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THE OBSERVATION OF MOLECULAR BOND RUPTURE DURING FRACTURE IN POLYMERS

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1. INTRODUCTION

ONE of the central themes in the development of materials science has been the search for atomistic models from which the macroscopic material strength can be inferred. It can be argued that an understanding of the molecular and supermolecular mechanisms underlying fracture can lead to advances in our ability to predict failure and even to develop materials more resistant to failure. Since the macroscopic strength of essentially all materials is orders of magnitude less than that calculated from a theoretical consideration of atomic bond strengths, it follows that these atomistic theories must be rather complex; they must in some way account for the defect structure of the material. As will be discussed in some detail, these analyses generally hypothesize the molecular mechanisms and then bring the theory into line with experimental fracture data by a "suitable" choice of the several constants in the formulae. Such agreement with experiments, however, may well be a fortuity arising from the number of constants to be selected; one really needs some means of observing experimentally the molecular mechanisms on which the model is based. Until recently, experimental techniques capable of providing this information were lacking, forcing one to rely on little more than educated intuition when hypothesizing the elemental molecular fracture processes.

In polymer materials one would expect the formation of two free radicals (unpaired electrons) upon homolytic scission of covalent backbone bonds. If formed in sufficient quantity these free radicals can be detected by electron paramagnetic resonance (EPR) spectroscopy. The use of EPR in the study of free radical chemistry is well known(1–3) and Campbell has published a review of EPR studies specifically of polymeric systems.(4) However, its application to polymer fracture is much more recent. Zhurkov(5–7) and his colleagues at the Ioffe Technical Institute, Leningrad, Russia, published the first such work and have continued as very active pioneers in the field. Since then EPR-fracture work has been reported in the United States by DeVries *et al.*(8) and Peterlin and Campbell(9) and in Germany by Kausch, Becht, and Fischer,(10–11) while some review articles on certain facets of the work have also appeared.(4,12–14)

Although EPR has proved to be an extremely powerful tool in polymer fracture studies, it does suffer from certain inherent limitations. This present review discusses these limitations in some detail, outlines means of reducing or working around them, and presents some of the many successful studies which have been completed.