STUDY ON THE FUNCTIONALIZED GRAPHENE MODIFIED WATERBORNE POLYURETHANE MATERIALS

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A new type of waterborne polyurethane (WPG) is fabricated using the functionalized graphene. The mechanical properties, wear resistance, and heat aging resistance of the modified polyurethane materials were tested. The results show that the initial thermal decomposition temperature (Td5) of polyurethane films increased from 217°C to 244°C, the mechanical property of modified polyurethane film firstly decreases and then increases with the increase of functionalized graphene. In addition, the wear resistance of modified polyurethane film decreases following the increase of functionalized graphene. Furthermore, the heat aging resistance is best when the content of functionalized graphene is 0.02% (wt). The centrifugal stability test shows when the content is less than 0.04%, the products are stable.

Keywords: waterborne polyurethane; functionalized graphene; heat resistance

INTRODUCTION

Graphene oxide is a functionalized graphene attained through the oxidation of graphite. The functional group just replaces few carbon atoms, meanwhile not destroying the crystalline cells of the whole graphene. Accordingly, graphene oxide still retains the crystalline characteristics of graphene. In the meantime, graphene oxide sheets contain extensive amounts of oxygen (hydroxyl, epoxy, glycol, ketone and carboxyl functional groups), which are capable of changing the van der Waals forces of their interaction, bringing to them enhanced compatibility with the organic polymers. At the edge of the sheet, there are also some carbonyl and carboxyl groups, making the graphene oxide sheets more hydrophilic, which make them more convenient to disperse in some solvents (Hou *et al.*, 2015; Yang *et al.*, 2016).

In the current paper, functionalized graphene modified polyurethane is employed for the preparation of high physical materials, which are capable of enhancing not only the heat resistance, but also the water resistance and aging resistance of waterborne polyurethane, in addition to improving the overall performance of materials. It is considered as quite helpful for developing the environment-friendly and high-performance composite materials.

MATERIAL AND METHODS

Materials

Graphene oxide (GO), prepared in the laboratory with the use of the Hummers method; Isophorone diisocyanate (IPDI), industrial grade, Bayer China Ltd.; Stannous octoate catalyst (T-9), industrial grade, Jining Huakai Resin Co., Ltd.; Polypropylene

glycol (PPG-2000), industrial grade (110 °C vacuum dewatering 2h), Jiangsu Hai'an Petrochemical Plant; 2,2-Dimethylolpropionic acid (DMPA), industrial grade, Jiangxi Southwest City Hongdu Chemical Technology Development Co., Ltd.; 1,4-butanediol (BDO), analytically pure, Komio reagent; Triethylamine (TEA), analytical grade, Tianjin Hengxing Chemical Reagent Manufacturing Co., Ltd.; Acetone, analytical grade, Beijing Chemical Plant; Universal Rally Machine, GT-AI-7000S, High Speed Rail Testing Instrument Co., Ltd.; Thermogravimetric Analyzer, Mettler TGA1100SF, METTLER TOLEDO Instrument Co., Ltd., Switzerland; Taber wear testing machine, GT-7012-T, High Speed Rail Testing Instrument Co., Ltd..

Experimental Methods

Preparation of Polyurethane Emulsion

In a 500-ml flask equipped with a stirrer, a thermometer, together with a condenser, IPDI 27 g, PPG-2000 30 g, DMPA 3.3 g was added; the temperature was raised to 85°C, followed by reaction under a N₂ atmosphere for a period of two 2 hours, and 8 g of GO/DMF solution was added. Subsequently, BDO 4.1g was added, followed by adding an appropriate amount of acetone in order to lower the viscosity, and the reaction was performed at a temperature of 75°C to react to a predetermined NCO value. Following cooling down to the room temperature, 2.5 g of neutralizer TEA was added. Subsequent to reacting for a period of 5 min, the reaction product was poured into an emulsified bucket, followed by addition of deionized water; moreover, the emulsion was attained with the help of high-speed stirring and shearing. The NCO value of the system during the reaction was determined by the di-n-butylamine titration. Eventually, acetone in the emulsion was distilled off subjected to the lowered pressure.

Configure GO/DMF solution: add a specific amount of dried graphene oxide to 8g DMF, together with dispersing it on a 600w power ultrasonic disperser for a period of 1h. The amount of GO is termed as the total weight of the material: 0% (G-0); 0.01% (G-1); 0.02% (G-2); 0.04% (G-3); 0.06% (G-4); and 0.08% (G-5).

Preparation of Cured Film

The prepared polyurethane emulsion was placed horizontally at the Teflon plate following 48h at the room temperature and placed in a vacuum drying oven. The sample was dried to a constant weight at a temperature of 60°C and, eventually, a film with the thickness of almost 100µm was obtained.

Characteristic Method

(1) The test of TGA

Mettler TGA1100SF thermogravimetric analyzer was employed for the purpose of testing TGA with a heating rate of 20°C /minute in nitrogen atmosphere. The sample weight is between 7~8mg and the temperature falls in the range between 25°C and 800°C.

(2) Tensile strength and elongation at break of the cured film

In accordance with GB/T 1040-2006 and GB/T 2918-1998, the tensile strength and elongation at break of the cured film were measured on the universal tensile machine.

(3) Determination of cured film hardness

In accordance with GB/T 6739-2006 paint and varnish pencil method, determine the hardness of the cured film.

(4) Cured film wear resistance test

Refer to GB/T 1768-2006 standard, use Taber instrument and rubber grinding wheel, load 500g, rotate 1000 rpm, measure sample quality prior to and subsequent to rotation, followed by calculating wear in accordance with the formula (1).

Wear $\square$ $m = \text{sample quality before test (m1)} - \text{sample quality after test (m}^2\text{)}$ (formula 1)

(5) Heat aging resistance (Huang, 2010).

In accordance with GB/T9349-2002B method (oven method), the sample was placed in an oven for heat aging for a period of 48 hours, followed by measuring the mechanical strength of the test piece.

RESULTS AND DISCUSSION

Polyurethane Film Heat Resistance

Figure 1. TGA curves of the polyurethane film

Fig. 1 is the TGA curve of the polyurethane film. Following the addition of GO, the thermal decomposition of the hard segment is delayed, and GO, as a modified material, is able to act as a partial hard segment.

As evident from Fig. 1, by increasing the amount of graphene oxide, the Td5 of the modified polyurethane manifests an increasing law; moreover, as the graphene oxide mass fraction is 0.08%, the initial decomposition temperature manifests an increase by 27°C. This is likely to be owing to the fact that graphene oxide is capable of providing additional heat capacity, requiring more heat in order to break the urethane bond (Khatua and Das, 2004).

Mechanical Properties

Tab. 1 presents the mechanical characteristics of the polyurethane film. The tensile strength and elongation at break of the polyurethane film increase first, followed by decreasing, which is due to the fact that by using graphene oxide for the modification of the polyurethane, the level of crosslinking of the polyurethane film is increased, and the tensile strength and elongation at break of the polyurethane film are increased as well.

Since the tensile characteristics of graphene are weak, accordingly, with the increase in the amount of graphene oxide, the tensile and tensile characteristics of the entire polyurethane chain decline.

Table 1. Mechanical characteristics of polyurethane film

NO.	G-0	G-1	G-2	G-3	G-4	G-5
Tensile strength /Mpa	20.1	23.9	19.6	16.5	16.5	14.4
Elongation at break /%	420	550	550	420	280	260
Hardness	2B	2B	B	B	B	HB

Polyurethane Film Wear Resistance

Figure 2. The test results of wear resistance of polyurethane film

Fig. 2 presents the test results of the wear resistance of polyurethane film. With the increase in the amount of graphene oxide, the wear of the polyurethane film manifests a gradual decline, which is owing to the robust interaction between graphene oxide and polyurethane molecular chains. In the meantime, the increase in the amount of graphene oxide gives rise to an increase in the hardness of the polyurethane film, lowering the deformation ability of the friction surface, and minimizing the area where the abrasion takes place. Besides, the bonding force between carbon atoms in layers is below the bonding force between adjacent carbon atoms in the same layer, making the graphene oxide layer have a lower coefficient of friction, accordingly enhancing the wear resistance of the modified polyurethane composite (Liu *et al.*, 2015; Sun *et al.*, 2016).

Polyurethane Film Heat Aging Resistance

Fig. 3 presents the tensile strength of polyurethane film both before and after the heat aging. As revealed by the experiments, when the amount of graphene oxide is 0.02%, the mechanical characteristics of the polyurethane film are less affected, and better heat aging resistance can be attained.

Figure 3 The tensile strength of polyurethane film before and after heat aging

CONCLUSIONS

In the current research work, graphene oxide was put to use for the modification of the polyurethane materials, together with investigating the effects of different amounts of graphene oxide on the mechanical characteristics, wear resistance and heat aging resistance of polyurethane.

As revealed by the results:

(1) The introduction of graphene oxide has the potential of improving the heat resistance, heat aging resistance and wear resistance of the polyurethane. Graphene oxide, being a hard segment in polyurethane, is able to enhance the hardness of the polyurethane film; moreover, when the amount of graphene oxide is small, the mechanical characteristics of the modified polyurethane film can be enhanced. However, with the increase in the amount, the mechanical characteristics of the polyurethane film are degraded.

(2) In this research work, the overall performance of polyurethane was optimized when the amount of graphene oxide was 0.02%.

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