

Application of Colloid Theory in Urea Formaldehyde Resin

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Abstract: Urea formaldehyde resin is an end-stage thermosetting resin in which urea and formaldehyde are polycondensated into an initial urea formaldehyde resin under the action of alkaline or acidic catalyst, and then an insoluble and non-fusible resin is formed under the action of curing agent or additives. Urea formaldehyde resin has the characteristics of colorless curing adhesive layer, good operation performance, low cost, good bonding performance and water resistance. Its use in the field of wood bonding is increasing. The cured urea formaldehyde resin is lighter in color than phenolic resin, translucent, resistant to weak acid and alkali, good insulation, excellent wear resistance and low price. However, urea formaldehyde resin is easy to decompose in case of strong acid and alkali, and its weather resistance is poor. There is a problem of formaldehyde emission in the manufacturing and use of wood-based panels produced by urea formaldehyde resin, so it must be modified. At present, urea formaldehyde resin is the largest adhesive used in wood industry, especially in the manufacture of various wood-based panels in wood processing industry, urea formaldehyde resin and its modified products account for about 90% of the total amount of adhesive. In this paper, the development and application of colloidal theory in urea formaldehyde resin are introduced, and the significance and Prospect of this theory are prospected.

Keywords: Urea Formaldehyde Resin, Colloid, Formaldehyde, Molar Ratio, Crystal, Settlement

1. Introduction

Urea formaldehyde resin, also known as UF resin adhesive, is the condensation polymerization of urea and formaldehyde into initial urea formaldehyde resin under the action of catalyst (alkaline or acidic catalyst), and then form insoluble and non fusible end-stage thermosetting resin under the action of curing agent or assistant. Urea formaldehyde resin (UF resin) was first synthesized by B. Tollens in 1844 and first applied after the research of C. gold Schmidt around 1896. In 1929, Ig company developed a UF resin condensation intermediate named kanritleim and can cure glued wood at room temperature, which attracted people's attention. Since then, the use of UF resin as an adhesive for manufacturing plywood and particleboard has expanded rapidly. In particular, UF resin has the characteristics of colorless curing adhesive layer, good operation performance, low cost, good bonding performance and water resistance, and its use in the field of wood bonding is increasing. The cured urea formaldehyde resin is lighter in color than phenolic resin, translucent, resistant to weak acid and alkali,

good insulation, excellent wear resistance and low price. However, urea formaldehyde resin is easy to decompose in case of strong acid and alkali, with poor weather resistance, poor initial viscosity, large shrinkage, brittleness, water resistance and easy aging. There is a problem of formaldehyde release in the manufacturing and use of wood-based panels produced by urea formaldehyde resin, so it must be modified. At present, urea formaldehyde resin is the largest adhesive used in wood industry, especially in the manufacture of various wood-based panels in wood processing industry, urea formaldehyde resin and its modified products account for about 90% of the total amount of adhesive [1-3].

Although UF resin is a kind of adhesive developed and applied earlier, due to the complex chemical reaction in the synthesis process of UF resin, it is difficult to determine the structural characterization of reaction intermediates and reaction end points. Up to now, people have not formed a unified understanding of the synthesis reaction mechanism [4].

2. Classical Theory of Urea Formaldehyde Resin and Its Existing Problems

The traditional view is that the synthesis of UF resin is usually carried out by two-stage reaction. The first stage carries out hydroxymethylation reaction under neutral or alkaline conditions, and the second stage polycondensates under acidic conditions. When the molecular weight reaches a certain degree, adjust the pH value of the reaction solution to 8 ~ 9 to obtain the initial condensation solution of UF resin. As for the reaction conditions and products of urea and formaldehyde, according to the research of Zigeuner, Fahrenhorst, Glauert and kadowaki, the generally widely recognized reactions are as follows. The reaction of urea and formaldehyde under alkaline conditions is the reaction of monohydroxymethylurea and dihydroxymethylurea. Under special conditions, trihydroxymethylurea or tetrahydroxymethylurea can also be produced when formaldehyde is excessive [5].

The molecular growth is caused by this condensation reaction to form an oligomer containing hydroxymethyl, which is used as an adhesive. Moreover, the curing of the adhesive is carried out under acidic conditions, and the resin further condenses to form giant molecules with three-dimensional structure. Under special conditions, intramolecular condensation also occurs to form a cyclic compound Uron.

Therefore, according to the classical theory, before curing, UF resin is a polydisperse polymer formed by alternating and repeating substituted urea and methylene or a small amount of dimethyl chain links. Depending on the reaction conditions, there are different degrees of hydroxymethyl or short branched chains on the molecular chain. During curing, these molecules react with -NH- to form -CH₂- cross-linking, forming a three-dimensional network structure. The classical theory has not clearly described the molecular morphology of UF resin. It is generally believed that due to the existence of hydroxymethyl branched chain, the resin should be in a disordered state of water-soluble or water dispersion. However, many problems in the properties of UF resin and the production process of UF resin cannot or are difficult to explain by classical theories. These problems are as follows [6-8]:

- 1) UF resin has unstable hydrolysis and formaldehyde smell. Liquid or solid UF resin is often milky white and opaque. Other formaldehyde series resins such as phenolic resin are resistant to hydrolysis and have no formaldehyde smell. Although they have color, they are transparent.
- 2) Typical UF resin can separate 35% solids by ultracentrifugal sedimentation, and the particles separated from the liquid phase are spherical.
- 3) Transparent UF resin can be synthesized or centrifugally deposited. When it is placed for a period of time, it will become mixed or dingy phenomenon will appear.
- 4) The cured product of thermosetting resin is glassy and

the fracture surface is smooth, while the cured UF resin has crystalline structure and its fracture surface has spherical structure.

- 5) Due to the above problems, the classical theory of UF resin is challenged. Therefore, some scholars put forward the colloidal theory of UF resin to better explain the structure and reaction process of UF resin.

3. Colloidal Theory of Urea Formaldehyde Resin

Colloid means that the size of dispersed particles is 5nm-1 μm. Dispersion system between. The molecular size of polymer compounds is close to or within this range. When polymer compounds are lipophilic, they are lipophilic colloids or polymer true solutions. If polymer compound becomes hydrophobic, it is hydrophobic colloid. The particle dispersion system of hydrophobic colloid has high specific surface and surface energy. It is thermodynamically unstable, and its stability depends on the attraction and repulsion between particles.

In 1983, Pratt and others first proposed the theory of UF resin colloid theory at the annual meeting of WSU adhesives. They believed that UF resin was linear polymer and formed colloidal dispersion system in water. When colloid stability was destroyed, colloidal particles coagulated and settled, and UF resin solidified or gel. The stability of UF resin is due to a layer of formaldehyde molecular adsorption layer or protonated formaldehyde molecular adsorption layer around the particles. When the colloidal particles condense, formaldehyde or hydrogen ions are released. Therefore, they put forward three important facts to support their theory: (1) during the curing process, the viscosity change of UF resin is discontinuous. (2) to make UF resin cured or gel, the concentration must exceed a minimum limit. (3) SEM showed that there was granular structure on the fracture surface of the cured UF resin [9].

In the analysis of the influence of the solid content of phenolic resin and UF resin on the gel time, it can be seen that the relationship between the gel time and the solid content of the phenolic resin obviously conforms to the classical condensation polymerization theory, while the UF resin is different. When the solid content is less than 40%, the solidified UF resin has no cohesion. Granular solid latex can not be hard solid particles or gel for reheating for several hours. This shows that the curing of UF resin requires a minimum concentration extreme value, and this minimum value decreases with the decrease of particles. The stable latex can be filtered out from the UF resin cured in dilute solution, and the shape seeking small particles are obviously formed by the aggregation of smaller rubber particles. Obviously, this kind of phenomenon cannot be explained by classical theory. From SEM photos, it can be seen that the cured structure of high concentration UF resin is different from other thermosetting resins and has granular nature. Its curing process is indeed the coalescence process of hydrophobic colloidal particles [10].

4. Configuration and Conformation of Urea Formaldehyde Condensate

After Pratt, dunker et al. Skillfully used the similarities between glycine polypeptide and UF resin model compound methylene polyurea to apply some knowledge of protein chemistry and its treatment methods to the configuration and conformation analysis of UF resin molecules, which provided a basis for the nucleation process of UF resin colloidal particles. The brief introduction is as follows:

¹³C-NMR analysis of UF resin with low molar ratio shows that there are few dimethyl ether links, so it is of practical significance to use methylene polyurea to represent the condensation product of UF resin. The following four conclusions can be drawn from the comparison of glycine polypeptide and methylene polyuria [11-13]:

- (1) When glycine, formaldehyde and urea form polymer compounds, they lose water molecules and reduce the solubility of polymers in water. If the curing of UF resin is a colloidal particle coalescence and sedimentation process, its solubility is required to be continuously reduced during the formation of urea formaldehyde polymer. Dunker believes that when two glycines form methylene, they lose two molecules of water and four hydrogen bonds. When urea and formaldehyde form methylene, 2 molecules of water are lost, that is, 8 hydrogen bonds are lost. Therefore, the formation of UF resin is the same as that of protein, and the solubility decreases gradually during the polymerization process.
- (2) Both peptide bond and substituted urea have planar configuration, which makes the configuration of urea formaldehyde polymer similar to that of protein. Because the polypeptide is in the electron pair plane of C=O. However, their dipole moments are different. The peptide group is 3.7d and the urea group is 4.6d. The rotational energy barrier caused by conjugation is 15-20kcal / mol. therefore, the peptide group is either trans or CIS. Due to steric hindrance, trans is dominant. Although urea group has two amide groups and there are two parts of double bonds with three configurations during conjugation, trans is dominant from the perspective of spatial loading model.
- (3) Steric hindrance and possible hydrogen bonds. After the plane configuration is determined, the Ramachandran diagram can be used to determine its steric resistance. The steric hindrance of the two polymers is similar. The conformational entropy of both polymers is smaller than that of free rotating polymers, which is conducive to the development of ordered structures in advanced structures. It has been found that proteins have two ordered structures, forming two hydrogen bonds, namely α - Intramolecular hydrogen bonds in helix and β - Intermolecular hydrogen bond in sheet structure. In urea formaldehyde molecules, although intramolecular hydrogen bonds and intermolecular hydrogen bonds can also be formed

due to the large steric hindrance of urea group, it is difficult β - Spiral sum α - Sheet structure.

- (4) Protein folding and possible urea formaldehyde molecular folding. Protein α And β The structure has been confirmed by protein chemistry, but this kind of folding of urea formaldehyde molecule has not been confirmed, but the above results are deduced theoretically, which still needs to be proved. Considering the release of bound water and dipole moment during folding, urea formaldehyde molecules are easier to form this advanced structure than glycine peptides.

According to the above analysis, urea formaldehyde molecule uses all hydrogen bonds within or between molecules, so it has stronger hydrophobicity. It can be explained that urea formaldehyde molecules polymerize to a certain extent to form nuclei insoluble in water colloidal particles. The Raman spectrum analysis of the cured UF resin with low molar ratio showed that there were no water molecules in the cured product. After curing, the resin has crystalline diffraction phenomenon, which also indicates the existence of colloidal ordered structure of UF resin.

Johns et al. analyzed the conformational characteristics of urea formaldehyde condensate by computer according to the law of minimum energy and using macromodel software package. This treatment is extended to long-chain methylene polyurea with branched chain CH₂OH.

The trimer is treated with two force fields. The main chain introduces hydroxymethyl, which is generally considered to increase the solvation ability, but it shows that the hydroxymethyl also forms an intramolecular hydrogen bond, which makes people believe that formaldehyde has a stabilizing effect on colloidal particles.

The lowest energy treatment by filling prepolymer showed that urea formaldehyde condensate formed an ordered tubular structure from four molecular chains. It is worth noting that hydroxymethyl has no effect on the tubular structure. It can be seen that linear or -CH₂OH branched urea formaldehyde condensate can be ordered to achieve a stable structural state.

The above theoretical derivation shows that UF resin has the conditions and possibility of colloidal particle nucleation, and the conformation or advanced structure of urea formaldehyde condensate should also be verified by experiments [14].

In order to confirm the existence of colloidal phase in UF resin, the nucleation process and growth of colloidal phase must also be suggested experimentally. Motter described the development process of precipitated phase in UF resin by TEM and SEM. The UF resin was analyzed by GPC technology, melting point determination method and X-ray diffraction technology. The size of colloidal particles in the clear liquid of centrifugal classification is 15-120nm. It is a mixture of basic particles and primary aggregates. It is clear that the primary aggregates are formed by the aggregation of basic particles, and the size of aggregates in the clear liquid has nothing to do with the storage period. The storage period of the settling phase becomes longer, and its particle

size becomes larger. Based on the above experimental results, the formation and development of UF resin particles can be obtained, which explains the colloidal nature of UF resin. X-ray diffraction also showed its crystal structure. It shows that polymethylene urea is the nucleus of the settling phase. GPC data show that the polymer part of UF resin has almost no change in the later stage of storage, and the increase of its viscosity is mainly due to the increase of the volume of dispersed phase, which is in line with the colloidal theory [15].

The above analysis and experimental structure shows that the main component of the settling phase is methylene polyurea with urea as the end group and containing 4-8 substituted urea. These polymers are formed by monomer reaction and are the source of sedimentation phase development. Through coalescence, the basic particles develop into primary coalescers, and then develop into secondary coalescers. In this way, they coalesce, settle and solidify. The colloidal essence of UF resin with low molar ratio was confirmed.

5. Conclusion

The colloidal theory of UF resin was put forward in recent years and has not been widely recognized in the world. The main reason is that the theory explains the problems and phenomena in the synthesis and curing process of low molar ratio UF resin clearly, but it needs to be confirmed for high molar ratio resin. However, at present, low molar ratio UF resin plays a leading role in industrial production, so the colloidal theory of UF resin is of great significance in practice.

According to the classical theory, the residual formaldehyde in the curing process and the formaldehyde hydrolyzed by the resin are the formaldehyde emission sources of UF resin. According to the colloid theory, the colloid releases formaldehyde in the condensation process, which is helpful to the stability of the colloid. However, whether the use of some other substances to protect colloids can replace and solve this problem needs to be explored.

In addition, colloidal theory also gives a new understanding to the properties, modification ways and interpretation of UF resin. Adding salt to UF resin can not only improve its curing speed, but also reduce its cost. Colloid theory explains this method: adding salt makes the double ion layer of colloidal particles thinner, colloidal particles unstable and coagulation accelerated, and satisfactorily explains the small change of pH value in the process. It can be seen that colloid theory has a new understanding of a series of properties of UF resin. Therefore, understanding the nature of these resins and being familiar with the principles of colloidal chemistry are of great significance to solve the above problems.

Conflicts of Interest

The author declares that he has no competing interest.

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