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The performance of biodegradable tung oil coatings

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ABSTRACT

Using immersion tests, viscosity measurements, FTIR and SEM, as well as biodegradation tests, biodegradable tung oil coatings were investigated. Results showed that the curing times for different formulae decreased as the amount of catalyst increased. During the curing process, there was an initial induction period where the viscosity remained more or less the same, and after a certain time, a sharp increase in viscosity was observed. The steady viscosity increased with time, revealing a continuous autoxidation process. Microorganisms in the soil attacked the surfaces of the tung oil films either uniformly on the whole plate or at specific weak points, leading to decreased volume, blurring of the small humps as well as holes. The weak point on the crosslinked chain was located at the carbonyl-containing groups, where chemical biodegradation occurred more easily and faster.

1. Introduction

In recent years, interest in biodegradable and environment-friendly materials has grown. The coating industry is especially focused on environment-friendly paints and coatings, since many products such as solvent-borne systems emit volatile organic compounds that are harmful to environment. As a possible environment-friendly coating, vegetable oil-based binders in formulations have the single, largest, easily available, low-cost, non-toxic, non-depletable, and biodegradable features [1]. Among vegetable oils, drying oils have received more attention than other renewable vegetable oils. Drying oils harden to a tough, solid film after a period of exposure to air through autoxidation instead of evaporation of water or other solvents. The use of drying oil in coatings is decades old and well-studied [2]. However, there were very few earlier papers associated with biodegration of coatings. Among them one reported on the dried oil film used in the controlled release fertilizer [3], and another in the composition for the wood flour [4]. Relatively more investigations about the vegetable drying oil focus on the cross-linking processes [5], application, extraction and analysis [6–8]. Due to the increasing environmental concerns, new knowledge about coatings made of vegetable drying oil has become more important.

Because of the existing and potential advantages of vegetable drying oil in the coating industry, commonly used products have included linseed (flaxseed) oil, tung oil, poppy seed oil, perilla oil, and walnut oil. In contrast to other drying oils, the three conjugated double bonds per fatty acid chain on the tung oil molecule [9,10] favor the formation of films by reacting with atmospheric oxygen. Thus, tung oil is broadly applied in the coating industry, and has been investigated in recent years. In 2010, tung oil-based polymers [11] and tung oil as a reactive diluent [12] as well as a modifier [13] were studied. In 2011, tung oil was applied as an autonomous repair agent in self-healing epoxy coatings [14]. In 2012, tung oil-based reactive diluents [15] and UV-curable tung oil [16] were introduced in alkyds. Since 2013, tung oil has been incorporated and studied in more advanced systems [17–22]. In these studies, the oil was used as an ingredient or a component of a coating system. In China, pure catalyzed tung oil has been traditionally utilized as a coating for hundreds of years in many applications, such as wood finishing for boats, strengthening rattan armor for ancient soldiers, surface coating for furniture, waterproofing materials, etc. In these traditional uses, the tung oil coating is biodegradable in environment after its service life has ended. However, the degradation process of tung oil coating remains an open problem, and compared to the huge potential in applications of environment-friendly materials, knowledge is lacking.

The aim of the present paper was to study the performance of biodegradable tung oil coating from liquid to solid film, through viscosity measurements, immersion tests, Fourier transformed infrared spectroscopy (FTIR), and scanning electron microscopy (SEM), as well as biodegradable measurements. The results will add to the knowledge of the theory and application of drying oil and biodegradable coating.

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2. Experimental

2.1. Materials

The tung oil used in experiment was a clear to yellowish commercial oil (Guangzhou Chenxin Chemical, China) that had a special smell of the tung oil, relative density (at 20 °C) 0.938 ± 0.005, refractive index 1.51 ± 0.01, impurity ≤0.15%, acid value ≤6.0 mg KOH/g, iodine value ≥163. The fatty acids composition of tung oil is shown in Table 1 (Taken from Wikipedia (the free encyclopedia at http://en.wikipedia.org/wiki/Tung_oil)).

Cobalt naphthenate, vanadium 2-ethylhexanoate, lead naphthenate were commercial products from Shanghai XiangZi Chemical Ltd. They are soluble viscous liquids in vegetable drying oil and have 4 ± 0.1% metal content.

Hydrochloric acid and sodium hydroxide were chemical grade.

2.2. Formulation and film

The coating was simply formulated by adding the designed amount of catalyst to 100 g tung oil with sufficient stirring at room temperature and was tightly stored for at least a week before the test. The formulae used for the coatings are listed in Table 2, in which they are indexed by the first letters of the component names and the amount of each drier. These simple formulae not only are designed for investigation but also can find practical usage in wood finishing and as slow-release coated fertilizers.

Films were prepared from the coatings by brushing them on glass sheets and curing them in air at 25 °C.

2.3. Methods

In this study, the properties of the coating and the film were tested with a general method, steady and oscillatory shear measurements, immersion in chemical solutions, scanning electron microscopy, biodegradable measurements, and Fourier transformed infrared spectroscopy.

Steady and oscillatory shear measurements were carried out with a rheometer DHR-2 (TA Instruments). A standard steel parallel plate with a 40 mm diameter was chosen. Viscosities were measured with variations of time at fixed shear and temperature.

The biodegradation tests were performed with the outdoor burial method. After the tung oil film samples were buried in outdoor soil for the chosen duration, the sample's performance was determined with a comparison with the initial state. For example, the weight loss ratio was calculated from the initial mass and the final mass, and the surface morphologies of the films before and after they were buried were examined with scanning electron microscopy (SEM, S-3000N, Hitachi), and so on.

FTIR spectra were recorded with a Nicolet NEXUS 670. Before the FTIR measurement, the samples were diluted with KBr to a weight ratio of 200:1 by mixing the them with KBr powder and pressing them into pellets less than 1 mm thick. The wave number was scanned from 4000 to 400 cm^{-1} at a resolution of 2 cm^{-1}.

Table 1
Major fatty acid composition of tung oil by Wikipedia.

Fatty acid	Composition (%)
Palmitic acid	5.50
Oleic acid	4.00
Linoleic acid	8.50
Alpha-eleostearic acid	82.0

Table 2
Formulae (in weight portion) of tung oil coatings in test.

Index	Tung oil	Cobalt naphthenate	Lead naphthenate	Vanadium 2-ethylhexanoate
TC1.0	100	1.0	–	–
TC1.5	100	1.5	–	–
TC2.0	100	2.0	–	–
TC2.5	100	2.5	–	–
TC3.0	100	3.0	–	–
TC3.5	100	3.5	–	–
TC4.0	100	4.0	–	–
TC4.5	100	4.5	–	–
TCL0.5	100	2.0	0.5	–
TCL1.0	100	2.0	1.0	–
TCL1.5	100	2.0	1.5	–
TCL2.0	100	2.0	2.0	–
TCL2.5	100	2.0	2.5	–
TCL3.0	100	2.0	3.0	–
TV1.0	100	–	–	1.0
TV1.5	100	–	–	1.5
TV2.0	100	–	–	2.0
TV2.5	100	–	–	2.5
TV3.0	100	–	–	3.0

3. Results and discussion

3.1. Curing performances

3.1.1. Drying time

Pure tung oil usually requires more than 5 days to dry, which is too long to be acceptable for application. To accelerate the drying speed, a catalyst is usually added to tung oil to formulate a usable coating. Commercial catalyst products for drying oil include metal salts. The most commonly used catalysts are metal naphthenate and 2-ethylhexanoate. Both can accelerate the autoxidation of the drying oil to form a polymerized macromolecule. However, the exact time required for tung oil to dry or cure differs. The set-to-touch time and dry-hard time as shown in Figs. 1 and 2 from the typical metal salts in Table 2 at 25 °C, reflects the rates of curing of the coatings. The curing times decreased as the amount of catalyst increased. The high efficiency for accelerating the drying velocity located in the low catalyst regime. The combined driers from cobalt and lead salts (indexed as TCL in Table 2) showed the best performed among the catalysts tested.

3.1.2. Viscous properties in drying process

While investigating the drying process of a coating, a rheological method has the benefit of continuously tracing the process. According to the type of shear, viscous features can be measured as steady and oscillatory viscosities. Steady viscosity is a traditional parameter measured under continuous shear. The oscillatory viscosity,

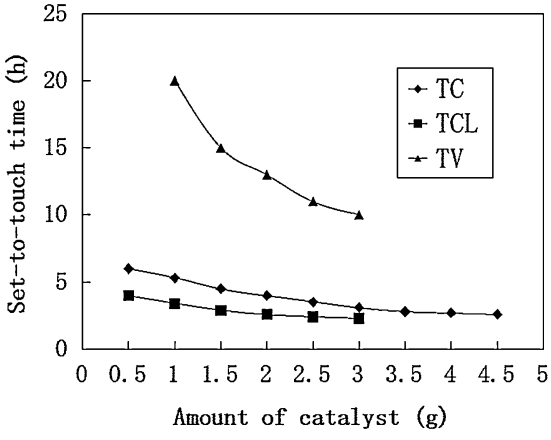

Fig. 1. Set-to-touch time over amount of catalyst for the formulae in Table 2.