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RESEARCH ARTICLE

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Preparation and characterization of rosin glycerin ester and its bromide

Abstract Rosin glycerin ester and its bromide were prepared from natural renewable rosin, glycerin and liquid bromine which were first subjected to an esterification reaction, followed by an addition reaction. Their structures were characterized by an infrared (IR) spectrum and their thermal resistance was conducted with thermal gravity (TG) and differential scanning calorimetry (DSC). It showed that the bromide in the rosin glycerin ester decomposed faster than the ester; hence it may be used as fire-resistant material.

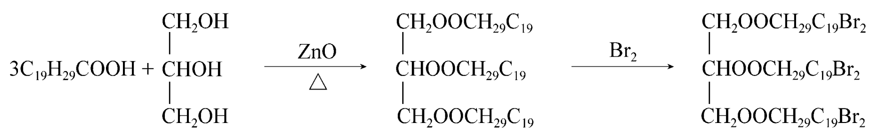
Keywords rosin glycerin ester, bromide, preparation, IR, TG-DSC

1 Introduction

As a natural and renewable resource, rosin and its derivatives have been used in paints [1], foam [2–4], elastomers [5–6], emulsions [7–8], adhesives [9], paper [10] and in drugs [11] for their film forming properties. But rosin is liable to oxidation because of its double bonds. Rosin can be modified by two different methods, based on its reaction with carboxyl groups and the unsaturated part of the rosin molecule. it can be modified either by an ether esterification reaction or by an addition reaction. In this paper, both these modified methods were used simultaneously to prepare the product with a C-Br bond, which may be used as fire-retardant. The reaction mechanism is as in scheme 1.

2 Experimental

Rosin was added to a 250ml four-neck glass reactor fitted with a reflux condenser, a stainless-steel stirrer, nitrogen gas inlet, thermometer and funnels. After heating the reactor to the melting temperature of the rosin with nitrogen, it was stirred. When the temperature reached 180°C ~ 200°C, the catalyst ZnO (0.2% based on the rosin weight) was added,



Scheme 1

and the glycerin (mole ratio: rosin/glycerin=1:2) was dripped into the reactor for 1h, Then the temperature was increased to 270°C for 30 min. When water-loss level reached the theoretic value needed, it was cooled to 250°C and the rosin glycerin ester product was poured out at once. The bromide was made as follows: a solution of rosin in CCl_4 was added to a three-neck glass reactor and kept in an ice-water bath, and a solution of liquid bromine in CCl_4 was slowly added to the reactor in drops for 30 min.Then the solvent was distilled and the product obtained. The IR spectrum was recorded on a Nicolet AVATAR 360 FT-IR spectrum, the product was made flake-like with KBr. TG-DSC was carried out on a NETSCH STA 449C synthesis thermal analyzer from Netsch Co. German.

3 Results and Discussion

Figures 1 and 2 show the formation of the rosin glycerin ester and its bromide, which are characterized by the disappearance of O-H at the 3000~3200cm^{-1} mark and a strong absorption peak, and the formation of C-O-C at 1300

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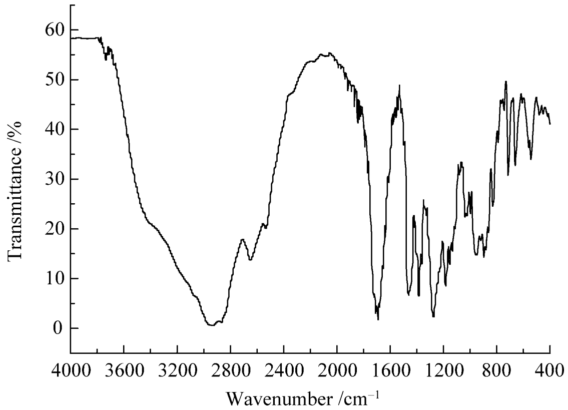

Fig.1 The IR spectrum of rosin

$cm^{-1}$and 1050 cm^{-1} in Fig 2 (above), the sharp absorption peak at 800 $cm^{-1}$is a sign of a C-Br bond in Fig 2 below. Figures 3 and 4 show that the initial decomposition temperature of the bromide is greatly decreased, further, the decomposition temperatures of rosin glycerin ester and its bromide are 435.7°C and 336.2°C, respectively, compared to that of rosin (343.9°C). The formation of an ester bond in the rosin glycerin ester accounts for its higher decomposition temperature than the carboxyl groups in rosin, and the high decomposition temperature of the bromide decreased due to the weak C-Br bond. Because of this, when it was added to the coatings, it decomposed first to HBr gas , and covered the surface of the firing area which is the function of a fire-retardant.

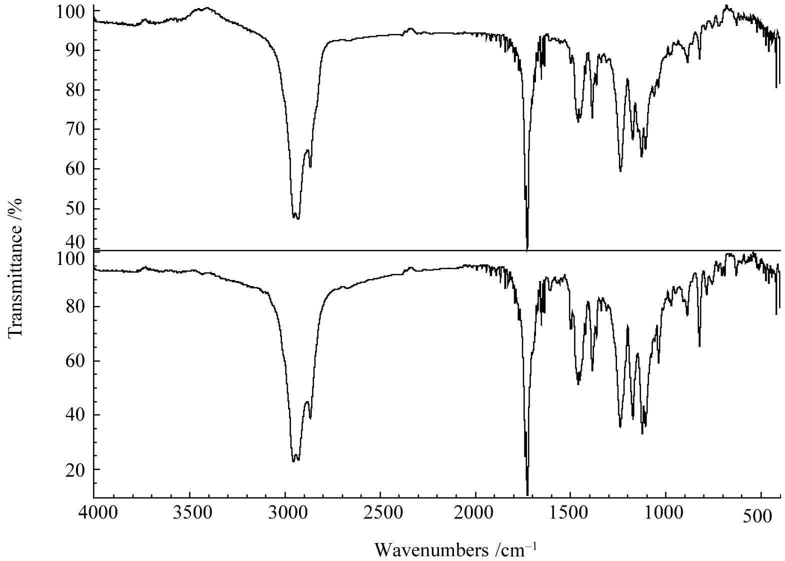

Fig.2 The IR spectrum of rosin glycerin ester(above) and its bromide

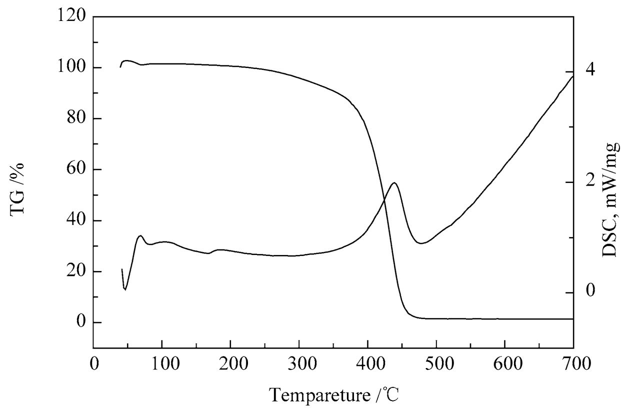

Fig.3 Thermal Gravity and DSC curve of the rosin glycerin ester

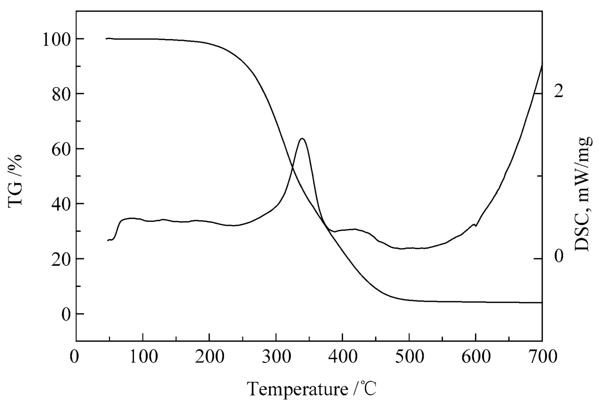

Fig.4 Thermal Gravity and DSC curve of the rosin glycerin ester bromide

4 Conclusions

Rosin glycerin ester and its bromide were prepared successfully from renewable rosin resources, An IR spectrum is characteristic of their structures. TG-DSC data showed that the bromide decomposed faster than rosin and its ester and hence it may act as a fire-retardant.

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