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Investigations on properties, types and existing problems of thermal stabilizers of polyvinyl chloride

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Abstract. Polyvinyl chloride is comprehensively utilized around the world for its use in various fields. However, it is sometimes thermally unstable so the addition of thermal stabilizers is indispensable. This paper investigates the properties and extant problems of lead salts, organotins, metal soaps, rare earths and organonitrogen thermal stabilizers, which are vital in preventing the degrading process. In detail, in this article, the literature review method and comparative method are used and some examples of experiments are given to study the thermal stability, light stability, colorability and environmental friendliness of heat stabilizers, and also analyze their mechanisms on polyvinyl chloride thermal decomposition respectively for the purpose of introducing the efficacies of these thermal stabilizers and provide foundation for future development. Investigations have shown that thermal stabilizers can reduce the degradation rate of polyvinyl chloride through their respective structural superiorities and therefore need to be thermally stable, photostable, highly lubricating, non-toxic and non-hazardous.

Keywords: Polyvinyl chloride, Thermal stabilizer, Property, Problems

1. Introduction

As is well-known, polyvinyl chloride (PVC) is one of the world's largest-produced plastics, only second to polyethylene and polypropylene in terms of its wide range of applications. Polyvinyl chloride is a macromolecule material derived from the addition polymerisation of vinyl chloride which is white and brittle as a pure form. However, due to its structural defects, polyvinyl chloride has a lack of thermal stability-generating hydrogen chloride continuously and forms conjugated double bond systems, and this is an obstacle that cannot be ignored when processing at high temperatures. As a result, scientists have developed a variety of thermal stabilizers hitherto to compensate for this thermal decomposition, the more common on the market are lead salt, organotin, metal soap, rare-earth and organonitrogen stabilizers. This paper aims to study the effect of different thermal stabilizers on the thermal stability of PVC by analyzing their properties, advantages and disadvantages on the environment, production costs, and reaction effectiveness to draw comparative conclusions. In this paper, we mainly use the literature analysis method, review method and comparative analysis method, by describing the structure of polyvinyl chloride and its thermal decomposition mechanism, corresponding it to different kinds of heat stabilizers and combining with the previous experiments. Therefore, this paper will be crucial to the popularization of social-economical benefits and the application value of polyvinyl chloride.

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2. Overview of polyvinyl chloride

2.1. Current status of polyvinyl chloride

Polyvinyl chloride is a synthetic resin first discovered by French scientist Henri Victor Regnault and first made on a large scale by a German company through emulsion polymerization. At present, the widely used production methods are the calcium carbide method and the ethylene method. Based on its preponderances in properties like mechanical, non-corrosive and flame retardant, it is widely used in architecture, communication technology, agriculture and other industries.

2.2. Molecular structure

PVC is formed from the addition polymerisation of its monomer chloroethene in the situation of ultraviolet (UV) light by free radical reaction with the repeating unit -CH2-CH(CH3)- and is therefore an artificial chain-growth polymer[1]. During the reaction, the carbon-carbon double bonds in chloroethene break down to form more stable single bonds instead. Nevertheless, at above 140 Celsius degrees, some defective structures such as branched chains, unsaturated end groups, tertiary chloride, etc, will degrade to release hydrogen chloride gas and result in unsaturated conjugated systems. Then a vicious cycle occurs as those hydrogen chloride (HCl) will contingently catalyze the conjugation[2].

2.3. Mechanism of thermal decomposition

The thermal decomposition mechanism of PVC is mainly divided into three types, free radical mechanism, ionic mechanism and single molecule mechanism[3].

The free radical mechanism consists of three processes- initiation, propagation and termination. In initiation, with the presence of UV light and heat, chlorine atom as a free radical is released so as the polymer itself. In propagation, due to homogeneous fission, the chlorine free radical has a single electron, which contributes to the detachment of hydrogen on beta-carbon to form HCl and a new chain radical. In termination, the new chain radical is so unstable that it will continue to strip chlorine atom (Cl) and produce conjugated double bonds. This theory is the most comprehensive.

The ionic mechanism proposes a viewpoint about bond polarity. As chlorine is highly electronegative to carbon, it will draw electrons towards itself, making carbon more positive. Subsequently, the beta-carbon is relatively negative and there will be an attraction between chlorine and the relatively positive hydrogen in the neighbouring position. Finally, this interaction promotes dehydrochlorination and the increased electron cloud deriving from emerging double bonds will exacerbate this phenomenon.

The single-molecule mechanism suggests that the thermal decomposition reaction follows molecular kinematics, starting with a four-membered ring (CH-CH-H-Cl) and adding new hydrogen atom (H) and Cl to form a six-membered ring to dehydrochlorate.

3. Properties, types and problems of thermal stabilizers

3.1. Functions and basic conditions of thermal stabilizers

The function of thermal stabilizers is mainly to maintain and enhance the advantageous properties of PVC, such as electrical conductivity, photo-thermal properties, and minimizing colouration problems.

Several conditions for thermal stabilizers are introduced:

First, they should substitute the chlorine atoms to minimise the release of HCl.

Second, their intrinsic structure should possess the ability to absorb HCl that is already detached from the polymer to mitigate further decomposition.

Third, the destruction of the conjugated polyolefin system by slackening the amount of double bonds is required. This behaviour is imperative in the inhibition of darker colour development.

Fourth, they are expected to assimilate free radicals for depression of the induction of the conjugated system[4].

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Those functions provide an idealised thermal stabilizer such that is non-realistic in daily life. However, through the cooperation of various modes of regulation, it is possible to manufacture more effective thermal stabilizers.

3.2. Types of thermal stabilizers and their impact on PVC

Current developments in thermal stabilizers have been successful hence a synthesis of diverse types. Lead salts, organotins, metal soaps, rare earths and organonitrogen stabilizers are analyzed in detail below.

3.2.1. Lead salt thermal stabilizer. Lead salt heat stabilizers were most widely used in the early days, which have been developed over 70 years, attributed to their superior heat resistance, light resistance, electrical insulation and lubricity, as well as being inexpensive and easy to colour. Therefore, it plays a significant role in the production of industrial PVC rubber. The commonly used lead salt stabilizers are classified into the following four types, tribasic lead sulfate, dibasic lead phthalate, dibasic lead stearate and dibasic lead phosphite[5]. During the reaction, they can absorb the HCl released and neutralise free radicals by changing the oxidation state of lead (2+) to lead (4+), thus producing lead chloride at the same time[6]. This product is non-reactive to those conjugated double bonds and free radicals, therefore restricting the process of self-decomposition. For UV shielding purposes, the example is dibasic lead phosphite, which inclines to antioxidation, therefore is an excellent application on UV absorbers and antioxidants. Some complex lead salts can also be enhanced by the addition of lubricants, such as metal soaps, a discovery that has led to more uniform dispersion of heat stabilizers in PVC, which makes it easier to quantify and increase production scale.

3.2.2. Organotin thermal stabilizer. Organotins, usually Sn4+, have the structural formula RnSnY4-n. R group always refers to methyl, butyl and octyl groups and Y often includes organic acids and thiols. Butyltin and octyltin will be formatted to produce alkyltin chlorides before binding to the anion, whereas methyltin is more straightforward, and more prevalent these days[1]. More specifically, each R group can be divided into cinnamates, maleates and thiols[6]. Similar to lead salts, organotins can easily absorb HCl from decomposition and form allotropes with unstable chlorine atoms in the long-chain polymer. After that, the chlorine atoms and conjugated double bonds can be displaced. Organotins have favourable heat resistance, transparency, and light stability, and can inhibit PVC colouring. Among them, thiol organotin is the most effective because it not only specialises in inhibiting colouration, but also generates the product organotin chloride that contributes no reaction to HCl. Maleate organotin is less useful on those two properties, but it can combine with heavy metal additives and represents better weathering performance. One benign point is that organotins are usually considered low toxicity, so they are quite environmentally friendly for adoption.

3.2.3. Metal soap thermal stabilizer. Metal soap thermal stabilizers, as advanced fatty acid metal salts, can be classified as chelating and ionic. The more common metal bases are calcium, barium (ionic), zinc, and cadmium (chelating), etc[7]. The reaction mechanism is largely identical to other stabilizers. It is capable of absorbing HCl escaping from degradation and replacing chlorine atoms with fatty acid roots under the catalytic effect of metal ions, thus reducing the activity of chlorine ions and preventing the continuous generation of conjugated structures[8]. One peculiarity is that metal soaps can mix up to elevate properties. For instance, a calcium/zinc composite system can be prepared under basic conditions according to Xibao Zhang when zinc nitrate hexahydrate, calcium chloride and acetylacetonate are used to synthesize calcium/zinc acetylacetonate composites[9]. The result of this experiment surprisingly showed a prolonged time for PVC to turn black. It has also been verified that calcium/zinc thermal stabilizers can increase the initial decomposition temperature of PVC, therefore restraining the decomposition process to an extent. In general, those thermal stabilizers are non-toxic, lubricating and contribute no negative externalities to sulfide contamination except cadmium, and they occupy the forefront due to benign thermal stability, light stability and transparency.

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3.2.4. Rare earth's thermal stabilizer. Rare earth's thermal stabilizers are synthesised by rare earth metals and fatty acid salt, such as stearic acid rare earth, neodymium trichloride, salicylic acid rare earth, etc[10]. They can undergo the following mechanisms. First, since rare earth metals are alkaline, they tend to react with HCl in an acid-base neutralization reaction, so it will greatly reduce the concentration of HCl and stabilize the overall system. Second, rare earth metal ions as central atoms always have empty d-electron orbitals to accept lone pairs from ligands, which enables the chelation between them and chloride ions. Lanthanum, for example, there is only a subtle difference in energy levels of 4f, 5d, and 6s orbitals, so it is possible for lanthanum ions to form up to 12 lone pair electrons and corresponding bonds[11]. Meanwhile, due to the large radius of lanthanum ion, it is easier to accept more ligands without steric hindrance. This stabilized structure results in increased intermolecular forces, improved plasticity, and a tighter, more compatible overall structure. Rare earths also absorb UV rays and have a certain degree of light transmission, thus ensuring the transparency of PVC. More predominantly, the complex structure promotes molecular polymerization and makes the polymer chain grow, which plays a role in enhancing product performance while removing impurities.

3.2.5. Organonitrogen thermal stabilizer. Organonitrogen thermal stabilizers belong to organic thermal stabilizers and can mainly be separated into urea, pyrimidine and cyanoguanidine. The earliest research began with barbituric acid, N.A.Mohamed found that the substance can absorb HCl very well, by the replacement of chlorine atoms by hydrogen atoms, thus stabilizing the PVC mechanism[12]. For the urea thermal stabilizer, it tends to displace chlorine atoms but more struggles to absorb HCl straightforwardly. This was conjectured to come from the electrophilicity of carbon-carbon bonds and therefore can be improved by inserting more electronegative groups. Pyrimidines are phenyl ureas with an amino group, such as 6- amino -1,3- diphenyl uracil, and in its comparison with 2,5-diphenyl-1,3,4-oxadiazole, it was found that the former has a more prominent effect on the thermal stabilization of PVC by the Congo red test and the heat ageing test[12]. This is because the metal ions can chelate with the atoms in the heterocyclic ring in the presence of other metal stabilizers such as zinc/calcium complexes. The higher the concentration of nitrogen, the more evident the effects on PVC. Cyanoguanidine, spiritlessly, is less remarkable to PVC so the addition of other reagents is necessary.

3.3. Comparison of problems between stabilizers

Although there has been great progress in thermal stabilizers, each of them remains self-defect to be researched and resolved. The most rigorous problem of lead salts is the toxicity they preserve that poses a threat to human health. What's worse, the lack of transparency limits them on the application of transparent or half-transparent PVC commodities. Organotins are expected to be ideal but some sulfur-contained organotins are less environmentally responsible and quite stinky. They are also too expensive to experience economies of scale. Metallic soaps usually play a significant role only if they work together, but the thermal stability of a single substance is mediocre. There is also zinc burn in calcium/zinc thermal stabilizer, which will cause blackening and charring. Rare earth heat stabilizers have similar drawbacks to metal soaps in that they are prone to colouration and suffer poor lubrication dispersion when used alone and therefore have discounted long-term stability. Organonitrogen thermal stabilizers seem to have the potential for development, which has the advantages of green environmental protection. However, cyanoguanidine is less thermally stable, while its transparency is better than 6-amino-1,3-dimethyluracil.

4. Conclusion

This paper focuses on the effects of various types of thermal stabilizers on the thermal stability of PVC and briefly describes their respective strengths and weaknesses. In summary, The function of heat stabilizers is to displace chlorine atoms and absorb HCl, preventing the catalysis of further conjugated structures, while changing the colourable nature of PVC. However, to date, it has not been possible to develop a thermal stabilizer that combines all desirable properties. Lead salts contain toxic heavy metals

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and are not resistant to vulcanization; metal soaps and rare earths are difficult to use on their own; organotins are sulfurous and expensive; and different organic nitrogen species vary in performance. Where this paper lacks is the lesser use of data analysis and further solutions for these problems. Therefore, future research can focus on how to compensate for the shortcomings of a single heat stabilizer and move towards a more economical, efficient, non-toxic and environmentally friendly direction of sustainable development.

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