A Composite Methodology for Multistage Degradation of Polymers

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SYNOPSIS

Five different analytical schemes for examining isothermal and nonisothermal degradation of polymers were reviewed and found inadequate for describing multistage decomposition. The different schemes were experimentally tested using thermogravimetric analysis data for an ethylene-vinyl acetate (EVA) copolymer, which exhibited a well-behaved two-step decomposition process in a nitrogen environment. Based on these experimental and analytical findings, a generalized methodology was developed capable of describing the exhibited complex decomposition behavior of polymers by combining two or more kinetic mechanisms in a series or parallel arrangement. This composite or combinational methodology thus extends established analytical schemes for describing complex decomposition of polymers in a rational manner, incorporating both experimental and theoretical considerations.

INTRODUCTION

Ethylene-vinyl acetate (EVA) copolymer is a model system by which degradation processes may be described using a thermogravimetric technique. EVA is also being considered as a matrix polymer in the manufacturing of ceramic polymer composite. For these systems, the debinding process of burning out the polymer is the rate-determining step. Characterization of the degradation kinetics of the binder polymer is one key issue that must be addressed in developing an optimum processing cycle. In this study, the degradation kinetics of EVA copolymer was investigated with several thermogravimetric analysis (TGA) kinetic models applicable to dynamic data.

Degradation mechanisms and their kinetics have been investigated extensively in the past for polyethylene (PE) and polyvinyl acetate (PVAc) systems. The degradation behavior of PE was recently reviewed by Davis and Mardosky. Davis reported that PE degrades by random scission or at weak links. Low-molecular weight product evolution was attributed to intermolecular or intramolecular free-radical transfer. Degradation of PE was found to be influenced by branching and molecular weight, as well as by the nature of polymer attributed to high-density or low-density PE. The activation energy of degradation has been reported in the range of 193–303 kJ/mol. Most recently Dickens reported activation energies of 262 ± 2 and 256 ± 3 kJ/mol for linear and branched PE by using the factor jump method.

For PVAc, it has been reported that initiation of thermal degradation takes place at the end of the polymer chain, resulting in a strong influence of the molecular weight on degradation rate. Barrales-Rienda, et al. reported the activation energies to be in the range of 145-184 kJ/mol based on an assumed autocatalytic reaction mechanism.

The degradation of the EVA block copolymer may be viewed as a composite degradation of each PE and PVAc block which results in a multistage weight loss. Accordingly, a series of dynamic TGA experiments were performed in order to elucidate this dual behavior and provide the data for modeling a multistage degradation process.

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