

Research Article

Research on the New Polymeric Plasticizer for the Food Industry

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Abstract: Aiming at researching on the new polymeric plasticizer for the food Industry, this study attempts polycaprolactone synthesis and study its optimal synthesis conditions. Polycaprolactone is a type of polyester plasticizer, it has good compatibility with the polymer properties and has excellent flexibility, processability and thermal stability. So it has been widely used in various fields of biodegradable materials and food industrial materials such as plasticizers. Through a single factor test to determine the synthesis of polycaprolactone optimum conditions are: 0.2% zinc acetate catalyst in the reaction system, the reaction 4 hours 120°C. Infrared, gel chromatography and a series of characterization methods are carried to figure out the structure and molecular characterization of polycaprolactone. The results show that the synthesized product is indeed the target product polycaprolactone.

Keywords: Food industry, polymeric plasticizer

INTRODUCTION

Some commonly used thermoplastic polymer having a glass transition temperature above room Temperature (T_g), at this temperature or higher, the polymer showed a greater flexibility, elasticity and impact strength; at this temperature, the glass exhibits the similar brittle state. The glass transition temperature of the polymer must be reduced to below the temperature before using practical value. To solve this problem, we introduced a class of polymer additives, such additives called plasticizers. Mode of interaction between the plasticizer and the polymer can be seen as both (Pommet *et al.*, 2005):

- As the resin molecule dipole-dipole interaction counteract gravity resin molecules correspondingly weakened;
- By a simple dilution effect, reduce the distance between the resin molecules, thereby forming a certain space. The results of the softness of the plastic article and the beginning of the impact strength are enhanced.

Therefore, the main function of the plasticizer is to weaken the secondary bonds between the polymer molecules, i.e., van der Waals forces, thereby promoting the mobile polymer chains to decrease the crystallinity, is a plastic polymer is increased. Specific performance: polymer modulus, hardness, brittleness temperature and softening temperature drops, flex, flexibility and elongation rate.

In order to have a good ductility of the polymer, as a plasticizer must be compatible with the resin material

or a certain dissolution of the resin. Most of these materials are low melting point solids or high boiling point organic liquid. Commonly used with phosphate or valerate, sometimes the use of epoxy compounds, halogenated hydrocarbons, ethers, hydrocarbons and the like. Broadly speaking, any resin can be uniformly mixed, does not produce any chemical reaction with the resin and the molding process remains the same; or can react with the resin, but can remain in the long polymers and enables some physical properties of the polymer material changes, may be referred to as a plasticizer (American Society, 2006).

Plasticizer is a kind of plastic used to increase the polymer resin, giving products softness additives, is currently the largest consumption of polymer production aids category. The main application for conventional plasticizers in polyvinyl chloride and a cellulose-based resin, but the other polar polymers are also widely used (Vieira *et al.*, 2001). Depending on the chemical structure of the plasticizer varieties so far should the city include phthalates, aliphatic dicarboxylic acid esters, trimellitic vinegar, polyol esters, Azusa lemon vinegar, phosphate esters, poly the chemical structure of type ester, epoxy fatty acids and their esters, phthalate plasticizers which yield maximum consumption, accounting for almost 70% of the total amount of the plasticizer. However, based on the environmental and health and safety reasons, to limit the century requires a global scale since the 1990s the use of phthalate plasticizers cries constantly, environmental protection, health, sustainable phthalates plasticized agents reported research and development of alternatives abound.

Therefore, the purpose of this paper is to study the development of alternative phthalates greater impact on the environment and human plasticizer to meet biodegradable plastic polylactic acid plasticized modified needs and to explore plasticizers plasticized process of polylactic acid.

MATERIALS AND METHODS

The selection conditions of plasticizer: A plasticizer cannot have a high plasticizing efficiency in the industrial production process, which is a plasticizer basic condition. But only with a condition that is not enough. If the product is called a plasticizer ideal plasticizer, then it must meet the following conditions should be:

- A high plasticizing efficiency, i.e., very little can be added in an amount to obtain a good plasticizing effect.
- Good compatibility with the resin, if they are not compatible, the plasticizer will be separated from the resin inside. Specific performance sweating, oozing, resin and plasticizer incompatible, then plasticizing efficiency is out of the question.
- Low volatility; reduce evaporation losses during storage products and the impact of the process of forming the product during storage as well as product performance. Wire and cable, automotive interiors and other areas of the volatile plasticizer has a higher demand.
- Durability, extracting water, oils and organic solvents and the like.
- Does not migrate, plasticizers within the article should not be spread to other solid contact with the media.
- Cold is good, which makes the resin at low temperature still has good flexibility. This is very important for agricultural products and outdoor use film.
- Heat resistance. It makes the use of the resin at high temperatures and processing temperature can remain stable.
- Non-toxic, tasteless, odorless, colorless.
- Fungal resistance, electrical insulation, flame resistance, good.
- Low price.

So far, no one plasticizer can fully satisfy all the above conditions. So, in the course of the practical application of the comprehensive consideration of various factors can only be based product application needs and price, to select the most superior product. In practice, in most cases choose two or more plasticizers, or with the use of other types of additives to be able to obtain good results. For example, in the automotive interior plastics, the need to prevent fogging, so should

choose low volatile plasticizer, such as trimellitic acid esters, plasticizers and polyester diisodecyl phthalate esters. If desired at low temperatures can still have good flexibility, it should be selected azelaic acid esters, sebacic acid esters or adipate plasticizer; if used as a food packaging material or the artificial leather at a polymer article, you should choose a good durability and non-toxic epoxy soybean oil or polyester plasticizer.

In summary, the choice of plasticizer for a polymer material, apart from a combination of factors to consider its use outside also need to consider the price, etc., in order to elect a good, suitable and economical plasticizer.

The classification of plasticizer:

Primary plasticizer, the secondary plasticizer and extender: According to the compatibility of different plasticizers and resins, plasticizers can be divided into two types of main plasticizer to secondary plasticizer. Primary plasticizer and the resin has good compatibility, not only to enter into the resin molecular chains in the amorphous regions, but also into the molecular chain of the crystalline region and does not cause blooming, bleeding and so on, may be used alone use; auxiliary plasticizer and resin compatibility is poor, the molecule can only enter the region of the molecule to the resin amorphous, crystalline regions can not be inserted, can be used and compatible plasticizer. There are some, such as chlorinated paraffin such a low price, also known as secondary plasticizer extenders.

Haplotype and polymeric plasticizers: The form of the molecular structure of the plasticizer based on it can be divided into two with the polymerizable monomer type, monomer type has a fixed molecular weight plasticizer, such as aliphatic dibasic acid esters, phosphoric acid esters, phthalic acid esters all haplotypes plasticizer. Also part of the plasticizer content of the component caused by the molecular weight range is not fixed, each consisting of a monomer which is not inside the polymeric molecules, such as epoxidized soybean oil, etc., are considered monomeric plasticizer category. In the industrial production of which, is a polymer of the polyester type plasticizer is only plasticizer, the plasticizer of such relatively high molecular weight, generally better durability.

General-purpose and special-type plasticizers: The plasticizer may be a part of commonly used, but not effect the performance of the general-purpose plasticizer is called plasticizers. Phthalates is a typical general-purpose plasticizer. In addition there are a number of plasticizer addition plasticizing effects, there are other additional features and such plasticizer is a special type of plasticizer. For example, the case of durable polyester type plasticizers, aliphatic dicarboxylic acid ester plasticizer hardy genus, the

genus phosphate flame retardant plasticizers, citric acid esters Azusa is non-toxic plasticizer, trimellitates belong heat resistant plasticizer.

Classification of plasticizers according to chemical structure: Classified according to chemical structure, the main types of plasticizers are:

- Acid esters including isophthalate, terephthalate and phthalic acid esters.
- Aliphatic dicarboxylic acid esters include adipates, sebacic esters, azelaic esters.
- Benzene multi esters, including trimellitate and pyromellitic acid ester.
- Esters of polyhydric alcohols include ethylene glycol, propylene glycol, dipropylene glycol and other glycols, glycerol, pentaerythritol esters of lower fatty acid and benzoic acid esters.
- Azusa lemon acid esters, fatty alcohols including Azusa kind of acid vinegar and citric acid esters Azusa acetylation.
- Phosphate, acetate, esters, including esters of pity, fatty alcohol phosphoric esters, chlorinated phosphoric esters and phosphoric acid mixed.
- Polyesters, polycondensation products of diol with dibasic acid, such as polycaprolactone and the like.
- An epoxy compound comprising an epoxy fatty acid esters, epoxidized oil.
- Other compounds, such as aliphatic monobasic acid ester, sulfonic acid esters, rosin esters, benzoic acid monoesters, fatty acid amides, sulfonamides, hydrocarbons, chlorinated hydrocarbons and the like.

The main factors affecting the plasticizers: Adding a plasticizer to the polymer which, when the molecule between the plasticizing influence on the crystallinity of the polymer is very large. A plasticizing effect on the polymer forces includes van der Waals interactions and oxygen bonding forces. Van der Waals forces are divided into dispersion force, induction force, orientation force. Dispersion forces exist between all the non-polar or polar molecules, due to the mutual action between minor and transient dipole-dipole impose so close to the suction generated at different poles adjacent to the state, but only in non-polar system, such as benzene, polyethylene or polystyrene, the dispersion forces will be accounted for relatively major position. When a dipole molecules another non-polar molecules among its neighbors, induced dipole-induced another when the inherent intermolecular dipole-induced dipole and called gravity between induced force.

Aromatic compounds, in the electron energy due to the height of the polarization, thus inducing very strong. Low molecular weight esters, such as inter-and polystyrene and polyvinyl acetate, or benzene, the major force is induced. Every time when the polar

molecules closes to each other due to the inherent orientation of the dipole and the force generated between the molecules causing, known orienting force. Just like polyester and PVC plasticizers interaction. Is a hydrogen group or a molecule containing -NH- -OH group, such as cellulose, polyvinyl alcohol, etc., can form hydrogen bonds between molecules (Galdeano *et al.*, 2004).

The hydrogen bond is a strong bond interaction between the polymer molecules whose presence would hinder plasticizer molecules inserted. Oxygen bond denser distribution along the molecular chain of the polymer, the more difficult plasticizer molecules corresponding insert, thus requiring similar can produce a strong interaction between the plasticizer and the polymer molecules. When the temperature increases, because the thermal motion of molecules hinder to molecular orientation the polymer, so that the effect of hydrogen will be a corresponding decrease.

Overview of polycaprolactone: Polycaprolactone is ϵ -ring-opening polymerization of caprolactone linear aliphatic polyester is semi-crystalline polymer, preferably the thermal stability, the decomposition temperature is significantly higher than the other polyesters. Meanwhile, it is a very good bio-degradable material and medical materials, the degraded product of polycaprolactone are water and carbon dioxide, which is non-toxic to the human body, therefore, polycaprolactone-a straight hot research people are. Initially, the additive can be used in polycaprolactone polyurethane, polyvinyl chloride or for a solid plasticizing agent. In recent years, along with the gradual increase public awareness of environmental protection, bio-degradable materials and more materials science has become a very active research topic among. Polycaprolactone many physical properties and general-purpose plastics are very similar and many are better compatibility with the polymer can be prepared by a variety of very good performance, or a copolymer blend. So, polycaprolactone biodegradable materials in this area have a very great value.

Polycaprolactone rigidity and relatively close to the density of the polyethylene, the color is white, with a wrong quality feel, with many types of polymers have a good compatibility. Polycaprolactone of melting point of about 6°C, a glass transition Temperature (T_g) of about -60°C, polar ester group containing one to five non-polar and its methylene repeating structural units, the molecular chain CC bond and C-O bond can rotate freely. Because with this type of construction, the softness of polycaprolactone is very good workability can be extrusion, injection molding, blown film, drawing and so on. Polycaprolactone mechanical properties and dilute hydrocarbon similar to 300-600% elongation, expansion intensity 12-30MPa. In addition, polycaprolactone and a variety of polymers can be copolymerized or blended and its thermal stability is

unmatched by other polyesters, the decomposition temperature is about 350°C, while the other polyester only 250°C. However, due to its low melting point, so that its heat resistance becomes poor, it has also become a serious limiting its development defects (Rotta *et al.*, 2009).

The Synthesis of polycaprolactone:

Synthetic method: The ε-caprolactone, ethylene glycol, or by three or pentaerythritol methacrylate, catalysts, dispersing agents according to the formula P ratio Ding flask equipped with a stirrer, thermometer, condenser spherical 250 mL four-necked flask, the stirrer, start of heating, the temperature control system does not exceed 140°C, slowly warmed reaction for 6 hours, the product was cooled to 80°C poured into a beaker, investigated the optimum reaction conditions and the molecular weight was measured under the optimum conditions of the synthesis product and IR spectra.

Determination the molecular weight of polycaprolactone:

The molecular size of the plasticizer will have a great impact on the performance of the application, therefore, is essential to control the size and distribution of the average molecular weight of the plasticizer. Because of different molecular size, so different rates through the column. Gel permeation chromatography is the separation of molecules by the application of the principle of different sizes and by detecting the spectrum obtained. The method can measure the average polycaprolactone vinegar inside the relative molecular weight plasticizer and the molecular weight distribution (Van Oosterhout and Gilbert, 2012; Galdeano *et al.*, 2011).

Gel permeation chromatography analysis using analytical instruments R1-201H Beijing temperature gel permeation chromatography, with four oxygen furan as eluent, the mobile phase THF, flow rate of 0.5 mL/min, measuring temperature 40°C, the column for three PL column in conjunction with, for refractive index detector, contrived narrow distribution polystyrene standards (Savenkova *et al.*, 2008).

The structure determination of polycaprolactone:

Infrared spectroscopy is a characterization and analysis of molecular structure is very important means of experiments using the United States PerkinElmer infrared absorption spectrum analyzer for testing, conditions and methods of measurement are as follows: wavelength range 4000-500cm⁻¹, the sample was applied in KBr scan measurement performed on a tablet (Sejidov *et al.*, 2012).

Effects of synthesis conditions on the product: The experimental conditions may have an impact on the molecular weight by changing various explore polycaprolactone synthesis optimum conditions.

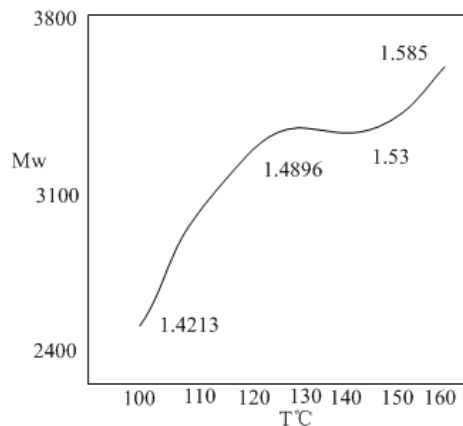


Fig. 1: The impact of reaction temperature on the molecular weight of PCL

Through single factor experiment of reaction time, reaction temperature, catalyst type and amount of product molecular weight and other factors such as performance of the situation.

The reaction temperature in this experiment is the first study conditions. Liu refining reaction conditions at 130°C 24h, to give the product polycaprolactone; reaction Daniel et 90-100°C 3h, then the reaction temperature was raised to 140-160°C 24-48 h, to obtain a molecular weight of about 3000 polycaprolactam ester; in Qiu Xia reaction at 120-200°C four h to get polycaprolactone products. The reaction temperature is too low, the reaction system activity is not enough, the reaction is extremely negative. The reaction temperature is too high will increase the variety of side effects which is shown in Fig. 1.

In this experiment, the reaction temperature is 12°C, n (ethylene glycol): n (ε-caprolactone) = 1:10, the choice of stannous octoate catalyst, the monomer added in an amount of 1%, the time of reaction was 3, 4, 5, 6 h relative molecular mass size and its distribution.

As the temperature increases, the relative molecular mass of the product has the following changes:

- Molecular weight gradually increased, starting from 120°C, changes gently, 120°C and 160°C molecular weight difference of about 250.
- Product color deepened, 100, at 120°C white, slightly yellow at 140°C, 160°C under pale yellow.
- Broadening the molecular weight distribution, because the higher the temperature, the more the side reactions. Taking all these factors, the reaction temperature selected 120°C. The influence of reaction time on molecular weight of PCL is shown in Fig. 2.

Relative molecular mass increases with reaction time after the first decrease in reaction time was 4h, the

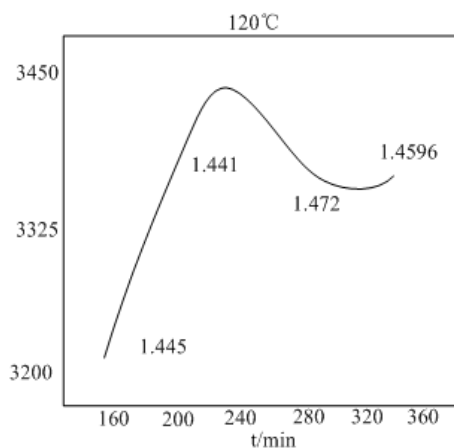


Fig. 2: The influence of reaction time on molecular weight of PCL

molecular weight of the maximum and the molecular weight distribution in the reaction of 4h minimum. This shows that, short reaction time, the reaction is not sufficient, the lower molecular weight; long reaction time, more side effects (such as transesterification, etc.), can cause a wide molecular weight distribution. Therefore, the reaction time is preferably 4 hours (Rosen, 1993).

In recent years, a lot of reports pay attention to the synthesis of poly-caprolactone, usually caused ϵ -caprolactone ring-opening polymerization catalyst used include: stannous octoate, zinc acetate and titanium tetraisopropoxide. In this study, respectively, stannous octoate, zinc acetate, isopropyl four iron as a catalyst under the same other conditions, the test three catalysts affect the reaction and determine the best catalyst and its dosage.

When 0.2% of the catalytic effect of the two catalysts, as the amount increases, the catalytic effect of the stannous octoate will get better. The amount of the catalyst was 0.2%, the synthetic product of consistent molecular weight and molecular weight distribution; in 0.3, 0.5% stannous octoate as the catalyst system, the synthesis of poly-caprolactone and its distribution is clearly higher than the molecular weight of zinc acetate, indicating that: (1) there is a certain relationship between the size and the molecular weight distribution (2) of catalyst in the case where the amount exceeds 0.2% stannous octoate for the synthesis of the side reaction (transesterification) play a catalyst.

In summary, selection of zinc acetate as catalyst and when it is used in an amount of 0.2%, the synthesis of poly-caprolactone and the theoretical molecular weight is close.

RESULTS AND DISCUSSION

The characteristics of polycaprolactone:

Gel chromatography of polycaprolactone: Respectively, with ethylene glycol, trimethyl propyl

burn pentaerythritol as the initiator, depending on the molar ratio of acetic acid as a catalyst front, in an amount of 0.2% of the total monomers at 120 °C conditions, the reaction synthesis of four hours number of different molecular weights were 404, 970,1700, 2300 arm polycaprolactone. Were recorded as 2-404, 2-970, 2-1700, 3-404, 3-970, 3-1700, 3-2300, 4-404, 4-970, 4-1700, 4-2300. Respectively, in reaction 1h, 2h, 3h, the molecular weight of the sample was measured at 4 h.

IR spectroscopy of polycaprolactone: Different numbers of arms of different molecular weight products is substantially the same IR spectrum, in which 3475/cm to the stretching vibration of the -OH shear vibration 1380/cm is -OH group. 1250/cm for the bending vibration -OH group; 2950 cm-1,2875/cm is -(CH₂)_n- stretching vibration, 1470/cm to -(CH₂)_n-plane shear vibration, 740cm⁻¹ is -(CH₂)_n- sided rocking vibration, 1300cm⁻¹ is -(CH₂)_n- non-planar vibrations; 1730/cm stretching vibration is C = O; 1190cm⁻¹ for C-O-C stretching vibration. Hence, it can be seen that the product of the polymerization reaction product was determined as the target polycaprolactone:

- Through the synthesis conditions polycaprolactone investigation and ultimately determine ethylene glycol, triple methylmalonic refining, pentaerythritol as the initiator synthetic polycaprolactone optimum conditions: temperature of 120°C, the reaction time was 4h, the catalyst for acid-feng, amount of catalyst is 0.2% initiator;
- By varying the monomer and the molar ratio of the initiator, the reaction under the optimum conditions to obtain different molecular weight polycaprolactone products. The molecular weight of the product was determined by GPC, the results obtained show a better reproducibility of the experiment;
- Infrared absorption spectrum analyzer detection, infrared spectra were basically the same and according to product analysis shows the characteristic peak of the target product was indeed polycaprolactone.

CONCLUSION

Through the synthesis conditions polycaprolactone investigation and ultimately determine ethylene glycol, triple methacrylate, pentaerythritol as the initiator synthetic polycaprolactone optimum conditions: temperature of 120°C, the reaction time is 4h the catalyst for zinc acetate, the amount of catalyst 0.2% initiator.

By changing the monomer and the molar ratio of the initiator, the reaction under the optimum conditions to give different relative points Sub polycaprolactone

quality products. GPC molecular weight determination by the product, the results obtained showed that the experimental reproducibility is better;

Infrared absorption spectrum analyzer through the detection, infrared spectra obtained consistent; described and according to the characteristic peak of the product was analyzed to obtain a target product which was indeed polycaprolactone;

As a new type of material, the degradation products of Polycaprolactone are carbon dioxide and water which is nontoxic to humans and the environment and has excellent resistance and mechanical properties of the drug-passing-through and it will have excellent performance and good prospects in biodegradable material and the food industry.

REFERENCES

- American Society, 2006. American Society for Testing and Materials-ASTM. West Conshohocken I: American Society for Testing and Materials, Standard D4274-05, 1(4): 16-22.
- Galdeano, M.C., M.V.E. Grossmann, S. Mali, L.A. Bello-Perez, M.A. Garcia and P.B. Zamudio-Flores, 2004. Effects of production process and plasticizers on stability of films and sheets of oat starch. *Mater. Sci. Eng.*, 29(2): 492-498.
- Galdeano, M.C., S. Mali, M.V.E. Grossmann, F. Yamashita and M.A. Garcia, 2011. Effects of plasticizers on the properties of oat starch films. *Mater. Sci. Eng. C*, 2(4): 32-538.
- Pommet, M., A. Redl, M. Morel and S. Guilbert, 2005. Study of wheat gluten plasticization with fatty acids. *Polymer*, 8(44): 115-122.
- Rotta, J., R.A. Ozorio, A.M. Kehrwald, G.M.O. Barra, R.D.M.C. Amboni and P.L.M. Barreto, 2009. Parameters of color, transparency, water solubility, wettability and surface free energy of chitosan/hydroxypropylmethylcellulose (HPMC) films plasticized with sorbitol. *Mater. Sci. Eng.*, 29(4): 619-623.
- Rosen, S.L., 1993. *Fundamental principles of polymeric materials*. John Wiley and Sons, Inc., New York, pp: 82-101.
- Savenkova, L., Z. Gercberga, V. Nikolaeva, A. Dzene, I. Bibers and M. Kalnin, 2008. Mechanical properties and biodegradation characteristics of PHB-based films. *Process Biochem.*, 2(35): 536-540.
- Sejidov, F.T., Y. Mansoori and N. Goodarzi, 2012. Esterification reaction using solid heterogeneous acid catalysts under solvent-less condition. *J. Molecular Catalysis A*, 2(1): 186-190.
- Vieira, M.G.A., M.A. Da Silva, L.O. Santos and M.M. Beppu, 2001. Natural-based plasticizers and biopolymer films I: A review. *Eur. Polymer J.*, 7(4): 254-263.
- Van Oosterhout, J.T. and M. Gilbert, 2012. Interactions between PVC and binary or ternary blends of plasticizers. Part I. PVC/plasticizer compatibility. *Polymer*, 12(5): 8081-8094.