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Kinetics of the thermally induced precursor curing to polymer via statistical analysis of TEM images

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Abstract

Thermally induced curing of the precursor to the cross-linked polymer was studied with transmission electron microscopy. The cured polymer was observed to have micro-domain morphology. Analysis of the microscopic images resulted in the statistical size distributions of micro-domains described subsequently using principles of irreversible thermodynamics. The statistical distribution parameters were determined to change with the curing temperature. A correlation of micro-structural and macroscopic parameters (the mean size of micro-domains and the dynamic Young's modulus), both varying during the precursor curing, was found and explained in terms of the kinetic concept of fracture.

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Keywords: TEM/STEM; Microstructure; Polymers and organics

1. Introduction

The curing is a process of deliberately cross-linking a low molecular weight precursor (e.g., liquid oligomer) to a hard and stiff polymer [1]. The term is practically referred to the cross-linking of unsaturated polyester [2] and epoxy resins [3], which used in many industrial applications, especially as matrices in reinforced composites. Recent investigations have been paid to create novel precursor compositions exhibiting improved properties after their curing. One of such a composition is known as the Rolivsan [4].

Of course, any changes in the chemical structure of a precursor during its transformation to a cured polymer cause variation of its morphology. It has long been realized that morphology is a key to understanding material properties. At the moment, microscopic techniques seem to reveal detailed micro-structure of a sample very carefully. Yet, *quantitative* interpretation of microscopic images is not always easy though many useful mathematical procedures for the image analysis have been elaborated and a qualitative correlation of material properties and parameters of mathematical morphology have been established [5].

The goals of the work are: (i) identification and size evaluation of the morphological entities in the Rolivsan precursor during its conversion to the polymer, polyrolivsan (PR), under heating; (ii) description of statistical size distributions of the morphological entities using principles of irreversible thermodynamics; (iii) analysis of the distribution parameters as a function of the curing temperature; and (iv) finding a correlation of micro-structural and macroscopic parameters varying during the precursor curing.

2. Experimental

The Rolivsan is a liquid precursor mixture containing the monomers M_1 (14%), M_2 (27%), and M_3 (25%); the oligomer Ol (32%); and an antioxidant (2%). Chemical structures of the precursor components are presented below:

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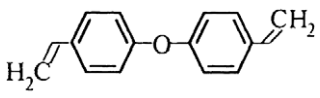
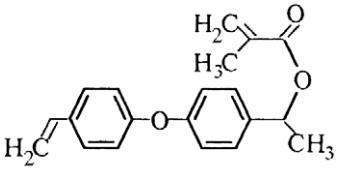
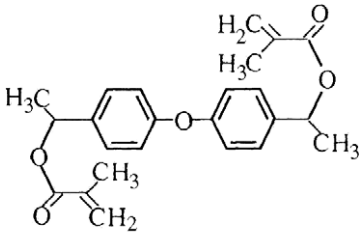


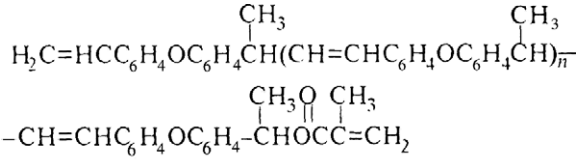
M_1



M_2

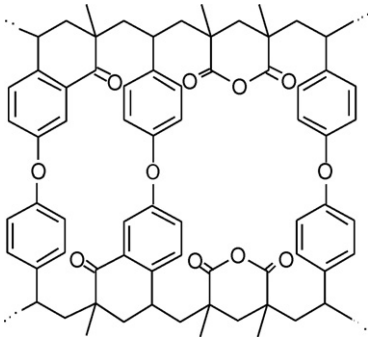


M_3



Ol

Being thermally cured, the Rolivsan precursor transforms to the thermally stable cross-linked polymer, PR. The primary polymer network obtained at 150 °C is converted upon further heating (⩾170 °C) to the final network. Its chemical structure can be presented as follows [4]:



Samples for studies were prepared by pouring of the liquid Rolivsan mixture into $50 \times 50 \times 10$ mm metallic/Teflon molds, followed by increasing heating at a rate of 5 °C min^{-1} to the final curing temperature T_c in the regimes: 150/5, 160/5, 170/5, 180/4, 200/4, and 250/4 °C/h. All the samples were solidified during their curing and consequently were subjected to transmission electron microscopy (TEM) analysis.

Before investigation with TEM technique, the samples were cleaved in liquid nitrogen and then were replicated: first, by a platinum (Pt) steam and, second, by vacuum evaporation from a carbon (C) arc. The final Pt–C replicas were detached from the surface with an aqueous solution of polyacrylic acid, which was subsequently removed by putting the replicas in distilled water. Afterwards, the Pt–C replicas in the form of thin films (30–40 μm) were deposited onto a copper grid, dried and examined with a Tesla BS-500 transmission electron microscope at the 20 000× magnification. The TEM images were then digitally analyzed using the Imagetool 3.0 software (Health Science Center, University of Texas, San Antonio, USA) to determine statistical size distribution of the morphological entities. The number of entities amounts from 600 to 4500 per each image ensuring good statistical representation. Afterwards, statistical distributions were described using the model of reversible aggregation.

The dynamic Young's modulus of the PR samples in the form of $34 \times 20 \times 8$ mm parallelepipeds was measured using a Metravib viscoelasticimeter, JLD Instruments, at 20 °C and at a frequency of 72 Hz.

3. Model

Based on principles of irreversible thermodynamics, the model of reversible aggregation gives a general characterization of micro-structure in different systems [6–8]. According to the model, stationary micro-structures are created by linking the energy-equivalent dynamic units in metastable clusters called aggregates. Aggregates are characterized by a definite lifetime, i.e., they are permanently formed and decomposed; this is a condition of the aggregates reversibility. In the liquid state, the configuration of aggregate ensembles continually fluctuates and after solidification, one of many possible, thermodynamically equivalent, configurations can be recognized. In the framework of the model, the statistical distribution function $h(y)$ is written as [6–8]

$$h(y) = ay^p \exp\left(-\frac{\Delta u}{kT}\right), \tag{1}$$

where y is the aggregate size, a is a normalizing parameter, p is the entropy factor related to the shape of the entities analyzed, Δu is the aggregate energy, k is the Boltzmann constant, and T is the absolute temperature. Eq. (1) can be interpreted as the probability density of a thermodynamic phase, i.e., as a Gibbs distribution [9]. Taking into account the dependence of the aggregate energy Δu on the aggregate size y ($\Delta u = y\,\Delta u_0$; Δu_0 is the standard aggregation energy) and existence of the embryonic aggregate with the size y_0, Eq. (1) becomes [8]