丙烯酸酯预乳化半连续法乳液聚合研究

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摘　要：用半连续乳液聚合法制备不同配方的丙烯酸类合成增稠剂，进行了性能测试和流变性研究。在氨水增稠后的丙烯酸乳液增稠剂具有优良的剪切变稀性。

关键词：丙烯酸　半连续乳液聚合法　合成增稠剂　流变性
中图法分类号：TS 102.33　　**文献标识码**：A

丙烯酸类增稠剂是80年代后发展最快及常用的一种乳液聚合物增稠剂[1]，文中设计了6种丙烯酸类合成增稠剂配方，采取预乳化半连续法进行乳液共聚，合成出6个不同产品，对其性能和流变性进行研究。

1　实验部分

1.1　原料

实验前将酸类单体减压蒸馏除去阻聚剂，将酯类单体用10%氢氧化钠溶液洗涤。用K_{12}和OP—10作为乳化剂，过硫酸钾作引发剂，碳酸氢钠作缓冲剂，蒸馏水作溶剂。合成增稠剂单体有：α-甲基丙烯酸、丙烯酸、丙烯酸丁酯丙烯酸丁酯、甲基丙烯酸甲酯、丙烯酸甲酯，由以上单体设计出6个配方。

1.2　丙烯酸(酯)乳液聚合

将乳化剂、混合单体、缓冲剂和水按一定顺序加入三口瓶，剧烈搅拌50min制备预乳液。取1/4预乳液和一定量新配制10%引发剂溶液加入到装有搅拌器、温度计、两个恒压滴液漏斗、回流冷凝管的500ml四口瓶中，用501型超级恒温水浴控温60℃，进行种子乳液聚合，氮气保护。待反应液出现蓝光(大约2h)，控温70℃，缓缓滴加剩余预乳液和引发剂溶液。加完料后恒温2h，加入少量阻聚剂，然后降温出料，过滤。用重新分析法[2~3]测得乳液含固量为27%左右，各样品的最终转化率均接近100%。

1.3　乳液性能测试

1.3.1　被氨水增稠后粘度　用NHD—79型旋转式粘度计(同济大学机电厂制造)。本实验为统一标准，所测粘度均为1g乳液用20mL规定浓度氨水增稠后的粘度。

1.3.2　乳液稳定性　1)机械稳定性：称取一定量乳液，在超高速离心机上以3500r/min转速下离心1h，用离心后沉淀占所取乳液质量的百分比表示[4]。2)化学稳定性：称取乳液M，滴加一定量电解质溶液，放置48h，过滤，洗涤滤渣，烘干称重W，其稳定性用W/M×100%表示[4]。3)稀释稳定性：将30mL稀释到固含量为3%的乳液倒入试管中放置72h，用沉淀部分体积占总体积的百分比表示稀释稳定性[5]。

1.4　乳液增稠后流变性

将乳液用0.5%氨水增稠后根据简易气压式毛细管法测定[6]。

2　结果与讨论

2.1　乳液聚合时间对增稠后粘度的影响

图1是按各配方进行乳液聚合时，自加料后每间隔25min取样，然后用氨水增稠测其黏度值。从图中可以看到6条曲线虽然没有明显规律，但值得注意的是都在加完料后50min和100min之间存在着一个峰谷，并且除配方5外，其余5条曲线自加完料后125min起均有不同程度的上升趋势。根据Harklins提供的关于乳液聚合理论，可以将乳液聚合分为三个阶段[5]：乳胶粒生成阶段、乳胶粒长大阶段、聚合反应完成阶段。在50min之前，乳液中已生成大量细小的乳胶粒，故增稠后粘度较大；在100min时处于乳胶粒长大阶段，氨水的加入破坏了水相和乳胶粒间的平衡，从而粘度下降；在125min时逐渐趋于聚合反应完成阶段，故增稠后粘度升高。由此可见，在采用本工艺时，自加完料后进行乳液聚合时间不得少于2h。

2.2　氨水浓度对丙烯酸乳液聚合产物增稠粘度的关系影响

图2和图3是在30℃条件进行乳液聚合2h所得产物其增稠黏度随氨水浓度变化曲线，6条曲线共同点是均在氨水浓度大约0.2%(pH为8)时突然升高，在0.9%(pH为11)时开始下降。这是由于该

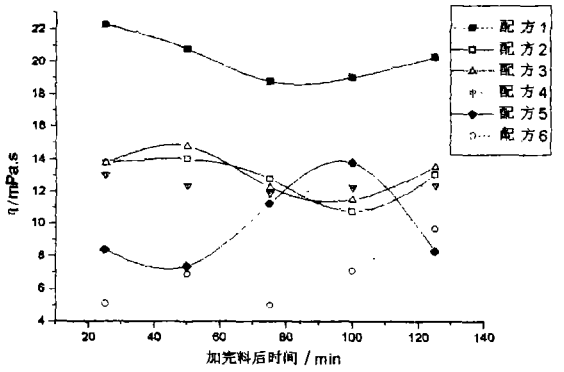

图 1 中间产品氨水增稠后粘度曲线(30℃)

增稠剂带羧基的分子链可溶于水相中,也可部分溶于乳胶粒中,而羧基较多部分伸向水相。在酸性或中性条件下,羧基以—COOH 形式存在,分子蜷缩成无规线团,加入碱以后,变成羧酸根离子,在同一条分子链上带上同号离子,由于静电斥力使无规线团伸展开,作用范围增大。在受外力而流动时使大分子链和乳胶粒间相互阻碍作用增大,宏观表现出乳液粘度升高[5]。本实验的结果表明了在碱性较强条件下聚合物大量溶解,导致乳胶粒尺寸有所降低,从而使粘度下降[7]。

图中看出,配方 1 和 6 在同等条件下黏度变化

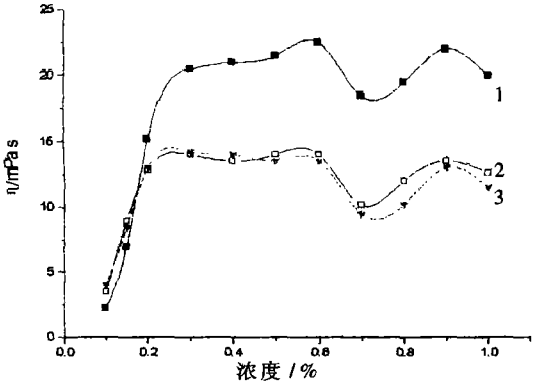

图 2 乳液增稠后粘度与所加入的氨水浓度关系

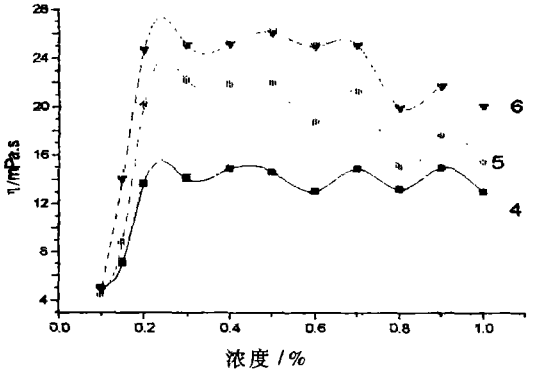

图 3 乳液增稠后粘度与所加入的氨水浓度关系(30℃)

十分显著,这是由于其配方中丙烯酸含量相对高的原因,此结果与碱增稠的理论相吻合,另外其他组分对乳液粘度也有较大影响。

2.3 丙烯酸乳液增稠剂的氨水增稠黏度与温度的关系

图 4 是取各配方产品 1g 加入 20mL3% 的氨水增稠后,考查增稠剂的黏度随温度变化的趋势。从图中可见,6 条曲线均随温度升高成下降趋势,这是由于乳液中粒子的热运动加剧,粘度随之下降。所以,不宜在高温下使用该系列产品。

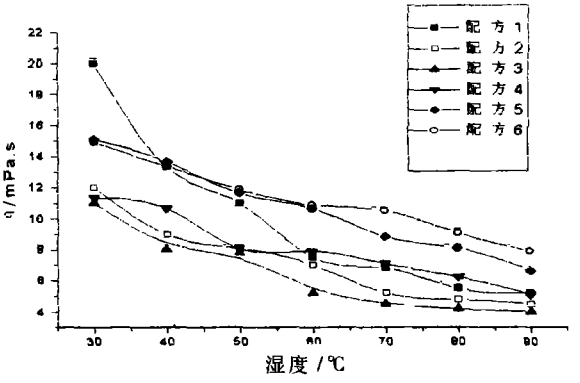

图 4 乳液氨水增稠后粘温曲线

2.4 乳液稳定性测试

附表 不同地方的乳液稳定性

	1	2	3	4	5	6
机械稳定性(%)	0.16	0.03	0.10	0.10	0.22	0.32
化学稳定性(%)	0.09	0.15	0.12	0.36	0.36	0.24
稀释稳定性(%)	0.02	0.003	0.01	0.02	0.05	0.03

从表中数据可以看出,整体上来说 6 个配方稳定性较好。但对于加入丙烯酸的配方 4～6,其机械稳定性和化学稳定性均不如配方 1～3。这是由于丙烯酸单体水溶性较强,预乳化时就已经开始在水中部分自聚,这样它和其余单体共聚的机会就降低了,从而导致稳定性下降。所以丙烯酸类比较适合在非水溶剂中进行反相乳液聚合[4]或采取后期集中滴加丙烯酸方式[8],使丙烯酸含量主要集中分布在"壳"层结构中,聚合物羧基离解,产生电荷斥力,使稳定性显著提高。

2.4 丙烯酸乳液增稠剂的流变性

丙烯酸乳液增稠剂碱增稠后的流变性质是衡量其色降印花效果的重要标志之一。图5为25℃下各配方氨水增稠后剪切应力与剪切速率的微分曲线。

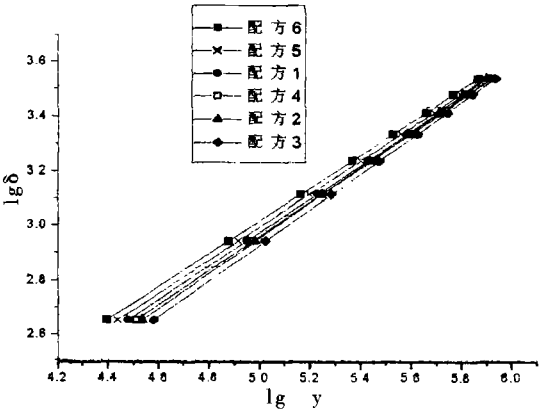

图 5　25℃时乳液氨水增稠后 $1g^{\delta}$-1gγ 曲线

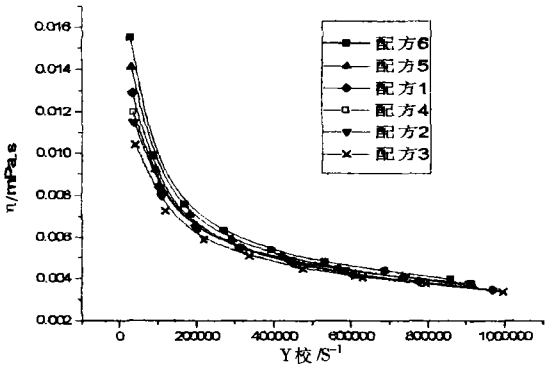

图 6　25℃时乳液氨水增稠后表观粘度-剪切速率关系图

几条曲线都有很好的线性关系且近似平行。由斜率求出非牛顿指数 n 值约为0.6～0.065，因 n 值较小，故各配方氨水增稠后具有良好的切力变稀性质。

图 6 为 25℃下各配方氨水增稠后的表观粘度与剪切速率的关系曲线（为减少出口剩余压降的影响，对剪切速率进行了校正）。实验表明，随剪切速率增大，表观粘度下降，表现出假塑性流体[9～11]的特征，数据回归的结果满足假塑性流体的剪切应力与剪切速率关系，即 $\delta = k\gamma^n$，式中 k、n 为常数，$0 < n < 1$，n 表征流体偏离线性行为的程度，n 越小偏离越明显。一般认为剪切增加分散粒子的能耗将导致切力增稠，而乳胶粒的剪切变形与取向、带电胶粒的表面双电层的剪切破坏引起流体力学体积减少则导致剪切变稀[11]。乳胶粒的变形性同聚合物的本体粘度有关，在 $T = Tg$ 时聚合物可视为等粘度状态，由 WLF[9]关系可知，在相同温度下 Tg 越低的聚合物，其本体粘度越小，变形性越大。丙烯酸乳液增稠剂表现的增稠后表观黏度随剪切力增加而下降这一性质有利于印花浆料透过网空，不易堵网。当剪切力消失，黏度马上恢复原始值，可以防止印花浆料在织物上渗化，保证花型轮廓清晰。

3　结　论

1. 预乳化半连续法进行乳液共聚法合成丙烯酸类增稠剂，反应过程易控制，操作简单，适合大型工业生产。用半连续乳液聚合法合成丙烯酸类增稠剂自加完料进行聚合时间不得少于 2h，这样有利于乳液聚合完全。

2. 氨水对丙烯酸乳液聚合物的增稠效果在 pH 为 8～10 最好，pH 值大于 11 时会使聚合物发生溶解，导致黏度下降。

3. 丙烯酸含量提高时碱增稠性提高，但随丙烯酸类物料增多乳液稳定性下降，所有产品随温度提高增稠黏度降低，因此适用于常温条件。

4. 该丙烯酸乳增稠剂具有良好的剪切变稀性质是印花行业较好的印花增稠剂。

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bility of the polyester, states in detail its functions of improvement on the spinnability and phase structure and the dyeable temperature decrease of pp/pe blended system, and predicts the applications of polysiloxane in the improvement on the dyeability of pp/pe blended fibers. ····· *You Gexin* et al(26)

Bulk-Copolymerization Kinetics Model of D_4 and Amio-silicone Monomer

In the paper, the copolymerization mechanism of D_4 and amio-silicone monomer was analysed and the copolymerization mechanism which is intermediate between chain and step reaction was proposed. Based on the classic conservation of mass, copolymerization kinetics model of D_4 and amio-silicone monomer was investigated. Finally the copolymerization kinetics character of the system was analysed by model simulation. ····· *Luo Zhenghong* et al(28)

A Comparative Study of Moisture Transfer Performance of Fabrics from Different Fibres

The moisture transfer mechanism of hydrophobic and hydrophilic fabric was tested and discussed in this paper. Theoretical analysis proves that hydrophilic fabric's inflation under sensible perspiration causes reduction of capillary radii of the fibers, so that moisture transfer and evaporation are negtively affected. On the contrary, hydrophobic fabrics can overcome this kind of defect. The validity of this theoretical analysis is proved by tests. ····· *Tang shijun* et al(31)

Study of the Inclusion Action of β-Cyclodextrin on Cationic Dyes

The inclusion action of β-Cyclodextrin on cationic dyes has been researched with UV spectrum, thermal analysis(TG/DTG, DSC) and X-ray diffraction and the inclusion has been analysed with respect to the configurations and sizes of the cationic dyes simulated by computer and β-cyclodextrin. ····· *Long Jiajie* et al(33)

The Analysis of New Model E-Shed Principle

Shedding is one of five motions of a loom. It is aimed to form shed where warp falls into two layers. The article analyzes electron-control four links shedding on a Toyota air jet loom. The analysis of the air-jet loom is aimed to know their work principle. ····· *Wu Weiting* et al(36)

Analysis of Geometric Parameters in Mathematic Model for Sleeve Flat Pattern

Based on the established mathematic model of sleeve flat pattern design and related operation formula, the article analyzes those important parameters that affect sleeve appearance qualitatively and quantitatively. ····· *Dai Wei* et al(38)

Technique of Manufacture

Application of the Digital Image Processing System to the Fiber Quantitative analysis

In this paper the method for testing blending ratio of ramie/cotton fibers by the digital image processing system was investigated, and the intelligent distinguishing of cashmere and other animal fibers was discussed. ····· *Liu Xiaoxia* et al(40)

Auto-designing System of Spinning Process Parameters

This paper introduces the function and features of auto-designing system, and in particular, deals with the key technique of system and quantitative adjusting algorithm during process parameters designing. All of these will have a referential value for further researching and developing auto-designing system of spinning process parameters. ····· *Ding Zhirong* et al(42)

The Research of the Testing Method for Blending Ratio of Two-Composition Blended Yarn by Uster Evenness Tester

The result, that there is a linear relationship between each sample's relative count per unit weight and blending ratio of two-composition blended yarn, was obtained by experiments and data analysis. It establishes the foundation to extend the application of Uster Tester by solving the theoretical problem of yarn testing with Uster evenness tester. ····· *Wen Yanqing* et al (44)

3D Circular fabric and Automatic Manufacture

This paper introduces the structure of 3D circular weaving machine and its principle of automatic weaving. The system has a simple construction, is easy to control and use, and suits the production of 3D circular fabric. ····· *Wang Yuecun* et al(46)

Copolymerization of Acrylate Semi-Continuous and Property

The synthetic thickening agent of acrylic copolymers of different formulation was prepared by using semi-continuous emulsion process. The property and rheology was studied. The emulsion of thickening agent of acrylic copolymers with ammonia water thickening had a very good property of shear thinning. ····· *Lu Tong* et al(48)

The Texture Design and Weaving of Tubular 3D Fabric

In this paper, was analysed the struture of tubular 3D Fabric, introduced the weaving technology, summarized the method of fabric texture design and discussed its weavability. ····· *Huang xiaomei*(51)

Effects of Transition Metal Compounds on Thermal Degradation of Chitin

Ferric chloride hydrate and potassium bichromate were respectively blended with home-made pulverized chitin. The effects of the additives on thermal degradation and thermo-oxidative degradation of chitin were studied with differential thermal analaysis (DTA). isothermal treatment. Thermogravimetry (TG) and infrared spectroscopy (IR). Ferric chloride hydrate accelerated thermal degration in nitrogen whereas potassium bichromate strengthened initial and thermo-oxidative degradation and decelerated thermal degradation. Both compounds modified extracts from condensed producte after isothermal treatment. ····· *Zhu Xinsheng* et al(53)

Investigation of Low Melting Point Copolyester

The melting point of Polyester is lowered by adding modifying component of alcyl of compounds to increase flexibility of molecular chain and to decrease the regularity of polymer. The melting point to lower is found with the increase of the degree of modifying component. A low melting point polyester is made by controlling the adding amount of modifying component. ····· *Hu Guoliang* et al(55)

Multiunit Synchronous Control System of Mercerizer

In this paper, the structure and principle of multiunit synchronous control system of a mercerizer were discussed. Meanwhile, the