

Research Article

Polyurethane Adhesives Used in Food Packaging Materials

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Abstract: Aim of the study is to introduce the development of polyurethane adhesive in food packaging materials. Research and application of polyurethane adhesive in food packaging materials is summarized; solvent-free and water-based polyurethane adhesive are highlighted, the merits and demerits are analyzed and the research and development tendency of products are also discussed, which provide technical basis for convenient foods.

Keywords: Food packaging materials, solvent-free polyurethane adhesive, solvent-based polyurethane adhesive, water-based polyurethane adhesive

INTRODUCTION

Polyurethane adhesive has rapidly developed since German industrialized over the past 60 years, with excellent adhesion, outstanding oil resistance, abrasion resistance, low temperature resistance and other characteristics (Lu and Sun, 2006). Solvent type polyurethane adhesive and various types of thin film has good wettability; the reasonable adjustment of the z formula can basically meet the temperature, resistance to boiling, resistance to erosion and other performance requirements. But the risk of fire and explosion is not in conformity with the increasingly stringent environmental regulations (Yan *et al.*, 2009). Now the overall development trend of polyurethane adhesive is to the high solid content, low toxicity, non-toxic solvent or no solvent and functional adhesive development (Du and Meng, 2005). Waterborne polyurethane adhesive composite packaging materials in the production process has not harmful solvent volatilization and eliminates the residual solvents fundamentally. And Waterborne polyurethane adhesive can reduce the cost in the production process easily (Liu *et al.*, 2008). So water based polyurethane is the most suitable food packaging adhesive. With the development of economy and the improvement of living standard, food packaging industry is developing rapidly. As the single film cannot satisfy the special requirements of food packaging, therefore, the composite films in packaging materials are increasingly welcomed and the amount of demanding of adhesives matching with them is increasing accordingly, among of which polyurethane adhesive is the largest (Ye, 2011). Polyurethane is a

kind of block copolymers with oligomer polyols being soft segment and isocyanate and chain extender being hard segment. There is carbamate bond, ester bond, urea bond as well as other polar bonds in its chemical structure (Li *et al.*, 2010), which endows it with excellent adhesion property and film forming property. Owing to the favorable mechanical property, service performance, heat-resistance property and high hygienic safety (Xu, 2010), polyurethane adhesives has been widely used in soft packaging materials, especially in instant food field.

The objective of this study is to present the development situation and existing problems of polyurethane adhesive in food packaging materials and to find the research and development tendency for the future, which is solvent-based adhesive is replaced by environmentally friendly adhesive.

MATERIALS AND METHODS

Experimental data, methods, formula as well as theoretical results, from several years of research in the subject recently, are presented and compiled in order to support conclusions.

RESULTS AND DISCUSSION

Polyurethane adhesives develop from solvent-based adhesive originally to solvent-free polyurethane adhesive and water-based polyurethane adhesive recently. However, that will result in environmental pollution and safety problems for solvent-based adhesive. For example, organic solvents are flammable

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explosive and poisonous, so they will result in air pollution. Moreover, during the production process of solvent-based adhesive, emission of solvents will not only pollute air and do harm to workers' health directly, but also a small fraction of solvents, remaining in packaging materials, cannot be removed thoroughly, which will damage the consumers. With the attention on food safety and the enhancement of people's awareness of environmental protection, solvent-based polyurethane adhesive will gradually withdraw from market and most adhesives in food packaging are transiting from the solvent-based one to solvent-free and aqueous polyurethane adhesives. The earliest adhesive used in food packaging in China is aromatic polyurethane manufactured in Shanghai, 1981, which is synthesized with aromatic isocyanate (toluene diisocyanate or diphenylmethane 4,4'-diisocyanate) being raw material. However, very tiny free monomer (TDI or MDI) as well as low molecular mass compounds decomposing from polymer adhesive can penetrate into food molecular through interior packaging material and will hydrolyze into aromatic amines. According to the research reports of National Cancer Institute, aromatic amines TDA and MDA which TDI or MDI hydrolyze into are carcinogenic. From the early 1980s, it is forbidden for steamed and boiled foods to use composite packaging materials manufactured by aromatic polyurethane adhesives. Therefore, the US and EU countries began to seek safe and healthy adhesives to process composite food packaging materials and Chinese researchers also made a lot of work in this field.

The promotion of public awareness of environment protection prompts people to develop solvent-free polyurethane adhesives for the composite film which is normally a two-part adhesive that constitutes of low-molecular weight polyol and polyisocyanate, or isocyanate prepolymer and polyalcohol or polyamine. Solvent-free polyurethane adhesives for the composite film have 100% solid content and do not exist solvent evaporation, so there is no need to remove the solvents in drying tunnels. Its production is environmentally-friendly and its application range is much wider, composite strength is better and it is more energy-saving than coextrusion films and hot-melt adhesives (Zhang *et al.*, 2010). Nevertheless, its technology and product quality for solvent-free composite film has not been widely recognized, the main problem is low initial adhesion, small stripped strength, high defective index and some equipment failures cannot be resolved. So solvent-free adhesives are not extensively used. Wang *et al.* (2010) utilized adipic acid, isophthalic acid, diethylene glycol, neopentyl glycol and butanediol as raw materials to synthesize polyester polyol, then polymerized with isocyanate to synthesize adhesives, which can be widely used in food packaging because solvent-free adhesives do not exist in solvent

evaporation. Yang and Ji (2013) synthesized castor oil modified polyester polyol with castor oil, phthalic anhydride and diethylene glycol being raw materials through esterification and polycondensation, which acts as curing agent of laminating adhesives, MDI and polyether glycol as raw materials to prepare solvent-free adhesive.

Water-based polyurethane was first successfully synthesized by German scientists Schlack in 1943, which means that adhesives formed in the way that polyurethane dissolves in water or disperses in water and mostly in emulsion and dispersion. As water-based polyurethane is used water as medium, so it is non-toxic, environmentally-friendly and low-cost (Yan and Fu, 2011; Yan *et al.*, 2008). In recent years, a lot of researches have been carried out and great progress has been made aiming at slow drying rate, poor wettability for non polar substrates, low initial viscosity and bad water resistance of water-based polyurethane adhesives (Qiao *et al.*, 2006). Chen *et al.* (2008) prepared stable aqueous modified polyurethane adhesive emulsion by copolymerization reaction with aqueous polyurethane emulsion and acrylic ester, which shows good storage stability and excellent mechanical properties. Polyurethane emulsion modified by acrylic acid is not only endowed with superior tensile strength, impact strength, flexibility and wear resistance of polyurethane, but also with good adhesive force and low cost of acrylic acid (Li *et al.*, 2000), as a result of which Polyurethane emulsion modified by acrylic acid is deemed as "the 3rd generation of aqueous polyurethane" and has a bright prospect in packaging and adhesion materials in food and medicine fields. Liu *et al.* (2010) prepared water-based polyurethane adhesive modified by acrylic ester and the adhesive strength, water resistance and heat resistance has obviously improved. Hu *et al.* (2009) prepared aqueous polyurethane with emulsion toluene diisocyanate (TDI), 1,4-diisocyanate(HDI), polyester diol(N-56) and Polyoxypropylene Propylene-Glycol (PPG) being main raw materials and it has good comprehensive performance. Research results show: if solid content increases to above 50%, it will have similar drying rate as ordinary polyurethane solvent adhesive when dried at 40~60°C. Wang *et al.* (2012) etc uses ester monomer emulsion process, which has the advantage of simple process, high bonding degree, safety and environmental protection, making polyurethane emulsion and acrylic ester monomer emulsion process synthesize waterborne polyurethane composite film emulsion.

But water-based polyurethane adhesive is poor coatibility and low adhesive force. In addition, as the heat capacity of water is large, which limits the product rate, increases production cost, meanwhile, water vapor leads to erosion of equipment.

The developing tendency of polyurethane adhesive overseas is to explore environmentally-friendly and safe sanitary solvents, aiming at the enhancement of comprehensive adhesion property and developing new varieties of functional and structural adhesives. Furthermore, the tendency of solvents used in polyurethane adhesive abroad mainly contains three kinds: water-based modified adhesive, hot melt adhesive, 100% liquid-reacted adhesive. Among of them, water-based modification has developed rapidly in western Europe countries and its type is typically aliphatic isocyanate, with good properties but expensive price that is 2~3 times as general polyurethane adhesives. Hot-melt polyurethane adhesive is rapidly developing in Japan and American etc., several hot melt polyurethane adhesives from some companies have come into market. 100% liquid-reacted adhesive is mainly applied in adhesion of plastic shell of cars, ships, household appliance and production line of composite films. Huang *et al.* (2016) prepared biodegradable polyurethane acrylates using isophorone diisocyanate, polycaprolactone glycol, hydroxyethyl acrylate and dibutyltin dilaurate under suitable reaction conditions.

Wu and Chen (2016) uses ϵ -caprolactone and dimethylol propionic acid to synthesize in low temperature liquefied dimethylol propionic acid. They succeed in synthesizing a series of waterborne polyurethane using liquefied dimethylol propionic acid and analyze them. Analysis of the polyurethane show: with the increase of liquefied dimethylol propionic acid content, the tensile strength and the elongation of the samples increased first and then decreased. The introduction of liquefied dimethylol propionic acid can reduce the degree of micro phase separation of aqueous polyurethane, which leads to the decrease of its mechanical properties. Although the mechanical properties of lwpu are slightly worse, lwpu is easy to be prepared and environmentally friendly and has very broad.

CONCLUSION

With the development of society and the rising of public awareness of environment protection, it is the inevitable tendency that solvent-based adhesive will be replaced by environmentally friendly adhesive, solvent-based adhesive will be gradually replaced by the adhesive with atoxic, low toxic high solid content and low viscosity in food packaging field. Solvent-based adhesive is still the leading products of multi-layer flexible packaging material. Therefore, it will be an important way for the future of polyurethane adhesive towards the environmental friendly direction to improve and perfect water-based polyurethane adhesive, solvent-free polyurethane adhesive and reactive hot melt

adhesive. Additionally, water-based polyurethane adhesive and solvent-free polyurethane adhesive will be popular research focus in the future.

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