference was acceptable, since the potential energy surface with respect to internal bond rotations is quite flat around this minimum. In order to determine the crystal packing of the molecule, one must freeze the internal molecular conformation, and adjust the lattice type, symmetry space-group, and lattice parameters to minimize the energy. In this program, this energy is computed from the sum of Lennard-Jones (6-12) potential energy functions, pairwise over the atoms, and, even though the electrostatic partial charges for each of the atoms is calculated for the gas-phase geometry, coulombic intermolecular interactions are negleced. Even specifying the space-group revealed by the crystallographic data, and some of the lattice parameters, this program did not give reasonable values for the remaining parameters. If different lattice types and different space-groups were specified, the energies were seen to be greater or less than that calculated for the *known* structure of the crystal. Thus, as far as this program is concerned, the known structure is not the minimum energy configuration. This raises serious questions as to the usefulness of this program in its current state to correctly calculate the energetics (and hence material and thermal properties) of candidate crystal structures, and thereby predict the crystalline structure of a novel polymer molecule which is, after all, much more complex than benzophenone.

Furthermore, it is uncommon to have a crystal of a polymeric material. Instead, we are interested in the behavior of materials which consist of microcrystallites embedded in an amorphous phase. Since the crystallites are very small, they are probably not well-modelled by this program, since this program assumes a crystal of infinite extent in at least one dimension.

Other difficulties encountered with this program include the fact that its interface to the semiempirical quantum calculation does not currently permit the user to control enough of the calculation to make it worthwhile. We have been in contact with Cambridge Molecular Design, and they are in the process of adopting a number of our suggestions in this regard.

Finally, over the period of this fellowship, some critical examinations were made into some of the theoretical underpinnings of calculations directed toward the prediction of the physical properties of polymeric materials. As a result of this process, the groundwork for a new approach was laid out and formalized into a proposal for funded research. We hope to soon be in a position to implement and demonstrate the utility of this new approach to explore the formation of microcrystalline domains in samples of high-performance polymers of interest to NASA.