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Hansen solubility parameters of polyglycolic acid and interaction parameters between polyglycolic acid and solvents

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ABSTRACT

This article focuses on the solubility parameters and interaction parameters of polyglycolic acid. 43 solvents have been used for polyglycolic acid to study the dissolution property. Then the Hansen three-dimensional solubility parameters and total parameter of polyglycolic acid were obtained by an optimization calculation. The values of δ_d, δ_p, δ_h and δ for polyglycolic acid have been obtained as 17.094 $(J/cm^3)^{1/2}$, 8.206 $(J/cm^3)^{1/2}$, 7.912 $(J/cm^3)^{1/2}$ and 20.546 $(J/cm^3)^{1/2}$. It was proved that the total parameter of polyglycolic acid is creditable by intrinsic viscosity approach and group contribution method. The values of the interaction parameter and the solubility parameter "distance" between polyglycolic acid and 43 solvents have been calculated. The results of the interaction parameters accords well with the standard of complete miscibility suggested by Flory–Huggins for polymers and solvents.

1. Introduction

Polyglycolic acid (PGA) was first manufactured as a synthetic absorbable suture material, and its success has led to development for other medical applications such as controlled drug release systems, orthopedic fixation and scaffolds [1,2]. In addition, PGA can also be used for beverage packaging material, as a composite container for packing beer, as a single (multi) layer of soft packaging material, and as agricultural biological degradable film, etc. [3]. Either application to medicine or application to industry and agriculture, the solubility or compatibility of PGA with other materials are always involved, that is, the interaction between PGA and other molecules will be touched on. As is known to all, solubility parameter can describe quantitatively the interaction between polymer molecules and other molecules. Therefore, it is necessary to study solubility parameter of PGA. However, to the best of our knowledge, there are very few reports on this investigation for PGA. In literature, only Abhishek et al. researched solubility parameter of PGA [4]. Abhishek et al. estimated the solubility parameters of PGA using intrinsic viscosity method, classical geometric method and group contribution and proposed an optimization method to obtain the Hansen solubility parameters of PGA.

However, the optimization method proposed by Abhishek et al. is very complicated. It contains many vectors functions, matrices functions and scalar functions. The calculation process is too incomprehensible to be convenient for application. Furthermore, Abhishek et al. used only eight solvents (three solvents and five nonsolvents) for PGA. The number of solvents is so small that the results obtained are not representative.

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In this study we measured Hansen solubility parameters of PGA experimentally using 43 solvents. Due to large amount of work, this measurement has not been explored yet. The aim is to acquire more accurate results. Simultaneously, we proposed a simple optimization method to determine the Hansen solubility parameters and compared them with those obtained by other methods.

The concept of a solubility parameter was first presented by Hildebrand. He considered that in a system where the dispersion forces were predominant, the solvent could dissolve the polymer when their parameters were close. However, the molecule polar as well as the hydrogen bonding interaction between the polymer and the solvent must be considered in the solutions of polar polymer–solvent system. In order to predict the miscibility of various polymer–solvent systems, various modifications have been made for the method of solubility parameter. It is the method of Hansen three-dimensional solubility parameters that are recognized widely at present. Hansen divided the total solubility parameter δ into three values – δ_d, δ_p and δ_h, where δ_d, δ_p and δ_h are the contributions of dispersion forces, dipolar forces and hydrogen bonding, respectively. δ can be calculated by $\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$. Only when the three-dimensional solubility parameters of the polymer and the solvent are all close, can the solvent dissolve the polymer. The objective of this work is to determine the three-dimensional solubility parameters for PGA precisely.

Total solubility parameters of solvents can be obtained from the definition $\delta = (\Delta E/V_m)^{1/2}$ by the energy of vaporization ΔE and the molar volume V_m. Since polymers cannot vaporize normally, total solubility parameters of polymers cannot be acquired by the definition. Their values of three-dimensional and total solubility parameters should be acquired by experiments.

The traditional experimental method to determine the three-dimensional solubility parameters of a polymer is as follows. First, a polymer is dissolved in various solvents under a certain concentration; second, the solvents are divided into good and bad solvents and the solubility parameters of the polymer are calculated using the solubility parameters of the good solvents.

2. Experimental

2.1. Materials

Triethylamine (99.5%), ethyl acetate (99.5%), anhydrous ethyl alcohol (99.7%) and chloroacetic acid (99.0%) were made by the Tianjin Kemiou Chemical Reagent Company (Tianjin, China). The other chemicals were purchased from Sun Chemical & Technology (Shanghai) Company Limited. All the chemicals are of analytical grade and used as received without further purification.

2.2. Synthesis of PGA

The synthesis method has been described in our earlier work [5]. Chloroacetic acid was dissolved in ethyl acetate. Triethylamine was added to the solution. The solution was refluxed with stirring for a period of time. Ethyl acetate was then distilled from the reaction mixture. After all solvent had been removed, the product mixture was obtained. From the product mixture, the byproducts were removed by washing with absolute ethanol. The residue insoluble polymer was PGA. The PGA was dried to constant weight at 60 °C.

2.3. Solubility test

The solubility tests were carried out in 43 organic solvents in order to classify them as good (one-phase systems) or bad (two-phase systems) solvents. The procedure was as follows: 0.1 g of PGA was placed in a glass bottle with 4.9 g of the test solvent [6]. The glass bottle was sealed with a suitable stopper to prevent solvent evaporation. Taking into account the dissolution equilibrium, the sealed solution was allowed to stand for three days at room temperature. The solutions were shaken for a certain time. In the case of solvent in which the solute did not appear to dissolve at room temperature, heat was applied and then cooled to room temperature [6,7]. The heating temperature was below the boiling point of the corresponding solvent. The solubility behavior of PGA was observed by a visual inspection and was judged as soluble or insoluble. Then each solvent was characterized as a bad or good solvent.

2.4. Intrinsic viscosity measurement

The relationship between molecular weight (M) and intrinsic viscosity ($[\eta]$) of PGA can be described by Mark–Houwink equation, $[\eta] = \beta M^{\alpha}$. $[\eta]$ measurements were performed with an Ubbelohde viscometer at 25 °C. The intrinsic viscosity of each sample was calculated according to the Solomon–Ciuta equation of a single point measurement [8]:

$$[\eta] = \frac{\sqrt{2\left(\frac{t}{t_0} - 1 - \ln\frac{t}{t_0}\right)}}{C} \tag{1}$$

where C is concentration of the solution; t is flow time of solution, t_0 is flow time of pure solvent.