Research and Development of Microwave Irradiation Technology in Polymer Synthesis

Xuelian Bai\textsuperscript{1,a} and Zhongguo Mu\textsuperscript{1,b}

Department of Underwater Weaponry and Chemical Defence, Dalian Naval Academy, Dalian, 116018, P. R. China
\textsuperscript{a}email: baixueian1971@163.com, \textsuperscript{b}email: muzhongguo-9@163.com

Abstract. The research status of microwave irradiation technology in polymer synthesis was reviewed. The application of microwave irradiation technology in bulk polymerization, emulsion and solution polymerization and functional polymer synthesis was introduced. In the aspect of polymer microwave curing, the microwave curing of epoxy resin and its composites is mainly introduced, and the microwave curing of other polymers is briefly introduced. Finally, the development trend of microwave technology in the future is discussed.

1. Introduction
Microwave application in chemical synthesis reaction began in 1986, Canadian R. Gedye et al. studied the esterification of benzyl alcohol and acid by microwave irradiation, and revealed the sequence of chemical synthesis by microwave. Starting from the date of the study, microwave synthesis has become research focus in the field of chemical synthesis. especially in the field of polymer synthesis more shows great potential for development. Microwave heating is the bulk heating caused by dielectric loss, and its energy is transmitted in the form of electromagnetic waves through space or media. With traditional high-energy radiation such as ultraviolet ray, r, compared with microwave on the depth of the effect of polymer, no damage, protection of macromolecular chain easy, has the advantages of the operation is simple, clean, safe, efficient.[1] Compared with traditional heating synthesis with easy temperature control, no heat effect, thermal gradient is small, the characteristics of material mechanics performance.[2]So the microwave method has become one of new means of synthetic polymer.

2. Microwave Application in Polymerization
2.1. Application of Microwave in Bulk Polymerization
Microwave is used for bulk polymerization. Many polymerized monomers are polar molecules, which have strong absorption effect on microwave and can be directly polymerized under microwave radiation. Joaquin Palacios et al.[3] from Mexico carried out bulk copolymerization of methyl propionic acid and one-difference ethyl methacrylate under microwave radiation. The polymerization reaction was completed in a short time and the high rate was obtained. Lu Jianmei et al. made polar maleic anhydride difficult to polymerize occur solid phase polymerization under microwave radiation. Low temperature solid phase polymerization makes post-treatment simple and reaction time greatly shortened. Chen[4] et al. used AIBN/CuBr\textsubscript{2}/2,2 pyridine/CH\textsubscript{3}CN and AIBN/CuCl/bPY as initiators to study the free radical polymerization of poly (methyl methacrylate). The results showed that microwave irradiation not only increased the polymerization rate, but also reduced the polydispersibility of the polymer in comparison with traditional methods, and the amount of catalyst...
was also reduced. Adinana[5] etc were studied a variety of monomers(ethylene propylene acid ester, styrene and methyl methacrylate and acrylonitrile) free radical bulk polymerization with nAIBI and phenoxy peroxide as catalyst, the study found that under microwave irradiation conditions, the rate of polymerization reaction only depends on the monomer structure, has little relationship with the microwave power, irradiation time and the heating mode. Philipp abbert et al found that microwave open-loop polymerization of ε-hexolidide can occur under the catalysis of tetrabutyl titanate, and its mechanism involves cationic polymerization and anionic polymerization. The results showed that the characteristic viscosity of the polymer was different in comparison with the tradition heating polymerization, and there was no significant difference in other polymers (such as relative molecular mass size, relative molecular mass distribution, etc.). YU[6] et al used carboxylic acid as initiator to prepare ε-hexanolactone by microwave irradiation. This reaction did not require metal catalyst under the effect of microwave. The polymerization increased significantly. When the chloroaetic acid is used as the initiaor in the process of microwave polymerization, degradation products can be found. It can inhibits degradation by using benzoic acid as the initiator.

2.2. Application of Microwave in Emulsion Polymerization
Zhu[7] studied the emulsion polymerization of methyl methyacrylate under the condition of pulse microwave irradiation. The research results show that the reaction rate of microwave irradiation method is faster than that of traditional methods at the same dosage of initiator. The relative molecular mass of the product is higher. When the pulse frequency is low, the average relative molecular mass of polymer is higher, it also illustrate that the pulse microwave polymerization of methyl propylene acid methyl ester is non-thermal effect, the microwave product and the traditional product have different physical properties and thermal performance. Zhang wenmin[8] et al. studied the microwave emulsion polymerization of polymer microspheres, and prepared various dispersible microspheres by means of polystyrene, polymethyl methacrylate and other polymer. The dispersible polymer microspheres prepared by microwave method had many advantages such as uniform heating, rapid reaction, small size and wider distribution of microsphere size.

2.3. Application of Microwave in Functional Polymer Synthesis
Microwave irradiation is widely used in the synthesis of liquid crystal polymer, medical polymer, optical material and conductive polymer.

In the field of the synthesis of liquid crystal polymers, H. Andersson[9] et al. had synthesized a monomer which contains both electron donors (ethylene oxide) and electronic acceptor (maleimide gel). This monomer can be directly polymerized and transform into nematic liquid crystal polymers without initiator under the condition of microwave irradiation,. Hurdue N[10] studied phase transfer polymerization by means of microwave heating, the product has characteristics of liquid crystal polymer, the whole reaction don’t need stirring, and the reaction time is shortened markedly.

The application of microwave is mainly used to prepared artificial teeth materials in medical field. The synthesis of denture by microwave method is mainly based on acrylic adhesives. The synthesis of denture by microwave method should not only be rapid in reaction with few monomer residues, but also have accurate and durable structure.

In optically conductive polymers, Shadpoar[11] et al. synthesized poly (ether-washing imide) and poly (amine-imide) with optical activity by microwave irradiation. Comparing with the traditional method, Microwave method is simpler and easier. The reaction can be finished quickly, internal viscosity is extremely low, The prepared optical material has good optical performance. O Cankmak[12] etc prepared the 2,4,6- fluorine sodium phenol polymer by microwave irradiation. The conductivity of the polymer is 0.3scm, and It can be used as a conductive polymer material. Luo zhexiang[13] synthesized the conductive polymer of phenyl phenylamine by microwave irradiation. The microwave product was not different from the traditional product in conductivity.

In addition, microwave irradiation has also been applied in the synthesis of high-temperature aromatic polymers. Yoshio[14] et al. rapidly synthesized heat resistant polyamides and polyimides with salt monomers and amino acids as raw materials in a household microwave oven. It is believed that the rapid synthesis of polymers is caused by the heat stored in the reactants.
3. Application of Microwave in Curing Reaction of Thermosetting Resin

The microwave curing reaction of polymer is mainly aimed at the microwave curing of epoxy resin, polyester polyurethane and other thermosetting resins and their composites.

3.1. Microwave Curing of Epoxy Resin

Microwave curing of epoxy resin is the most studied topic of polymer microwave curing. There have been a lot of literatures in this aspect. The epoxy/curing agent systems studied include primary amine, tertiary amine, sulfone, imidazole, anhydride and so on.

In terms of microwave curing of epoxy/primary amine systems, F. Y. C. Boey [15,16] et al. studied the effect of curing agent on the glass transition temperature of epoxy/primary amine systems, with DDS, DDM, mPDA as curing agent. The results show that the epoxy system with DDS as curing agent has the highest curing percentage and largest $T_g$. It is caused by relatively slow reaction between the DDS and epoxy, in contrast, DDM and mPDA system have stronger reactivity, compared with thermal curing. Microwave curing can shorten reaction time and is more effective in reducing mPDA system total cure time. Yarlagada[17] studied the microwave curing of different types of bisphenol-A epoxy resins with iso-formaldehyde and cyclohexylamine as curing agents. The results showed that the bending properties and vitrification transition temperature of microwave curing products were higher than those of thermal curing products. Gu xiaoli[18] used DDM, DDS and imidazoles as curing agents to study the microwave curing of epoxy, and found that the microwave curing rate was faster. Zhong fachun[19] et al. prepared polyamide/epoxy foam material by microwave method with water as the foaming agent. The material has excellent compression performance and good resistance.

Epoxy/tertiary amine system is studied even later in comparison with epoxy/primary amine system. The microwave curing reaction of epoxy/tertiary amine is very severe, and the curing products can only be obtained by intermittent irradiation. The microwave curing process of epoxy/ethylene triamine was studied by the method of intermittent microwave irradiation. Mu zhongguo et al. studied the intermittent microwave curing of epoxy/DMP30 system, determined the best process of microwave curing reaction, and analyzed the curing process and product structure by infrared spectroscopy, and compared the mechanical properties of thermal curing products and microwave curing products. The results showed that the curing speed was significantly increased and the bending property of microwave curing product is higher than the thermal curing product, and the impact property is slightly lower.

In terms of the microwave curing of epoxy/anhydride system, Wu ke[20] et al. studied the microwave curing conditions of epoxy/anhydride system, the mechanical properties and thermal properties of the microwave curing system. Zhou[21] et al. studied the microwave curing of epoxy E-44/maleic anhydride system, and showed that microwave curing could significantly shorten the curing time. The mechanical strength of microwave curing product was higher than that of microwave curing product, but its break elongation and deflection were lower.

The progress was made in microwave curing of epoxy composites, and its research mainly focuses on epoxy/glass microspheres, the epoxy/silica, the epoxy/glass fiber and epoxy resin/graphite system. S. L. Bai[22] et al. studied the interfacial properties of microwave curing compound. Based on the analysis of experiment results and the observation of the damage and failure process, it can be seen that the microwave curing compound has stronger fiber-matrix interface than the heat curing compound. C.Y.YUE[23] et al. studied the influence of thermal and microwave processing on mechanical and interfacial properties of glass/epoxy composites. Chawasakoo[24] added fly ash treated with coupling agent into the epoxy resin prepolymer, and took isofurone as curing agent to study microwave curing and thermal curing of the system. The results show that microwave curing shortens the reaction time and improves the mechanical strength and fracture strain of the system. Lu xianxiao et al. prepared the water acoustic gradient functional material of epoxy resin/razor clam by microwave irradiation. Chem minghua studied that the microwave curing of carbonized fiber/epoxy system. The results showed that the microwave curing time was short and the shear strength of the product was high. Sgruccia[25] et al. studied the microwave curing of different kinds of natural fiber/epoxy resin composite system. The results showed that the curing degree of linen fiber/epoxy composite system was the highest under microwave irradiation. Wang et al. studied the microwave
curing of epoxy conductive adhesive filled with metal powder under the action of frequency conversion microwave. Comparing with single-frequency microwave, the application of variable frequency microwave curing is less likely to cause local overheating and burning. Yalagaddala[26] has studied microwave curing of aluminum powder/epoxy systems and has concluded that curing time and temperature depend on the amount of aluminum powder and curing agent. Liu xueqing and Ding tao et al. studied the phase structure, compatibility and thermal expansion performance of microwave cured epoxy/phenol terminated polyurethane system, and found that microwave curing could improve the compatibility between epoxy and polyurethane components, while the thermal expansion performance of microwave curing products was slightly reduced.

3.2. Other Thermosetting Polymer Research
In addition to epoxy resin and its composite material, Other thermosetting polymer microwave curing has also made certain progress, Its research mainly focuses on unsaturated polyester, bimaleimide, pulse aldehyde resin and so on. H. KU[27] discussed the microwave curing of vinyl ester resin. The results showed that microwave curing could significantly reduce the shrinkage of resin. Qin yan et al. studied the microwave curing characteristics of unsaturated polyester resin, and found that the gelation time of the resin was significantly shortened by microwave method, and the mechanical properties and thermal properties of the resin were not different from the thermal curing products. Alazard[28] et al. studied the microwave curing reaction of unsaturated polyester resin and determined the optimal reaction conditions by measuring the glass transition temperature of curing products. Zainol[29] studied the effects of microwave curing and thermal curing on bimaleimide resin. The results showed that the vitrification temperature of the thermal curing product was higher than that of the microwave curing product. Zhao qiong et al. substituted glucose for formaldehyde and synthesized green and environment-friendly glucose biuret resin adhesive similar to urea formaldehyde resin under acidic conditions by microwave method, and obtained the optimal reaction conditions by orthogonal experiment. Compared with the traditional method, microwave method can improve the curing speed and has a wide application prospect.

4. Conclusion
Although microwave irradiation has shown potential application value and prospect in the field of polymer synthesis, the research on the mechanism of microwave action is not clear enough and the factors affecting microwave heating are not well understood. Due to the limitations of existing microwave processing devices, the microwave synthesis of most polymers is still limited to the laboratory research stage, and it is difficult to achieve large-scale production. The existence of these problems has affected the progress of polymer microwave synthesis to some extent. In the future, the microwave synthesis of polymers well focus on solving these problems and develop towards the following aspects:

1. Strengthening the research on the mechanism of polymer microwave polymerization; the kinetics of microwave synthesis is studied. The influence of microwave power, pulse frequency and pulse mechanism on microwave synthesis are studied. The influence of microwave non-thermal affect on polymer synthesis is studied.

2. The relationship between microwave irradiation process and polymer material structure, morphology and mechanical properties should be studied. The great effort is made to realize the optimization design of microwave synthesis process and product properties.

3. The relationship between polymer structure and microwave absorption characteristics is further studied, and the molecular design is organically combined with the microwave irradiation process.

4. The more efforts will be made in improving the polymer microwave irradiation device, selecting more suitable polymer microwave synthesizers, strengthening the safety and scale expansion of the device research in order to achieve the industrialization of polymer microwave synthesis technology.

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