



Study on waterborne acrylate coatings modified with biomass silicon

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ABSTRACT

Silica that originated from the calcination of rice husks, which is a source of biomass silicon, was added as a reinforcing agent to waterborne polyacrylate wood coatings to improve their coating performance, and especially their mechanical properties. The morphology of the rice-husk ash, aggregation and dispersion of modified silica in the polyacrylate emulsion and the surface roughness of the coating on wood were characterized by scanning electron microscopy, transmission electron microscopy and atomic force microscopy. The film mechanical properties and performance were investigated. The rice-husk ash calcined at 650 °C exhibited a particle size of 5–20 μm. Silica modified by silane coupling agent KH-570 was dispersed in waterborne acrylate coatings with a submicron scale. For a 2 wt% modified silica loading, the surface roughness of the coating on wood was influenced slightly and the elongation at break, the tensile strength, the elastic modulus, and the pencil hardness of the polyacrylate film were 303.06%, 48.673 MPa, 6.672 MPa and 2H level, respectively. The adhesion strength was enhanced significantly to level 0 with an increase in modified silica loading. The changes of film abrasion loss and gloss for the five groups are not obvious. The silica-modified coating exhibited slightly hydrophobic properties and a better lipophilicity. This paper provides a feasible route for the value-added utilization of rice husk.

1. Introduction

Acrylate waterborne coatings are one of the main varieties of wood coatings with many advantages, such as a light color, a high transparency, brightness and a high solids content, strong adhesion, good construction performance and safe use [1]. However, because of their disadvantages of hardness, wear resistance and mechanical properties, acrylate waterborne coatings have been limited in their applications [2,3].

In recent years, organic–inorganic nanocomposites have combined the advantages of inorganic materials (such as rigidity and thermal stability) and organic polymers (such as flexibility, ductility and processability) and improved the material properties. Nowadays, the use of silica to prepare organic–inorganic nanocoatings has been studied widely. Because nanoscale silica has a large specific surface area that can increase the interfacial area significantly as a filler, polymer can be contacted with silica and improve nanosilica agglomeration [4–6]. Related studies have been carried out with nanosilica, in which

research has indicated that the introduction of nanosilica to the system can improve the hardness, mechanical properties, wear resistance, corrosion resistance, heat resistance and hydrophobicity [7–19].

The traditional preparation of nanosilica is by the sol–gel and microemulsion methods [20], but rice husk, which is a natural raw material and an agricultural waste, can be used as an alternative biomass silicon source. It contains 65–75% organic matter and 15–20% inorganic matter, and 95–98% of the inorganic matter consists of hydrated amorphous silica. Hence, rice husk is an ideal silica biomass source [17]. Rice-husk resources are abundant globally; approximately 600 million tons of rice husk are generated annually and China produces 45 million tons per year, but the utilization of rice husk is very low. Most rice husk is abandoned as waste or is used as a low-level fuel, which results in environmental pollution. The utilization of rice-husk resources, an increase in its value and the conversion of waste into value is of great practical significance to promote the efficient recycling of rice-husk resources. Silica, which is the main component of rice husk, has a very large specific surface area and a smooth, non-porous surface,

Abbreviations: RH, rice husk; RHA, rice-husk ash; MMA, methyl methacrylate; BA, n-butyl acrylate; AAEM, 2-(methacryloyloxy)ethyl acetoacetate; KH570, methacryloxypropyltrimethoxysilane

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Preparation and characterization of a melamine-urea-glyoxal resin and its modified soybean adhesive

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ABSTRACT

Although polyamidoamine-epichlorohydrin (PAE)-modified soybean meal (SM) adhesives exhibit desired bond properties and technological applicability, their commercial application is still limited by the high cost of PAE resin. In this study, a formaldehyde-free crosslinking agent, melamine-urea-glyoxal (MUG) resin for SM adhesive, was developed based on investigations of the effects of melamine content and storage time on the structure and properties of MUG resin and MUG-modified SM adhesive. The test results confirmed that melamine could effectively copolymerize with glyoxal and urea to form an aldehyde-terminated MUG resin that was crosslinkable to soybean protein. The melamine content in MUG had important effects on the bond properties of the SM adhesive, attributed to the incorporation of aromatic triazine rings into the aliphatic urea-glyoxal chains and the greater reactivity and functionality of melamine than urea. However, the addition of melamine at more than 10% led to a shorter storage time of MUG resin and worse bond properties of MUG-modified SM adhesive. Owing to the further reactions of residual aldehyde and amino groups of MUG resin, the water resistance of the MUG-modified SM adhesive decreased with the storage time of the MUG resin. The allowable storage of the optimal MUG-10 resin was 3 weeks to ensure an acceptable bonding quality. Due to the much lower cost of MUG resin than PAE resin, it is beneficial for the wide commercial applications of formaldehyde-free SM adhesives in wood composites.

1. Introduction

Formaldehyde-based adhesives, including those based upon urea-formaldehyde (UF), phenol-formaldehyde (PF) and melamine-formaldehyde (MF) resins, are extensively used in wood-based composites owing to their low cost, water solubility, high reactivity and allowable adhesion properties [1–3]. However, the utilization of these formaldehyde-based adhesives not only consumes non-renewable petrochemical resources but also leads to hazardous volatile compound emission issues that are detrimental to the human body and negatively impact the living environment [4,5]. Consequently, the development and application of biomass-derived adhesives without formaldehyde addition is an available approach to eliminate formaldehyde contamination of wood-based panels and to replace petroleum-based synthetic adhesives [6].

Soybean meal (SM), an agricultural byproduct of soybean oil production, is considered an ideal raw material for the preparation of bio-based wood adhesives owing to its advantages of low price, abundance, renewability and degradability [7]. However, conventional SM adhesives usually exhibit insufficient water resistance and bonding strength owing to their inherent structure with high hydrophilicity and weak intermolecular interactions [8]. Therefore, various strategies have been proposed in recent years to promote the bonding strength and water resistance of SM adhesives, such as the physical blending method [9,10], chemical cross-linking modification [11,12], and enzymatic treatment technology [13,14]. Among these, cross-linking modification presents an efficient and promising performance enhancement for commercial applications.

Polyamidoamine-epichlorohydrin (PAE) resin is a new-generation crosslinking agent and dispersant that has been commercially applied

Abbreviations: SM, soybean meal; MUG, melamine-urea-glyoxal; PAE, polyamidoamine-epichlorohydrin.

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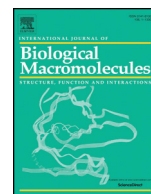
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Development and investigation of novel antifouling cellulose acetate ultrafiltration membrane based on dopamine modification

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ABSTRACT

In this contribution, a novel cellulose acetate modified with dopamine (CA-DA) membrane material was designed and prepared by a two-step route consist of chlorination and further substitution reactions. The chemical structure of the prepared CA-DA material was determined by FTIR and ¹H NMR, respectively. The CA-DA ultrafiltration membrane was subsequently fabricated by the scalable phase inversion process. Compared with cellulose acetate membrane as the control sample, the introduction of dopamine improved the porosity, pore size and hydrophilicity of the CA-DA membrane, which was helpful to the water permeability (181.2 L/m²h) without obviously affecting the protein rejection (93.5%). According to the static protein adsorption and dynamic cycle ultrafiltration experiments, the CA-DA membrane displayed persistent antifouling performance, which was verified by flux recovery ratio, flux decline ratio and filtration resistance. Moreover, the water flux recovery ratio of the CA-DA membrane was retained at 97.3% after three-cycles of BSA solution filtration, which was much higher than that of the reference CA membrane. This new approach provided a long life and excellent ultrafiltration performance for polymer-based membranes, which has potential application prospects in the field of separation process.

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1. Introduction

Today, people are paying more and more attention to water pollution with increasingly tight resources [1,2]. Among the various water treatment methods, ultrafiltration technology is considered to be one of the most economical, effective and cleaner separation methods due to their unique separation principle and many attractive advantages. Up to now, ultrafiltration process has been widely used in sewage treatment, drug separation and other industrial separation processes [3,4]. The high-performance membrane material is an essential and important part of ultrafiltration membrane, and it controls membrane performance consist of permeability and selectivity. At present, ultrafiltration membranes have been fabricated from various polymers, including polyacrylonitrile (PAN) [5], polyvinyl chloride (PVC) [6], polyvinylidene fluoride (PVDF) [7], polyethersulfone (PES) [8] and cellulose acetate (CA) [9], etc. However, the intrinsic hydrophobicity of these polymers

restricts water permeability and leads to membrane fouling, which are two major obstacles to the applications of membrane technology.

Membrane fouling is caused by the adsorption and deposition of contaminants on the membrane surface and pores during membrane separation process [10], which leads to permeate flux reduction, selectivity and service life deterioration [11,12]. Recently, almost all the researches on ultrafiltration have focused on improving its antifouling performance, especially introducing hydrophilic materials into ultrafiltration membrane [13]. Zhang et al. grafted zwitterions to the polyimide membrane surface through a two-step reaction, thereby improving the hydrophilicity and antifouling performance of the membrane [14]. Lv et al. fabricated an ultrafiltration membrane by blending hydrophilic cellulose nanocrystals (CNC) and hydrophobic polyvinylidene fluoride, which showed good water permeability and antifouling performance [15]. Liu et al. also blended amino-functionalized SiO₂ and TiO₂ nanoparticles with polyacrylonitrile to prepare composite membrane [16]. The results exhibited that the PAN-TiO₂ composite membrane had better hydrophilicity, higher porosity, larger average pore size, and superior antifouling performance. In addition to nanocellulose [17], zwitterionic materials [18] and inorganic nanoparticles [19] mentioned above, dopamine has also attracted increased attention.

Dopamine is a newly discovered hydrophilic substance [20]. The presence of a large number of hydroxyl groups in the dopamine

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Exploration of antifouling zwitterionic polyimide ultrafiltration membrane based on novel aromatic diamine monomer

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ABSTRACT

In this study, a new kind of aromatic diamine monomer named as 1,4-bis(4-aminophenyl)piperazine (BANPZ) was particularly designed and synthesized, and then the novel zwitterionic polyimide (ZPI) was prepared through a two-step process including polycondensation and quaternary amination reaction. The chemical structures of the prepared monomer and polymers were identified by FTIR and ¹H NMR measurements, respectively. Meanwhile, the inherent viscosities, molecular weights, solubility behaviors and thermal properties of two obtained polymers were thoroughly characterized. Compared with the control polyimide (PI) membrane, the presence of zwitterionic groups considerably improve the hydrophilicity of the ZPI membrane, thereby enhancing the water permeability to some extent without obviously affecting the rejection ratio. Based on the static protein adsorption and dynamic cycle ultrafiltration experiments, the ZPI membrane exhibited persistent antifouling property, which was demonstrated by the flux decline ratio and filtration resistance. In particular, the water flux recovery ratio of the ZPI membrane was retained at 96.0% after a three-cycles of BSA solution filtration, which was much higher than that of the PI membrane (76.7%), suggesting excellent long-term performance stability. This new approach provided a valuable strategy of combining polymer chemical structure optimization and mature non-solvent induced phase separation (NIPS) method, which could greatly drive the development and application range of separation membranes.

1. Introduction

Water is the most important natural and strategic resource in the world. The demand for clean water supply is becoming more and more urgent with the continuous growth of population and rapid development of science and technology [1]. Compared with other water treatment method, membrane separation technology has many advantages of low energy consumption, simple operation, high separation efficiency and water production. It is very suitable for large-scale wastewater treatment, water regeneration and desalination, and is also beneficial to ensure the safety of drinking water and the recycling of water resources [2]. Ultrafiltration is currently the most developed and widely used membrane separation technology based on pressure-driven and physical sieving principle, which can effectively remove rust, sediment, suspended matter, colloid, bacteria, macromolecular matters and other

harmful substances in wastewater [3]. The preparation of ultrafiltration membranes is mostly based on synthetic organic polymers, such as polyvinyl chloride (PVC), polyacrylonitrile (PAN), polyvinylidene fluoride (PVDF), polysulfone (PSF) and polyethersulfone (PES) [4], etc. But these polymers are not the most ideal and suitable membrane materials because their inherent extremely hydrophobicity restricts water flux and leads to unavoidable membrane fouling, which are two major obstacles to the application and development of ultrafiltration technology [5]. Therefore, many researches on ultrafiltration have focused on hydrophilic modification to improve water flux and antifouling performance, especially the introduction of zwitterionic materials into ultrafiltration membrane in recent years [6].

As well known, zwitterionic membranes remain overall electrically neutral due to equivalent positive and negative charges, and generally contain the groups of sulfobetaine, carboxylbetaine or phosphobetaine,

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Article

Mechanical Properties of a Soy Protein Isolate–Grafted–Acrylate (SGA) Copolymer Used for Wood Coatings

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Abstract: Changing demands have led to rapidly growing interest in the modification of waterborne wood coatings. To improve the performance of a polyacrylate wood coating, especially the strength, hardness, and abrasion resistance of the film, a soy protein isolate–grafted–acrylate (SGA) copolymer was prepared in an aqueous solution with ammonium persulfate (APS) as an initiator and sodium pyrosulfite (SPS) as an unfolding agent for the soybean protein isolate (SPI). The emulsion was characterized using transmission electron microscopy, Fourier-transform infrared spectroscopy (FTIR), and a particle size analyzer. Furthermore, the mechanical properties of the film, including the tensile strength, elastic modulus, elongation at break, and pencil hardness, were measured. The results showed that the glass transition temperature of the polyacrylic resin decreased to 35 °C after the SPI grafting. The elastic modulus of the film increased from 0.317 to 46.949 MPa, and the elongation at break decreased from 453.133% to 187.125% as the addition of SPI varied from 0 to 4 g, respectively. The pencil hardness of the wood coating increased from HB to 3H. This paper proposes a feasible route for the utilization of SPI for wood coatings.

Keywords: soy protein isolate; polyacrylate; graft copolymerization; waterborne wood coating

1. Introduction

In recent years, waterborne wood coatings have frequently been used in the decoration of homes, hotels, and wood furniture in China because they are non-toxic and environmentally friendly, and they release low amounts of volatile organic compounds (VOCs) [1,2]. Polyacrylate waterborne coatings are one of the main varieties of wood coatings with many advantages, such as exhibiting strong adhesion, forming colorless coatings, exhibiting high transparency, and possessing high solid contents. However, further applications of acrylate waterborne coatings are limited by their low hardness values and poor mechanical properties [3–5].

Various efforts have been made to improve the mechanical properties of polyacrylate waterborne coatings, such as copolymerization with polyurethane [6–10], silicone modification [11], treatment with nanoparticles [12–14], epoxy modification [15], microemulsion polymerization, microemulsion hybrid polymerization [16,17], and other methods [18,19]. The hardness values and mechanical properties of the obtained coatings were improved by these methods, but nonrenewable and nondegradable petrochemical-based materials were consumed. In the past few years, it has become a development



Preparation of effective ultraviolet shielding poly (lactic acid)/poly (butylene adipate-co-terephthalate) degradable composite film using co-precipitation and hot-pressing method

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ABSTRACT

Biodegradable poly (lactide) (PLA) and poly (butylene adipate-co-terephthalate) (PBAT) composite films were made by a co-precipitation and hot-pressing method. The property of composite films like the chemical interaction, phase morphology, mechanical properties, and thermal properties were studied. The Fourier transform infrared spectroscopy (FTIR) test manifested that there was a small amount of the transesterifications between the PBAT and PLA during hot pressing, which could improve the compatibility of the two phases. The tensile strength of the film only reduced by 7.4%, while the elongation at break was increased by 119.1% compared with PLA after adding 4%wt PBAT. The composite films showed a high Ultraviolet-visible (UV) light barrier property. The UV blocking rate of the composite after adding 4%wt PBAT was 6.95 times higher than that of pure PLA at 380 nm. The PLA/PBAT composite films with excellent thermal stability, satisfactory mechanical properties and UV-light barrier have high a possibility for an UV screening packaging application.

1. Introduction

In order to reduce the harm of non-degradable plastics such as polyethylene (PE) and polypropylene (PP) to the environment and living beings [1,2], biodegradable polymers were investigated as alternatives to traditional petroleum-based polymers [3]. In these biodegradable polymers, the largest output is polylactic acid (PLA), because its excellent performance can be comparable to that of PP. The main advantages of PLA are high mechanical strength, high transparency, and easy processing [4–6], which make PLA has great prospects in the packaging, electronics and automotive industry files [7]. However, the shortcomings of PLA are also very obvious, such as brittleness and low resistant to ultraviolet rays [8,9]. These shortcomings inhibit PLA from being more widely used in daily life, especially thin film as the packaging materials. Therefore, decreasing the inherent brittleness and enhancing UV resistance of PLA have aroused widespread attention and interest [10,11].

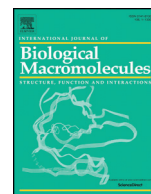
Many strategies were used to improve the properties of PLA, which included plasticization, grafting, and compatibilization [12–16]. Among these strategies, blending other flexible polymers with PLA to obtain

desirable properties was one of the best solutions. These strategies had a wide range of utility, especially in industrial-scale applications [17,18]. Poly (butylene adipate-co-terephthalate) (PBAT) is a kind of biodegradable polymer with highly flexible [19]. In addition, the large amount of benzene rings in PBAT molecular chains also provides the possibility to improve the UV resistance of PLA. However, large content of PBAT reduce the transparency of PLA/PBAT composites, and the compatibility of PLA and PBAT is not good [20]. After the twin-screw mixing, the mechanical strength of the PLA/PBAT composites was greatly reduced due to the difference in polarity and the vast difference in the molecular chain segment structure. Although the use of solvent volatilization to prepare composite films has been widely used, this method is only suitable for laboratory preparation and not for industrial large-scale production. Because the solvent used, such as methylene chloride, is harmful to the environment. And it is also difficult to recycle and the cost of the solvent is pretty high. Solution precipitation method was used to prepare PLA/PBAT composites in this study [21]. Under appropriate conditions, precipitation of a hydrophobic compound solution in a non-solvent could generate a dispersion of particles [22]. The

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Development and investigation of novel antifouling cellulose acetate ultrafiltration membrane based on dopamine modification

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Original Article

Study on the properties of PLA/PBAT composite modified by nanohydroxyapatite



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ABSTRACT

Poly(lactic acid) (PLA) and poly(butylene adipate-Co-terephthalate) (PBAT) show high and excellent biocompatibility, which are promising materials used in bone tissue engineering field. In this research, n-HA/PLA/PBAT/MCC composites were prepared by solution blending method. Nano hydroxyapatite (n-HA) was used as nucleation, and microcrystalline cellulose (MCC) was added to improve the degradation performance of the materials. Compared with the composite without n-HA, the crystallinity of the composites with 6% n-HA was increased by 62%. The scanning electron microscopy (SEM) and the transmission electron microscopy (TEM) showed that the n-HA was evenly dispersed in the composites when the addition ration of n-HA was lower than 6%, while obvious agglomeration of n-HA appeared at the addition ratio of 10%. The tensile test demonstrated that the tensile strength of the composites with different addition ratio transcended the needs of bone tissue engineering materials. The introduction of n-HA in obtained composites simulated the composition and structure of native bone, which suggested a potential utility and application prospect in bone tissue engineering.

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1. Introduction

Bone defect repair surgeries in tissue engineering methodologies have been widely used to treat common and uncomplicated bone fracture, which required bone graft replacement to strengthen the ability of the repair in the defect. According to statistics, in recent years the incidence of fracture in China has surpassed 1000 per 100,000 people [1]. Currently the metal materials (mainly titanium) are used for bone tissue engineering maturely in surgery. Although scaf-

folds, there are inherent defects such as inability to degrade, corrosion, and aseptic inflammation as the traditional metal bone tissue engineering scaffolds would be remaining in the human body and need to be removed through surgery after a period of implantation [2]. The native bone mainly consisted of organic components such as collagen and inorganic components such as hydroxyapatite. Fibers, polysaccharides, growth factors and hydroxyapatite excreted by bone-end cells constitute the extracellular matrix [3–5]. To facilitate the attachment and proliferation of bone cells, mature bone tissue scaffold should have good biocompatibility and porosity [6]. Poly(lactic acid)-based biomimetic material contained hydroxyapatite could replace the metal to make the bone tissue engineering scaffolds, which compensates the deficiency of the metal

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Synthesis of Grafting Itaconic Acid to Starch-Based Wood Adhesive for Curing at Room Temperature

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Abstract

A new biodegradable, renewable, and environmentally friendly starch-based wood adhesive that can be used at room temperature was synthesized by grafting of itaconic acid (IA) monomer onto cassava starch. When the addition of IA was 5% (starch basis), we can obtain the optimal mechanical properties of 15.38 MPa in dry state and 4.56 MPa in wet state. Compared with unmodified starch adhesive, the shear strength of grafted starch adhesive improved by 43.6% in dry state and 93.2% in wet state, respectively. The improved performance of the grafted starch-based wood adhesive was characterized by the measurement of viscosity and solid content, Fourier-transform infrared (FTIR), Thermogravimetry (TGA), X-ray diffraction (XRD) and scanning electron microscopy analyses (SEM). The results showed that there was a new characteristic peak of ester at 1700 cm^{-1} in the infrared spectrogram, which indicated the successful grafting of IA onto starch. After grafting modification, the storage stability and thermal stability of starch adhesive were improved. From SEM images and XRD patterns, we can witness that the morphology and crystallinity of starch particles were changed, which as a supplement of FTIR, confirmed the improvement of bonding strength and water resistance of the adhesive.

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蓖麻油基 UV/空气双重固化水性聚氨酯 木器漆的制备及性能研究

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摘要:目的 由紫外光固化/空气后固化构成双重固化体系,以弥补单一紫外光固化存在固化速度慢及边角
棱固化不充分的缺陷。方法 将具有气干固化性质的蓖麻油引入两端带有 C=C 双键的水性聚氨酯中,使水
性聚氨酯体系不仅能进行紫外固化,还可进行空气后固化。通过控制光引发剂、催干剂的添加量,制得了
紫外光固化、紫外光/空气双重固化、空气/紫外光双重固化的水性聚氨酯木器涂料,研究了不同水性聚氨酯
乳液配方、固化方式对涂膜、漆膜性能的影响。结果 制备的水性聚氨酯分散体具有良好的储存稳定性且 90
天内无沉淀、分层现象。DMPA 质量分数为 6.5%,CO 质量分数为 15.24%时,乳液较稳定,且涂膜耐水性
和力学性能好。紫外光/空气双重固化涂膜拉伸强度为 13.06 MPa,断裂伸长率为 22.53%,弹性模量为
11.39 MPa,紫外光/空气和空气/紫外光双重固化体系木器漆膜硬度均达到 4H,附着力均为 0 级。结论 与空
气/紫外光固化、单一紫外光固化两种固化方式相比,紫外光/空气双重固化涂膜力学性能最优异,热稳定性
介于两者之间。紫外光/空气和空气/紫外光双重固化体系木器漆膜硬度、附着力优于传统单一紫外光固化的
漆膜。

关键词: 蓖麻油; 水性聚氨酯; 氧化聚合; 紫外光/空气双重固化; 固化方式

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Synthesis and Properties of Castor Oil-based Waterborne Polyurethane Wood Coating Cured through UV/Air Dual Process

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ABSTRACT: The work aims to develop an UV/air dual curing system by ultraviolet curing and air post curing so as to make up

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UV 固化硅溶胶改性水性聚丙烯酸酯木器涂料的制备

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摘要:用硅溶胶改性、紫外光固化构成的体系, 弥补水性纯聚丙烯酸酯木器涂料力学性能不佳、硬度较低、固化速度较慢的缺陷。通过将具有环氧基团的 KH-560 硅溶胶引入带有活性羟基的水性聚丙烯酸酯乳液中, 以提高水性聚丙烯酸酯膜的力学性能及附着力; 进而通过调控功能性单体季戊四醇三丙烯酸酯 (PETA) 的添加量制得紫外光固化硅溶胶改性水性聚丙烯酸酯木器涂料。研究了不同水性聚丙烯酸酯乳液配方对漆膜、涂膜固化速度及性能的影响。结果表明: 硅溶胶含量为 10%、PETA 含量为 12% 时, 制备的硅溶胶改性水性聚丙烯酸酯分散体具有良好的贮存稳定性, 且 90 d 内无沉淀分层现象, 乳液有效粒径为 250 nm, 固含量达到 44.98%, 紫外光固化涂膜玻璃化转变温度为 21.78 °C, 拉伸强度为 21.98 MPa, 断裂伸长率为 31.5%, 凝胶率为 92.62%, 漆膜紫外光固化时间 10 s, 硬度达到 3H, 附着力达到 1 级。与传统水性纯聚丙烯酸酯体系相比, 紫外光固化硅溶胶改性聚丙烯酸酯体系制得的漆膜力学性能优异, 硬度较高, 固化速度明显提高。

关键词: 硅溶胶; 水性聚丙烯酸酯; 乳液聚合; 紫外光固化; 木器涂料

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Synthesis of UV cured waterborne polyacrylate wood coatings modified by silica sol

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Abstract: Modified by silica sol, the UV cured waterborne pure polyacrylate (PA) wood coating was developed, which could address the drawbacks of traditional wood coatings, such as unsatisfactory mechanical properties, low hardness and slow curing rate. The mechanical properties and adhesion of waterborne polyacrylate film could be improved by introducing KH-560 silica sol with epoxy group into aqueous polyacrylate emulsion with active hydroxyl groups. Furthermore, the UV cured waterborne polyacrylate wood coatings modified by silica sol were synthesized by adjusting the loading of functional monomer pentaerythritol three acrylate (PETA). The effects of different waterborne polyacrylate emulsion formulations on the curing rate and properties of film were characterized. The results showed that the PA had good storage stability with no precipitation and delamination within 60 d with 10wt% silica sol and 12wt% PETA. The effective particle size of the emulsion was 250 nm and the solid content reached 44.98%. The glass transition temperature of the UV cured coating was 21.78 °C, the tensile strength was 21.98 MPa, the elongation at break was 31.5% and the gelation rate was 92.62%. The UV curing time, hardness and adhesion of the paint film were 10 s, 3H and 1st grade, respectively. The UV cured waterborne polyacrylate film modified by silica sol had excellent mechanical properties, higher hardness and faster curing speed compared with the traditional waterborne pure polyacrylate system. With the improvement of people's consciousness of environmental protection and the progress of waterborne wood coatings preparation technology, solvent-based coatings with high VOC have been phased out. Waterborne coatings have become the mainstream trend in the development of wood coatings due to their less VOC and less pollution. The UV curing method can improve the curing speed of coatings, greatly improve production effi-

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试验与研究

TEST AND RESEARCH

环氧化木质素改性环氧树脂的性能研究*

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摘要:将玉米秸秆木质素环氧化后用于环氧树脂的共混改性。借助力学性能测试、扫描电镜观测、红外光谱分析和动态力学分析等方法研究了环氧化木质素在聚乙二醇助溶作用下对环氧树脂/聚酰胺体系力学性能、微观相容性、动态力学性能的影响。结果表明,环氧化木质素与环氧树脂/聚酰胺体系的相容性较好,能够参与并促进环氧树脂的固化,并可与聚乙二醇协同增韧环氧树脂。随着环氧化木质素添加量的增加,环氧树脂固化物的抗弯强度、抗冲击强度、储能模量和玻璃化转变温度呈现先增加后减小的趋势,当环氧化木质素添加量为8%时,环氧树脂固化物的力学性能和耐热性能提升较大。

关键词:环氧树脂;聚酰胺;环氧化木质素;聚乙二醇;性能

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Study on the Properties of Epoxy Resin Modified by Epoxidized Lignin

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Abstract: The corn straw lignin is epoxidized and used for the blending modification of epoxy resin. The effects of epoxidized lignin on the mechanical properties, micro-compatibility and dynamic mechanical properties of epoxy resin/polyamine system under the solubilization of polyethylene glycol are studied by means of mechanical properties test, scanning electron microscope observation, infrared spectrum analysis and dynamic mechanical analysis. The results show that the epoxidized lignin has better compatibility with epoxy resin/polyamine system, and can participate in and promote the curing of epoxy resin, and can toughen the epoxy resin with the polyethylene glycol synergistically. With the increase of the amount of epoxidized lignin added to epoxy resin, the bending strength, impact strength, energy storage modulus and glass transition temperature of epoxy resin cured product increases firstly and then decreases. When the amount of epoxidized lignin added to epoxy resin is 8%, the mechanical properties and heat resistance of epoxy resin cured product can be improved greatly.

Key words: Epoxy resin; polyamine; epoxidized lignin; polyethylene glycol; property

前言

环氧树脂因其良好的物理机械性能、成型加工性能、耐热性能以及优异的粘结性能而在航空、航天、电子和机械领域得到了广泛应用^[1]。环氧树脂自身结构的特点使其固化物脆性较大,抗冲击强度和断裂韧性较差^[2],并且其最终固化物的性能很大程度上取决于与之相配合的固化剂和添加剂^[3],因而采用适宜结构的固化剂和添加剂与之相配合提高环氧树脂的最终性能一直是人们关注的热点,尤其是

以低成本的代价提高环氧树脂的力学性能、热性能和耐老化性能。

作为自然界唯一能提供芳香基团的生物质资源,木质素来源广泛、种类丰富、可再生、可降解^[4],其分子链段中的芳香基团及酚醚结构使其在聚合物改性中可以赋予聚合物较好的耐热性及耐紫外老化性^[5-7]。研究表明^[8],来自玉米秸秆生物炼制副产物的木质素与环氧树脂混合后可以促进或参与环氧树脂的固化,提高环氧树脂的耐热性和耐老化性,这也为较低成本代价下提高环氧树脂的性能提供了新的途径。对木质素进行环氧化处理,可以在

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尿素-乙二醛树脂的优化合成及其 对大豆胶黏剂的改性

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摘要:当前人造板工业化应用的无甲醛添加大豆胶黏剂主要是由环氧氯丙烷-聚酰胺多胺(PAE)树脂改性脱脂豆粕所得,由于交联剂PAE的原料价格昂贵,导致大豆胶黏剂的成本较高。为降低大豆胶黏剂成本以促进其在木材工业中的广泛应用,笔者以价格较低的尿素(U)和乙二醛(G)为原料,优化制备一种无甲醛添加大豆胶黏剂使用的新型交联剂尿素-乙二醛(UG)树脂,通过傅里叶变化红外光谱(FT-IR)表征、热重分析、溶胶-凝胶测试以及胶合性能评价,确定G/U摩尔比对大豆胶黏剂的结构和胶合性能的影响。结果表明:通过乙二醛与尿素反应产物残留醛基与大豆蛋白胺基之间的反应,UG能对脱脂豆粕进行有效交联,从而改善胶黏剂的耐水性能;G/U摩尔比对UG改性剂的结构以及改性大豆胶黏剂的交联密度、胶合性能和热稳定性有着重要影响,以G/U摩尔比为2.0时所合成UG树脂具有最佳胶合性能,但G/U摩尔比为1.6时具有适宜的耐水性能和更低的原料成本。所优化的UG树脂改性大豆胶黏剂,其耐水性能完全满足国家标准GB/T 9846—2015《普通胶合板》中的II类胶合板的要求,而交联剂UG树脂的原料成本比当前工业化大豆胶黏剂所用的PAE树脂降低了43.8%。

关键词:尿素-乙二醛树脂;交联改性;大豆胶黏剂;胶合性能;合成摩尔比

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Optimal synthesis of urea-glyoxal resin and its crosslinking modification on soybean-based wood adhesive

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Abstract: Formaldehyde-based synthetic adhesive is widely used in the wood-composite industry because of its low cost, excellent bonding strength and good water resistance. However, the formaldehyde-based synthetic adhesive is derived from non-renewable fossil resources and releases toxic formaldehyde, which results in high intention by both academia and industries to the development and application of bio-based adhesives from renewable, non-toxic and sustainable bio-resources. As a popular bio-based adhesive, commercial formaldehyde-free soybean adhesives in the current wood-composite industry are mainly prepared from the defatted soybean meal flour and polyamidoamine-epichlorohydrin (PAE) resin that is synthesized from diethylenetriamine, adipic acid and epichlorohydrin. The soybean adhesives have higher cost than other commercial adhesives such as the urea-formaldehyde resin due to the expensive raw materials for PAE. In order to reduce the cost of the soybean-based adhesive and promote its wide application in wood composites, a formaldehyde-free urea-glyoxal (UG) resin as the crosslinker for the defatted soybean meal flour-based adhesive was optimally synthesized using the low-cost urea and glyoxal. Based on the examination results from the Fourier transform infrared spectroscopy (FT-IR) analysis, thermogravimetric analysis (TGA), sol-gel test and bond-property determination, the effects of G/U molar ratio on the structures and properties of defatted soybean meal flour-based adhesives modified by UG resin were evaluated. The UG resin could effectively crosslink defatted soybean meal flour and improve the water resistance of the defatted soybean meal flour-based adhesive, attributing to the crosslinking reaction between amino groups of soybean protein and residue aldehyde groups of UG resin. The G/U molar ratio had important effects on the structures of UG resin and the crosslinking density, thermal stability and bond

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研究报告——生物质材料

射流等离子体放电气氛对木塑复合材料 表面性质的影响

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摘要: 利用空气、氮气、氧气 3 种不同气氛的射流等离子体放电对聚乙烯木塑复合材料(PE-WPC)表面进行处理以改善其胶接性能,其中空气、氮气、氧气气氛处理后的试样分别记为 PE-WPC-A、PE-WPC-N 和 PE-WPC-O。通过对剪切强度、表面接触角、表面形貌、表面官能团以及表面元素含量的测试与表征,研究了不同气氛射流等离子体处理对 PE-WPC 表面物理化学性质的影响。研究表明:射流等离子体处理可以通过改变 PE-WPC 的表面性质,进而大幅度提高材料的胶接剪切强度,由未处理样品的 0.62 MPa 提高到处理后试样的 11.32~13.79 MPa。对于胶接性能来说,不同气氛的射流等离子体处理效果差别不大;而对于处理后材料表面的微观结构,不同气氛射流等离子体的处理效果存在差别,氮气气氛处理以表面化学改性为主,在材料表面引入更多的含氮基团;氧气气氛处理以表面氧化刻蚀为主,在材料表面引入更多含氧基团;空气气氛处理则是以上 2 种作用的综合体现。

关键词: 聚乙烯木塑复合材料;表面处理;表面性质;射流等离子体放电;放电气氛

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Effect of Jet Plasma Discharge in Different Atmosphere on Surface Properties of Wood-plastic Composites

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Abstract: The surface treatment of polyethylene wood-plastic composite(PE-WPC) was carried out to improve the adhesion properties by jet plasma discharge in three different atmospheres of air, nitrogen and oxygen, respectively. Among them, the samples treated with air, nitrogen and oxygen atmosphere were labelled as PE-WPC-A, PE-WPC-N and PE-WPC-O, respectively. The effect of different atmosphere jet plasma treatment on the surface properties of PE-WPC was studied by using shear strength test, contact angle test, surface morphology observation, Fourier transform infrared spectroscopy(FT-IR) analysis and X-ray photoelectron spectroscopy(XPS) analysis. The results showed that the bonding shear strength of PE-WPC was improved obviously after the surface treatment of jet plasma discharge due to the change on the surface properties for the PE-WPC, which was increased from 0.62 MPa to 11.32-13.79 MPa. For the bonding strength, there was slight difference between the jet plasma discharges in different atmospheres, and for the surface microstructure of the treated PE-WPC, there was evident difference between the jet plasma discharges in different atmospheres. The plasma discharge in pure nitrogen atmosphere was mainly surface chemical modification, which introduced more nitrogen-containing groups on the surface of PE-WPC. Surface oxidation etching was dominant in oxygen atmosphere jet plasma treatment, which introduced more oxygen-containing groups on the surface of PE-WPC. The jet plasma discharge in air atmosphere was combined with the above two effects.

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