

Research Status and Prospect of Polyvinyl Alcohol Film

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Abstract

The unique advantages of polyvinyl alcohol (PVA) film in environmental protection, degradability and other aspects make it a hot spot of current research. It is a common goal at home and abroad to develop new production process and prepare PVA film with excellent performance. In this paper, the advantages, characteristics, types and main uses of PVA film are described in detail. The development of production technology and market prospect of PVA film in recent years are analyzed. The development status and application trend of PVA film are summarized.

Keywords

PVA; Film; Production process; Application; Overview.

1. Introduction

Although the use of many new materials makes human life more convenient, it also brings a lot of pollution waste, thus accelerating the deterioration of the environment. With the increasingly prominent problems of energy and environment, the research and development and production of degradable materials have attracted people's extensive attention. It is an extremely effective way to solve the problem of environmental pollution, and it will play an important role in human survival, health and development. The research of degradable materials is a new field which integrates environmental science, polymer chemistry and medical research. Its development and application have been paid more and more attention by the government, enterprises and scientific research institutions^[1-6].

Polyvinyl alcohol film has excellent microbial decomposition performance, can be decomposed into carbon dioxide and water, does not pollute the environment, but also has some unique properties, can meet the various requirements of various industries for the film, so it has caused a boom in development and application at home and abroad. The common production method of polyvinyl alcohol industrialization is to polymerize vinyl acetate into polyvinyl acetate, and then alcoholysis. The physicochemical properties of PVA vary with the degree of saponification and polymerization. The solubility of PVA in water depends on alcoholysis degree and polymerization degree, especially alcoholysis degree. During the alcoholysis of polyvinyl alcohol, the hydrophobic vinyl acetate group (CH₃COO-) in the molecule decreases, while the hydrophilic hydroxyl group (HO-) increases, so the partially alcoholized PVA shows that[7-9]. With the increase of alcoholysis degree, the number of hydrophilic hydroxyl groups, the hydrogen bond association between hydroxyl groups, and the crystal part which is difficult to be immersed in water increase correspondingly, so it does not show cold water solubility but warm water solubility. On the contrary, when the alcoholysis degree is low, PVA is difficult to dissolve in water because the proportion of nonpolar groups in the molecule increases. Therefore, for the processing of PVA film, PVA resin with different alcoholysis degree, crystallinity and polymerization degree should be selected according to its different use requirements^[10]. In recent

years, some companies in Japan and Europe and the United States have made breakthroughs in the development of PVA films, creating favorable conditions for the wide application of PVA films. With the special requirements of barrier, transparency and packaging in China, PVA film industry has further developed. Therefore, the advantages, characteristics, types and main uses of PVA film are described in detail, and the production process development and market prospect of PVA film in recent years are analyzed.

2. Properties, types and applications of PVA films

2.1 Properties of PVA films.

PVA film has excellent biocompatibility and degradation, which can be decomposed by microorganisms in nature, and the degradation speed is fast, which can completely solve the problem of packaging waste treatment. The degradation mechanism of PVA can be divided into two steps: the first step, PVA dissolved in water can be decomposed by bacteria in the soil to produce secondary alcohol oxidase (SAO), under aerobic conditions, PVA hydroxyl is oxidized to ketone compounds. In the second step, pva-oh, under the action of PVA secondary alcohol hydrolase (BDH), generates intermediate degradation products such as - COOH and - CH₃, and PVA molecular chain breaks gradually. The fatty acid compounds produced are absorbed into the cells by microorganisms for digestion, as the nutrients for their own growth, and finally excluded from the body by microorganisms in the form of carbon dioxide and water. Polyvinyl alcohol film has very excellent antistatic performance, which will not cause electrostatic dust problems like other packaging films.

In the dry environment, polyvinyl alcohol film has excellent barrier to oxygen and nitrogen, can completely maintain the composition and smell of packaging products, has strong permeability to water vapor, is extremely advantageous to packaging products prone to produce water vapor, and can avoid the formation of fog drops on the inner surface of packaging film. However, the barrier property of the film will change with the change of the relative humidity of the environment. With the increase of the relative humidity of the environment, the water vapor transmittance will increase greatly, and the barrier rate of oxygen and nitrogen will decrease, which will affect the quality of the packaging products. Therefore, it is necessary to explore the relationship between the barrier property of PVA film and the relative humidity of the environment, so as to improve the basis for the rational use of PVA film packaging products with selective barrier of different gases.

The mechanical properties of PVA film are better, with higher tensile strength, tear strength and impact strength. With the increase of humidity, the modulus of elasticity and tensile strength decrease, but the elongation increases because the film becomes more flexible under the action of water molecules. Polyvinyl alcohol film as a packaging material needs to have good heat sealing performance, which can achieve the effect of product protection. The film can be resistance heat sealed and high frequency heat sealed. PVA film has good oil resistance and can be used to pack oil food. In addition, the film is resistant to all organic solvents except DMSO, and can be used for packaging chemical raw materials and intermediates. Polyvinyl alcohol film has excellent printing performance and strong film polarity. It can be printed directly. Clear characters and patterns can be obtained by conventional printing methods.

2.2 Types of PVA films.

PVA film can be divided into water-soluble PVA film, insoluble PVA film and biaxially stretched PVA film according to the polymerization degree, alcoholysis degree and processing method of PVA resin. The water-soluble PVA film is processed by partial alcoholysis PVA resin with alcoholysis degree of about 88%. Because the macromolecular chain contains a certain volume of vinyl acetate, which hinders the molecular chain from approaching each other, and weakens the association of hydrogen bonds between hydroxyl groups on the molecular chain, so that there are more hydroxyl groups interacting with water, so it has higher or lower alcoholysis degree than PVA Well, the film is also excellent. Through slight heat treatment, the crystallinity of the films can be adjusted slightly, and various kinds of soluble films from cold water soluble to warm water soluble can be obtained.

Insoluble PVA film is a kind of UN stretched film with strong water resistance. It usually contains about 10% polyol plasticizer, and its thickness is 20-70 μ m. It is processed by polyvinyl alcohol resin with polymerization degree more than 1000 and alcoholysis degree more than 98%. The film has good transparency, high glossiness, no electrostatic charge, strong toughness, moisture permeability, oil and organic solvent resistance, and good printing performance.

As a result of stretching, the cohesion between molecules of biaxially stretched PVA film is enhanced, the mechanical strength is improved, and the strength and toughness are similar to that of cellophane. It can be compounded with other films into two, three or more layers of composite films to meet the needs of food packaging. In addition, biaxially stretched PVA film has the best gas resistance, including O₂, CO₂, N₂, SO₂, H₂S and other gases; its dimensional stability, heat resistance, cold resistance, transparency, glossiness and other aspects are significantly improved compared with those of other production methods; it is suitable for vacuum aluminum plating, gas replacement packaging, vacuum packaging, Deoxidizer packaging, etc.; it can also be used for polyester molding Release film and agricultural film.

2.3 Applications of PVA films

Due to many excellent properties of PVA film, it has been widely used in various fields, the market is very broad, so it has been widely valued by developed countries in the world. However, due to the complex process of PVA film, the development of PVA film in China is still relatively slow, and foreign products have a great impact on the industry. This requires us to fully understand, determine and locate the production and development direction of PVA film in the future. Therefore, it is of great significance to understand the new trend of PVA film application at home and abroad. It has been nearly 30 years for foreign countries to study this field, and their research and production have been ahead of our country. For example, the United States, Canada, Brazil, Germany, Japan and other countries have made different progress in the development and application of PVA films.

In recent years, Japan, the United States and other advanced countries have adopted the new technology of pesticide packaging. The main principle is to use a new type of environmental PVA film as the packaging material, and pack the large packaging products into small film packaging. Due to the unique properties and environmental protection characteristics of PVA plastic film, it is widely valued by developed countries in the world. PVA pesticide environmental protection packaging bag has the following advantages: (1) the water-soluble speed can be designed and selected. Non toxic, pollution-free, cold water soluble. (2) It can greatly reduce the impact of toxic or irritant substances such as pesticides and industrial chemicals on human body and environment. (3) It can effectively solve the problem of increasing production and transportation costs due to heavy glass bottles, as well as the waste caused by the loose sealing of bottle plugs, easy leakage and difficult recovery. (4) It has excellent oil resistance, fat resistance and organic solvent resistance. (5) Good anti-static performance, packing powder, will not absorb powder and dust. (6) The measurement is accurate, so as to avoid excessive or insufficient use of pesticides, which may lead to enhanced resistance of pests and pathogens. Based on the above characteristics, PVA pesticide environmental protection packaging bag is quickly recognized by pesticide manufacturers all over the world, and widely used. 2) PVA medical packaging laundry bag environmental protection medical packaging bag is a new environmental protection product developed in Europe and America in recent years. The aim is to avoid contamination and cross infection between medical staff and patients. In the past 30 years, a large number of infectious medical wastes have been produced in the process of nursing hospital patients. The commonly used packaging materials for waste disposal often contact with pollutants. Therefore, it is likely to contain pathogenic bacteria and infectious substances. If the pollutants are dissolved in the disinfection medium, it is easy to treat them, and it can greatly reduce the burden of landfill and incineration, and at the same time eliminate the pollution of bacteria and infectious substances to the environment and human body. In recent years, it has been widely used in Europe, America and other developed countries, and found that PVA environmental protection medical packaging bag produced by PVA environmental protection material has ideal wear-resistant and

environmental protection characteristics. PVA environmental protection medical packaging laundry bag has the following advantages: (1) once packed, the contents will not touch the outside during the process of self handling, cleaning and drying, and will be completely isolated. (2) The film of packing bag is completely dissolved in water, without residue, and the water quality is not polluted. (3) Due to the high barrier of water-soluble medical packaging bags, it can ensure that medical personnel are not infected by bacteria and viruses during the handling process. (4) Water soluble medical packaging bag has the properties of anti-static, non-toxic and thorough degradation. A large number of experiments have proved that bacteria and viruses can not penetrate the film, which is very conducive to medical packaging. 3) The packing cement additive of cement additive has strong alkali, strong acid and high concentration. It is usually used outdoors. It is easy to touch workers' eyes, skin and pollute the environment due to the influence of wind dust. In the past, workers used to wear appropriate protective equipment to avoid being polluted by cement additives, which brought great inconvenience to construction operation. If pollutants touch the body, it is easy to cause harm to human body. In recent years, the western developed countries have widely used PVA film packaging cement additives, completely avoid pollution, simple operation, accurate measurement.

Based on the excellent characteristics of PVA film, such as good transparency, high gloss, non-static, strong toughness, oil resistance, organic solvent resistance, and good printing performance, it can be used in the following fields: 1) temporary protective packaging of transport products; 2) packaging of electronic components and anti dust pollution, such as: packaging of high-performance dry batteries; 3) manufacturing of polarizers of LCD; 4) packaging of textiles ; 5) protective film on metal surface; 6) composite film with polyethylene, polypropylene, nylon, polyester, polycarbonate, etc. 7) When unsaturated polyester, epoxy or other thermosetting resins are used to make automobile parts, tanks and other articles, PVA film can be used as a kind of film remover with excellent performance; 8) PVA film can be used as a food fresh-keeping film with excellent performance because of its excellent oxygen barrier and air permeability.

3. Production process of PVA film

PVA is a kind of polyhydroxy polymer. Because of its regular structure, strong hydrogen bond and high crystallinity, the melting temperature of PVA is higher than the decomposition temperature, so it is difficult to process. Since the appearance of PVA film in Japan in the early 1960s, the main production methods of PVA film include solution casting, water melt extrusion, anhydrous melt extrusion, water melt extrusion blow molding, continuous biaxial orientation and dry extrusion blow molding. The characteristics of solution casting are high precision, transparency and glossiness. At present, most PVA films on the market are produced by tape casting. However, the low concentration of solution, low production capacity, high equipment cost, large floor area, high labor intensity and high energy consumption of workers in this production method limit the popularization and application of PVA film.

In order to reduce the viscosity of PVA resin melt and increase its plasticity, proper amount of water, glycol and glycerol were added into PVA resin. After melting and defoaming, the film is formed by extrusion, film making and heat treatment of T-head. The equipment and operation conditions of the water melt extrusion method and the solution casting method are different. The water solution concentration of the raw resin used in the water melt extrusion method is high, and the production capacity is improved accordingly. The PVA resin was heated and melted, extruded by T-head, and then quenched to form film. The PVA film produced by this method is cooled immediately after extrusion at high temperature, so the transparency and glossiness of the film are good, and the production speed is fast, and the thickness of the film is easy to adjust. However, this method is only suitable for thin films which are easy to be oriented in the forming process, and the equipment cost is high.

The PVA solution with water content of 20% - 60% was extruded from the ring head after extrusion and mixing, then blown, dried, and then rewound to produce the film with water content less than 7%.

The strength, stability and appearance of the film prepared by this method are better than those obtained by T-head. In order to solve the problem of producing PVA film by continuous biaxial drawing process, people combined the tube method with biaxial drawing process to produce PVA film successfully. Given the initial deformation and longitudinal orientation under the optimum humidity and temperature conditions, it is possible to achieve the best orientation balance of PVA film by adopting the continuous biaxial orientation process. In addition, high temperature heat treatment can improve the crystallinity and other physical properties of PVA film, such as the decrease of equilibrium water content and the increase of dimensional stability under various humidity conditions.

After vacuum drying for 24 hours, PVA, plasticizing modifier and film forming agent are mixed evenly in a high-speed mixer according to a certain proportion, and then extruded and pelletized by a modified single screw extruder, and then defoamed and blown, and the product is obtained after finalizing treatment. The dry extrusion blow molding method not only retains the excellent properties of PVA, such as permeability resistance and biodegradation, but also has the advantages of simple process, low energy consumption, high efficiency and low investment compared with the wet process and casting process technology. At the same time, PVA can be used in the production of multi-layer coextrusion composite films and injection molding hollow containers. This technology is innovative, fills the gap of PVA melt processing technology in China, widens the application field of PVA resin, and has a good market prospect.

4. Conclusion

PVA film is a product with high technology content and high added value. No matter in the selection of raw materials or in the process of processing and consumption, it does not or does not release any toxic and harmful substances, which is conducive to environmental protection and green consumption. It is an environmentally friendly product with good application prospects. In recent years, domestic PVA film products are in short supply. According to experts, the global average annual growth rate of PVA film in the next few years is 8% - 10%. Therefore, investment in PVA film project can not only promote the application of PVA film in China, but also have good economic benefits. With the new round of accelerated development of China's economy, the consumption of PVA film in environmental protection materials, packaging and other industries will continue to increase. For PVA film industry, we should see the existing problems and the gap with the international level; we should increase and accelerate the investment in science and technology, expand the production scale, and continuously launch products suitable for the market demand; we should develop high value-added products, improve the competitiveness of the international market, and promote the development of PVA film industry in China.

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