Thermochimica Acta 562 (2013) 11–21

Contents lists available at SciVerse ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Model free kinetics—Thermal degradation of bisphenol A based polybismaleimide–cloisite 15a nanocomposites

R. Surender[a,b], A. Mahendran[c], A. Thamaraichelvan[b], S. Alam[d], C.T. Vijayakumar[a,*]

[a] Department of Polymer Technology, Kamaraj College of Engineering and Technology, S.P.G.C. Nagar, K. Vellakulam Post 625 701, India
[b] Post Graduate and Research Department of Chemistry, Thiagarajar College, Madurai 625 009, India
[c] Wood Carinthian Competence Centre, Kompetenzzentrum Holz GmbH, Klagenfurterstrasse 87-89, A-9300 St. Veit an der Glan, Austria
[d] Defence Materials and Stores Research and Development Establishment (DMSRDE), G.T. Road, Kanpur 208 013, India

ARTICLE INFO

Article history:
Received 10 July 2012
Received in revised form 23 March 2013
Accepted 25 March 2013
Available online 1 April 2013

Keywords:
Bismaleimide
Cloisite 15a
Nanocomposites
TGA
Model free kinetics
TEM

ABSTRACT

Bismaleimide (2,2-bis[4-(4-maleimidophenoxy phenyl)]propane) is prepared, blended with cloisite 15a (1, 2, 3, 4, 5, 7 and 9 wt%) by ultrasonically and thermally polymerized. The FTIR studies reveal that the clay particles affect the maleimide ring and ether linkage of the polybismaleimide. Thermogravimetric studies of cured materials show that the incorporation of clay particles does not affect the degradation temperature values at low levels of clay loading. At higher loadings, the degradation temperature decreases compared to pure polybismaleimide. Degradation kinetics is performed using Vyazovkin and Friedman methods. At lower loadings of clays the apparent activation energy for thermal degradation is nearly constant ($\alpha = 0.1–0.8$) and at higher loadings the trend is similar to pure polybismaleimide, but the values are lower. This is due to the aggregation of nanoclays leading to microcomposites. The clay particles are well dispersed in the polybismaleimide matrix as evidenced by SEM and TEM studies of the nanocomposites.

1. Introduction

Inorganic/organic hybrid materials are used in the polymeric matrix systems to achieve unique properties. The materials have both the advantages of inorganic material (rigidity, high thermal stability) and the organic polymer (flexibility, dielectric, ductility and processability) and overcome the disadvantages of these two materials [1]. Only a small amount of these particles drastically enhances the properties of the polymer matrix. Nanoclays is one of the important filler used in the polymer matrix to improve the thermal stability of the polymer matrix systems. Of the different polyimides, bismaleimides are one of the addition polymers having excellent properties such as thermo-oxidative stability, high mechanical strength, high modulus, excellent chemical and corrosion resistance, hot-wet performance and electrical properties [2].

The technical and commercial importance of a polymer is in part based on the thermal stability of the material. Hence, kinetic analysis of the thermal degradation of polymeric materials plays an important role in assessing the reliability of the materials for high temperature applications. A thermal analysis method, mainly thermogravimetric method is extensively used to study the thermal degradation of the polymers. The kinetic parameters [activation energy (Ea), pre exponential factor (A) and reaction model (n)] of thermal degradation of polymers give an idea regarding the decomposition mechanism of the materials [3,4]. In the beginning, researchers are using single heating rate kinetic methods for evaluating the kinetic parameters of the materials and it gives only a single set of kinetic triplets [5]. The International Confederation of Thermal Analysis and Calorimetry project (ICTAC) 2000, ruled out the single heating rate process and suggests the multiple heating rate processes for evaluating the kinetic triplets [6].

Model fitting kinetic methods are used to determine the kinetic triplets using multiple heating rate programs and the kinetic triplet obtained from these methods for non-isothermal condition is highly uncertain and cannot be compared with the kinetics triplet obtained from isothermal condition [5,7]. Vyazovkin model free approach through use of isoconversion method leads to a trust worthy way of obtaining reliable and consistent kinetic information from non-isothermal data from DSC and TG studies. The variation of the activation energy with the extent of conversion helps to reveal the complexity of multiple reactions taking place during thermal degradation of materials [5,8–11].

In our previous investigations, different types of 3% weight of nanoclays are incorporated into the bismaleimide, 2,2-bis[4-(4-maleimidophenoxy phenyl)]propane and the curing and thermal stability of these materials was investigated. Among the clays,

* Corresponding author. Tel.: +91 94420 57674.
E-mail addresses: ctvijay22@yahoo.com, ctvijay22@gmail.com (C.T. Vijayakumar).

0040-6031/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tca.2013.03.037

cloisite 15a nanoclay reduces the curing exotherm window and imparts excellent thermal stability to the cured nanocomposite [12]. From these results, different weight levels (1, 2, 3, 4, 5, 7 and 9%) of cloisite 15a (C) were incorporated into the bismaleimide matrix system and the curing behavior of these materials were investigated by DSC and the apparent activation energy for the polymerization of these materials was obtained using three model free kinetic [Flynn–Wall–Ozawa (FWO), Vyazovkin (VYZ), Friedman (FRD)] methods. The added nanoclay particles influence the thermal curing behavior of the bismaleimide material and the variation in the trend of change in the apparent activation energy [13]. Hence in the present work it is intended to investigate the variation in the apparent activation energy for the thermal degradation of the thermally cured bisphenol A based bismaleimide having different loading of nanoclay (cloisite 15a). The two model free kinetic methods (VYZ and FRD) are used to evaluate the apparent activation energies and the results are presented and discussed.

2. Experimental

2.1. Preparation of bismaleimide (BMIX)

The synthetic procedure (Scheme 1) for the preparation of bismaleimide, 2,2-bis[4-(4-maleimidophenoxy phenyl)]propane, is already presented in detail in the previous work [12].

2.2. Organoclay, cloisite 15a

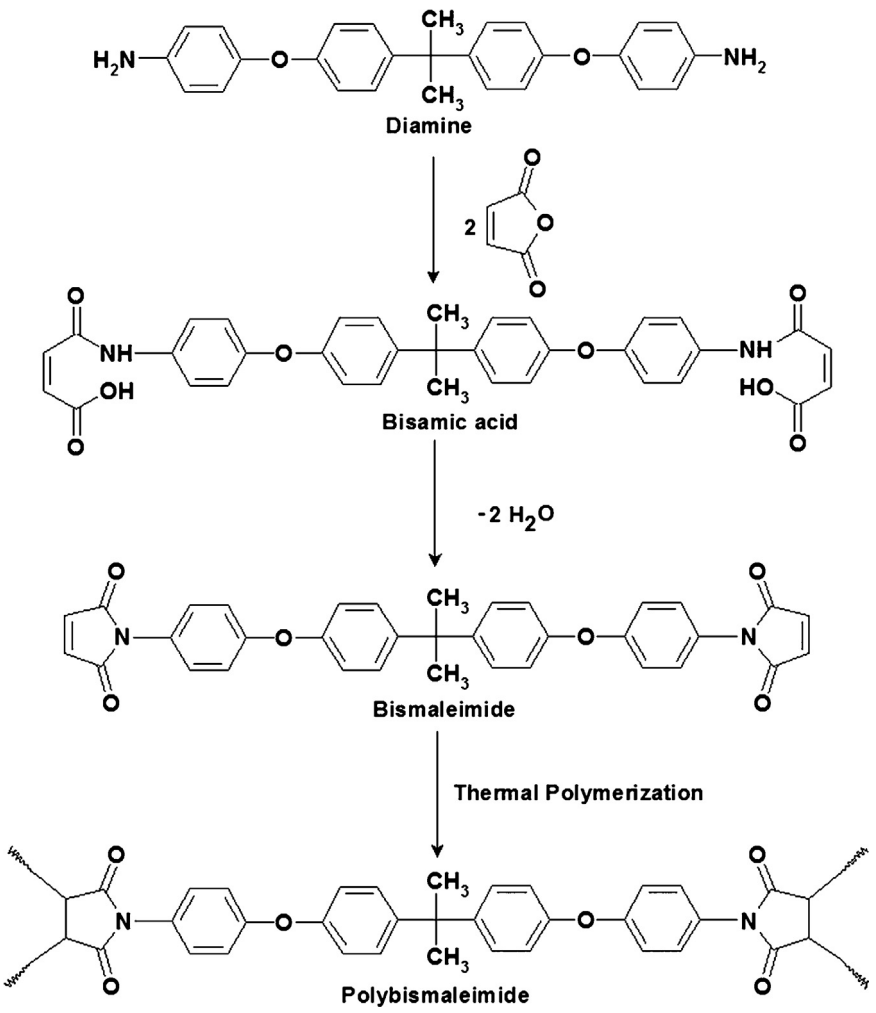
Cloisite 15a is an organically modified montmorillonite system in which the clay layers are modified with dimethyldihydrogenated tallow quaternary ammonium salt. The hydrogenated tallow consists of about 65% C18, about 30% C16, and about 5% C14. It should be mentioned that 100% of Na^+ ions in natural montmorillonite have been exchanged [14]. The *d*-spacing of the montmorillonite clay is around 10 Å without any water layers [15] and is around 31.5 Å for the Cloisite 15a clay layers [16]. Cloisite 15a was supplied by Southern Clay Products, Inc., Gonzales, Texas, USA.

2.3. Blending of organoclay with bismaleimide (BMIX)

Organo clay, cloisite 15a was dried at 110 °C for 24 h in a hot air oven. Different weight ratios (1, 2, 3, 4, 5, 7 and 9%) of dry cloisite 15a nanoclay was mixed with bismaleimide dissolved in minimum quantities of acetone. The solutions were sonicated for 6 h and then the solvent was evaporated in vacuum and the dry blended materials were stored in a desiccator for further work [13].

2.4. Thermal curing

The pure bismaleimide and its cloisite 15a blends were taken in separate micro test tubes and flushed with dry oxygen-free nitrogen (Scheme 1). The materials were thermally polymerized at



Scheme 1. Preparation and polymerization of BMIX.