Chapter

6. Conclusions and Future Work

The research summarized in this dissertation has detailed the development of a methodology which facilitates prediction of material properties of a polymer based only on knowledge of its environmental history and initial properties. This prediction is predicated upon a parameter which describes the degree of environmental exposure, τ, that is defined as the product of the rate at which the degradation occurs and the time the polymer is exposed to this environment. This study shows that mathematical relationships can be developed relating τ to molecular weight distribution and then to properties of interest and allowing calculation of this parameter for any degree of exposure.

The methodology introduced in this thesis specifically addresses the thermally initiated degradation of bisphenol A polycarbonate in a nitrogen environment. For this case, τ corresponds to the degree of degradation of the sample and is a product of the kinetic first order rate constant of thermal degradation and the time of degradation. The kinetic rate constant was found through the use of thermogravimetric analysis where samples were degraded for specific times at certain temperatures. Molecular weight distribution changes were measured by gel permeation chromatography, and then related to τ. Other properties of interest in this study included tensile strength, melt viscosity, and glass transition temperature. A relationship between each of these parameters and τ was developed. In addition, master curves were prepared for both molecular weight distribution and melt viscosity such that these quantities could also be predicted based only on knowledge of τ and the initial properties of the polymer. One other area of investigation concerned an attempt to determine the chemical mechanisms responsible for the degradation. Data were obtained in an effort to support one of the theories currently espoused in the literature for this degradation. However, the results were inconclusive, and the exact chemistry involved in the process is still in question.

Future work applying this methodology to the thermal degradation of polycarbonate may focus on improving the predictive tools for the properties investigated with a goal of more accurate representation of the material performance. Particular areas for improvement include the master curves developed for both molecular weight distribution and melt viscosity, as well as tensile strength predictions. Further study of the chemical mechanisms of the degradation, using more sophisticated techniques, might also be pursued. Knowledge of the mechanism may allow more accurate ascertainment of the kinetic rate constant through changes in chain lengths instead of the indirect method of TGA utilized in this dissertation.

While the present methodology was developed for the specific case of thermal degradation, it is important to note that the technique is general to other material systems and other degradation modes. For example, this analytical scheme could be utilized to describe the mechanical degradation of ultra high molecular weight polyethylene (UHMWPE), such as that encountered in total knee joint replacements. In fact, this technique should describe property changes accompanying any degradation, whether chemical, mechanical, thermal, or radiation-induced, as long as the kinetics of the degradation can be mathematically modeled.

Caution should be used when applying this methodology to new systems. For example, in systems where crosslinking may be occurring during the degradation, such as with polyesters, one would expect the kinetic rate constant to have a negative value which would in turn lead to a negative τ. Predictive models for such a system would have to account for this negative value in order to provide accurate representations of the data. In an even more complex system where simultaneous scission and crosslinking is taking place, the kinetics may be very difficult to adequately describe, and so this methodology may not be applicable. Another issue which may complicate property prediction is changes in crystallinity as may occur in polyethylene. Certain properties, such as tensile strength, are known to depend on the level of crystallinity present in the sample, so the model would not only have to account for changes in molecular weight but also in crystalline content. Clearly, the more complex the degradation, the more care should be taken when attempting to apply this methodology since these situations are often difficult to understand or model.

Future work with this technique may more closely examine its application to various modes of degradation such as chemical or radiation induced degradation. Furthermore, while only a few material parameters were predicted in the present study, the approach should be applicable to any property which is dependent on molecular weight. Future research, then, may address the changes in density or impact properties which accompany environmental exposure. With such a broad range of situations where the methodology could apply, one can imagine a multitude of unexplored areas that may be of interest to future researchers.

By allowing a researcher to calculate a value for a given property merely from information regarding the environmental history, the power of this technique is immense. Such a technique may have applications in such diverse areas as accelerated aging and predicting the useful service lives of parts leading to fewer device failures and more efficient use of existing materials.