Degradation of polyacrylic elastomers: Theoretical and experimental studies

Tuhin Saha [a], Anil K. Bhowmick [a, *], Takeshi Oda [b], Toshiaki Miyauchi [b], Nobuhiko Fujii [c]

[a] Rubber Technology Centre, Indian Institute of Technology, Kharagpur, 721302, Kharagpur, West Bengal, India
[b] Polymer Research Department, Denka Company Limited, Chiba, 290-8588, Japan
[c] Elastomers Department, Denka Company Limited, Tokyo, 103-8338, Japan

ABSTRACT

A series of Reactive Force Field (ReaxFF) molecular dynamics simulation was performed on poly-acrylicester terpolymer for the first time to understand its thermal decomposition characteristics. The effects of time and temperature on the evolution of various products were analyzed. Alkyl radicals were discovered as dominant products at low temperature along with carbon dioxide. Additionally, alkenes were also detected in the final products at higher temperature. Other small molecular products including alkoxy radicals and carbon monoxide were also noticed in the end products. Evolution mechanisms of dominant products (alkyls and alkenes) were explored in detail based on the simulation approach. The fracture of ester linkage is the typical initiation step for the formation of alkyl radicals. The pathway for yielding alkenes mainly consists of the β-hydrogen elimination from the side chain ester groups. The products during the thermal decomposition processes of polyacrylicester predicted theoretically were in agreement with the experimental results from thermogravimetry coupled with fourier transform infrared spectroscopy (TGA-FTIR) and simultaneous thermal analysis coupled with gas chromatography and mass spectroscopy (STA-GC-MS). The apparent activation energy for thermal decomposition of polyacrylicester obtained from the ReaxFF simulation was also consistent with the experimental results.

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1. Introduction

Acrylic rubbers are mainly synthetic polymers, composed of acrylic acid alkylester (ethyl or butyl) and/or ethylene. Acrylic rubbers are mainly known for their high heat and outstanding hot oil resistance properties. Since they do not have unsaturation in their main chain backbone, they show good weatherability and ozone resistance. However, the current challenge is to improve the heat resistance of these elastomers further in view of the stringent application requirements. The thermal degradation of polyacrylates and their co-polymers has been investigated by many researchers in oxygen as well as in nitrogen atmosphere [1–10]. But for the first time, the degradation characteristics of a ter-polymer containing both ethylacrylate and butylacrylate units as the main constituents have been studied in this work. Also, a novel theoretical approach has been taken to understand the degradation phenomenon of acrylic elastomers by using molecular dynamics simulation (MDS).

Grassie et al. [1–3] investigated thermal degradation behaviour of several poly (alkylacrylates) by analysing both the liquid and gaseous products formed during pyrolysis of poly (alkylacrylates) using gas-liquid chromatography (GLC), mass spectrometry and infrared (IR) spectroscopy. They proposed the degradation mechanism via formation of tertiary hydrogen atom during the initial stage of decomposition.

Gunawan et al. [4] studied the pyrolysis of polymethyl acrylate and proposed the degradation mechanism initiated by random homolytic scission of the chains. Haken et al. [5] analyzed the pyrolysis of poly (n-butylacrylate) by gas chromatography-mass spectroscopy (GC-MS) and identified the major degradation products as carbon dioxide, 1-butene, monomer and saturated as well as unsaturated dimers.

Recently, Czech et al. [6–8] proposed that the degradation of poly (alkyl methacrylate) takes place via the production of mono-mer as a main degradation product. Özlem and Hacaloglu suggested that the degradation of both poly (n-butylacrylate) and poly (t-butylacrylate) takes place by β-hydrogen transfer fron the side chain butyl group via elimination of 1-butene and isobutylene respectively [9,10].

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* Corresponding author.
  E-mail address: anilkb@rtc.iitkgp.ernet.in (A.K. Bhowmick).

Almost all the previous workers had used analytical techniques such as thermogravimetry (TGA), pyrolysis gas chromatography-mass spectroscopy (GC-MS), thermogravimetry coupled with fourier transform infrared spectroscopy (TGA-FTIR) etc. TGA is a classical technique to study the weight loss of a polymer over a wide range of temperatures (30 °C–800 °C) and estimate the thermal degradation of polymers and also allow to calculate the degradation kinetics [11–16]. Kinetic parameters from TGA can be obtained by performing two different methods, isothermal and non-isothermal methods. Isothermal method is performed at constant temperature. On the other hand, non-isothermal method involves heating the material from low to high temperature at different heating rates. Several mathematical approximations are required to calculate the kinetic parameters by non-isothermal method. The approximation methods developed by Friedman [19], Flynn-Wall-Ozowa (FWO) [21,22] and Kissinger-Akahira-Sunosa (KAS) [24,25] are more frequently used. In this study, a comparison among these three methods has been done.

Degradation of polymer is always a complex method and without thorough computational methods, detail products formed

$$E_{system} = E_{bond} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{conj} + E_{tors} + E_{vdW} + E_{coulomb} \tag{1}$$

may not be identified. ReaxFF reactive force field method proposed by van Duin is an effective force field method for describing complicated chemical processes via bond breaking and bond formation [26–29]. Recently a few articles have been published in the area of polymers using ReaxFF force field technique to understand the pyrolysis mechanism of polymers subjected to high temperature heating. Stoliarov et al. [30,31] performed the pyrolysis simulation first on Poly (methyl methacrylate) and then on polyisobutylene to understand the degradation mechanism and the major degraded products. Recently, Diao et al. [32] applied the ReaxFF force field simulation on epoxy resin and acquired the detail chemical reactions involved. Lu et al. [33] carried out the molecular dynamics study based on the pyrolysis of polyimide and calculated the activation energy for pyrolysis.

In this present study, an acrylate type ter-polymer model consisting of randomly placed monomer units was built. Ten of the above model chains were placed in a cubic lattice and then subjected to degradation by molecular dynamics simulation to describe the thermal decomposition of the ter-polymer. Detailed study of the formation mechanism of dominant products was done with the help of ReaxFF MDSs. The results were correlated with the experimental data obtained from TGA-FTIR and simultaneous thermal analysis coupled with gas chromatography and mass spectroscopy (STA-GC-MS). Kinetic analysis of pyrolysis was also done at different high temperatures during the simulation. The results were then compared with those from the non-isothermal kinetics with the help of TGA analysis at different heating rates. The results obtained from this study can provide an in-depth recognition of complicated pyrolysis process of acrylic rubbers, which can be useful in industrial applications.

2. Experimental

2.1. Material

The elastomer used in this experiment is DENKA ER. It was kindly supplied by DENKA Company Limited, JAPAN. This was dissolved in methylethylketone (MEK) and the solution was then dried to obtain the purified rubber. The experimental work was performed on the purified raw elastomer or gum (and not on the vulcanized rubber). DENKA ER is designated as ACM. It is a terpolymer of ethylene and acrylate esters. The acrylate esters contained ethyl acrylate and *n*-butyl acrylate. The generalised structure of ACM is shown in Fig. 1.

2.2. ReaxFF reactive force field computational approach and simulation details

2.2.1. Overview of simulation

ReaxFF reactive force field concept, proposed by van Duin [26] in order to reproduce Quantum Mechanical energies for a variety of reactions, is based on bond order introduced by Tersoff [34]. ReaxFF reactive force field is an effective method for complicated chemical reactions and other complexed phenomena under drastic conditions.

The system energy function for ReaxFF is a function of various energy terms and is described as:

Here, E_{system} denotes the system energy and E_{bond} represents the bond energy. Other energy terms, such as E_{over}, E_{under}, E_{val}, E_{pen}, E_{conj}, E_{tors}, E_{vdW}, $E_{Coulomb}$ are over-coordination energy, under co-ordination energy, penalty energy, conjugation effects to molecular energy, torsion energy, non-bonded van der Waals interaction and Coulomb interaction respectively.

2.2.2. Model construction

ACM, a random terpolymer of ethylene and acrylic esters is a high molecular weight polymer containing numerous acrylic ester side groups. According to the molecular structure obtained from ¹H NMR study, which is discussed in the following section (Section 3.1.1), a single model chain consisting of 1 unit of ethylene, 6 units of ethyl acrylate and 3 units of *n*-butyl acrylate (ACM10) in a randomly placed orientation was built. To designate this acrylate based system, the "adf" package in Amsterdam density function (ADF) was used. The geometry and energy optimization packages in ADF were utilized to optimize the model shown in Fig. 2.

2.2.3. Simulation details

A total of ten ACM 10 polymeric chains were placed in a periodic box of 32 Å × 32 Å × 32 Å, giving an initial density of 0.514 g cm⁻³. The pictorial representation of the periodic box before and after optimization is shown in Fig. 3.

The pyrolysis simulation was performed on ten monomer units (decamers). To understand the degradation mechanism of high molecular weight polymers, pyrolysis simulation on a single model chain consisting of 20 monomer units (ACM20) and 30 monomer units (ACM30) respectively was also executed.

High simulation temperature would be of great help to facilitate sufficient collisions between molecules and would also help in detecting thermodynamically possible reactions at lower temperatures within acceptable picoseconds simulation. Although high temperature simulation may cause some uncertainty in degradation mechanism, it drastically reduces the simulation time. The