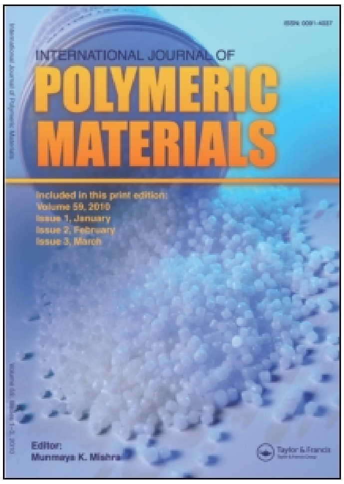


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

THE ACID VALUE OF THE POLYCONDENSATE FROM ADIPIC ACID AND DIETHANOLAMINE AND ITS DISPERSING PROPERTY IN PREPARING PHYSICAL BLOWING MICROCAPSULES

Wu Minghua[a]; Luo Yan[b]; Chen Shuilin[b]
[a] Zhejiang Institute of Science & Technology, Hangzhou, China [b] Donghua University, Shanghai, China

Online publication date: 16 August 2010

To cite this Article Minghua, Wu , Yan, Luo and Shuilin, Chen(2004) 'THE ACID VALUE OF THE POLYCONDENSATE FROM ADIPIC ACID AND DIETHANOLAMINE AND ITS DISPERSING PROPERTY IN PREPARING PHYSICAL BLOWING MICROCAPSULES', International Journal of Polymeric Materials, 53: 2, 119 — 129
To link to this Article: DOI: 10.1080/00914030490267555
URL: http://dx.doi.org/10.1080/00914030490267555

International Journal of Polymeric Materials, 53:119–129, 2004

ISSN: 0091-4037 print/1543-5253 online
DOI: 10.1080/00914030490267555

THE ACID VALUE OF THE POLYCONDENSATE FROM ADIPIC ACID AND DIETHANOLAMINE AND ITS DISPERSING PROPERTY IN PREPARING PHYSICAL BLOWING MICROCAPSULES

Wu Minghua
Zhejiang Institute of Science & Technology, Hangzhou, China

Luo Yan
Chen Shuilin
Donghua University, Shanghai, China

Factors affecting the polycondensation of adipic acid and diethanol amine were investigated by means of orthogonal and single factor methods. The particle size, size distribution and the morphological structure of physical blowing microcapsules prepared with such a polycondensate as a dispersant were observed with optical microscope and electronic microscope, respectively. The results showed that the factors influencing the acid value of the polycondensate with different intensities during polycondensation were the temperature, time, vacuum level, and the mass of p-toluene sulfonic acid. The acid values of polycondensates suitable for dispersant in preparing physical blowing microcapsules with single-cored structure were 75.7–104.0 mg KOH/g.

Keywords: adipic acid, diethanol amine, polycondensate, physical blowing microcapsules

INTRODUCTION

The polycondensate with suitable acid value of adipic acid and diethanol amine is a water-soluble polymer and possesses good dispersion property. It is mostly used in organic synthesis, textile printing, dyeing and microcapsule preparation [1]. Under suitable conditions, the adipic acid and diethanol amine polycondensate are formed by

Received 14 January 2002; in final form 29 January 2002.
Address correspondence to Wu Minghua, Zhejiang Institute of Science & Technology, Hangzhou 310033, China. E-mail: Minghua_wu@etang.com

condensation polymerization. The performance of the polycondensate as a dispersant is related closely to its degree of polymerization.

In this paper, the condensation polymerization of adipic acid and diethanol amine was studied. Additionally, the dispersion property of the polycondensate in preparing a physical blowing microcapsule was also discussed.

EXPERIMENTAL

1. Reagents Used

Adipic acid (AR), diethanol amine (AR), p-toluene sulfonic acid (AR), vinylidene chloride (AR), acrylonitrile (AR), methyl methacrylate (AR), azobisisobutyronitrle (AR), PVP(K17, available from BASF Co., Ltd) and colloidal silica (available from Shanghai Petroleum Chemicals Co., Ltd).

2. Laboratory Apparatus

High-speed shearing emulsifiers, model BME100L; autoclave, model GCF-2; refrigerator, model DYH-15; vacuum filter.

3. Condensation Polymerization

Under suitable conditions, the condensation polymerization between adipic acid and diethanol amine occurred [2].

$$nHOOC\text{-}(CH_2)_4\text{-}COOH + nNH(CH_2CH_2OH)_2 \xrightarrow[\Delta]{(Cat.)}$$

$$HO\text{-}(\text{-}CH_2CH_2\text{-}NH\text{-}CH_2CH_2\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_4\text{-}\overset{\overset{O}{\|}}{C}\text{-})_n\text{-}OH \quad +2nH_2O$$

As the condensation polymerization went on, the polymer molecular weight became larger and the acid value became lower; the acid value could be regarded as the indicator of the extent of the reaction.

In order to understand the factors affecting the acid value of the polycondensate, both orthogonal and single factor experiments were carried out, respectively.

4. Preparation of Physical Blowing Microcapsules with Polycondensate as a Dispersant [3]

According to the formula, the vinylidene chloride, acrylonitrile, methyl methacrylate were mixed homogeneously and the azobisisobutyronitrile was dissolved in to form the oil phase, while colloidal silica, polycondensate, common salt and $NaNO_2$ were dissolved in distilled water and acidified to form the aqueous phase. Then both the oil phase and aqueous phase were emulsified with a high-speed mixer at a speed of about 2,500 r.p.m for 5 minutes under cooling. The emulsified system was transferred into an autoclave, sealed, and pressurized with N_2 gas until an initial pressure of 0.2–0.5 MPa was obtained. The system was heated slowly to a temperature of about 60°C, and the temperature was kept for over 20 hours to finish the microencapsulation.

5. Measurements and Tests

5.1 The Acid Value

The acid value was determined according to GB (the national standard of China) 1668-81, in mgKOH/g.

5.2 Emulsifying Efficiency [4]

20 ml 1% polycondensate was transferred into a 100 ml graduated cylinder with plug, then 20 ml hydrocarbon oil were added. The mixture was shaken for 30 s, and stood for 1 min. This procedure of shaking and standing was repeated five times, and then the time for separating 10 ml clear water was recorded.

Usually, the longer separating time implies the higher emulsifying efficiency.

5.3 Particle Size and Size Distribution of Physical Blowing Microcapsules

These were measured with XSP-BM microscope and Panasonic photographic finder with digital picture analysis system.

5.4. Morphological Structure of Physical Blowing Microcapsules

The morphological structure was observed by JSM-5600LV (Japan) electron microscope.

RESULTS AND DISCUSSION

1. Factors Affecting the Polycondensation

1.1 Results of the Orthogonal Method of Multiple Factors

Based on the main factors of polycondensation, temperature, time, pressure and quantity of p-toluene sulfonic acid(catalyst) were chosen as four factors of the system. The model of orthogonal table was L9 (3^4). The selected conditions, parameters and the result of the orthogonal experiment are shown in Table 1.

TABLE 1 The Four Factors and the Three Levels Chosen and the Results of the Orthogonal Method

	Factor			
Level	Temperature (°C)	Time (hour)	[a]Quantity of catalyst	System pressure (mmHg)
1	120	1	0	760
2	140	2	0.001	Under normal pressure for first half time and then under a pressure of 120
3	160	4	0.002	120
Result of the orthogonal method (as intensity of affecting on acid value)	Strongest	Stronger	Week	Average

a: quantity of catalyst is mole ratio of p-toluene sulfonic acid to adipic acid

The results of the orthogonal experiment revealved that the influence degrees from strong to weak on the acid value of polycondensate were the temperature, time, system pressure and the quantity of p-toluene sulfonic acid, thus the temperature and the time should be taken into account first when controlling the acid value of polycondensate.

1.2. The Results of the Single Factor Experiments of Polycondensation

1.2.1. Effect of temperature on the acid value of polycondensate Table 2 shows that different reaction temperatures resulted in different acid values. The higher the reaction temperature was, the lower the acid value of polycondensate would be. Therefore, if a relatively

TABLE 2 Effect of Temperature on the Acid Value of Polycondensate

Temperature (°C)	Acid value of polycondensate (mgKOH/g)
120	185.4
140	117.5
150	102.4
160	87.9

Conditions: time 4th; normal pressure; mole ratio of p-toluene sulfonic acid to adipic acid 0.001

TABLE 3 Effect of Reaction Time on the Acid Value of Polycondensate

Reaction time (hour)	Acid value of Polycondensate A (mgKOH/g)	Acid value of polycondensate B (mgKOH/g)
1.0	181.8	228.6
1.5	147.7	214.5
2.0	135.7	205.6
3.0	110.3	186.3
4.0	87.9	185.4

Conditions: Polycondensate A: temperature 160°C, normal pressure, mole ratio of p-toluene sulfonic acid to adipic acid 0.001

Polycondensate B: Temperature 120°C, normal pressure, mole ratio of p-toluene sulfonic acid to adipic acid 0.001

low acid value of polycondensate was preferred, an elevated reaction temperature should be used.

1.2.2. Effect of the time on the acid value of polycondensate. From Table 3 it can be drawn that at 160°C, with a prolonged reaction time, the acid value of polycondensate was significantly decreased. But at 120°C, the acid value of polycondensate decreased only slowly. This implies that under atmospheric pressure relatively large amounts of water, one of the polycondensation products, remained in the reaction system and slowed down the reaction. As the reaction temperature elevated, e.g. 160°C, less water remained and the reaction proceeded faster, giving a faster decline of the acid value. As the time prolonged, the system gelled. Thus, if a relatively low acid value of polycondensate was desired, the temperature had to be higher. However, at a higher temperature, as a matter of fact, this reaction would be hard to control.

1.2.3. Effect of quantity of p-toluene sulfonic acid on the acid value of polycondensate. Usually, the p-toluene sulfonic acid acts as a catalyst in common polycondensation [5]. But from Table 4 it can be

TABLE 4 Effect of Quantity of p-toluene Sulfonic Acid on the Acid Value of Polycondensate

p-toluene sulfonic acid(mol)/ adipic acid (mol)	Acid value of polycondensate (mgKOH/g)
0	66.9 (gel)
0.001	87.9
0.002	104.1
0.010	112.6

Conditions: temperature 160°C; time 4 h; normal pressure

TABLE 5 Effect of Removing Water from the Reaction System on Acid Value of Polycondensate

Pressure of the reaction system (mmHg)	Acid value of polycondensate (mgKOH/g)
760	87.9
120	63.2 (gel)

Conditions: temperature 160°C; time 4 h; normal pressure; mole ratio of p-toluene sulfonic acid to adipic acid 0.001

seen that with increasing quantity of p-toluene sulfonic acid, the acid value of polycondensate became higher at a reaction temperature of 160°C. It seems that the catalytic effect of the p-toluene sulfonic acid is more negative than positive under such conditions.

1.2.4. Effect of removing water of condensation from the reaction system on the acid value of polycondensate. Table 5 shows that under the condition of vacuum supply, the reaction balance shifted toward the reaction products because more water was removed. As a result, the acid value of polycondensate decreased faster.

2. Emulsifying Properties of Polycondensates Prepared

From Table 6, it can be seen that the emulsifying property of polycondensate decreased with increased acid value. Thus, within the scope of our experiments, the polycondensate with an acid value of 75.7 mgKOH/g possessed the best emulsifying property of the polycondensates, even better than the PVP (K17).

TABLE 6 Comparison of Emulsifying Properties between Polycondensates and PVP (K17)

Sample	Acid value (mgKOH/g)	Stability of emulsified system (time)
Polycondensate	75.7	40 min
Polycondensate	104.0	50 sec
Polycondensate	112.6	23 sec
Polycondensate	131.1	23 sec
Polycondensate	160.7	23 sec
PVP (K17)	–	6 min

TABLE 7 The Relationship between the Acid Value of Polycondensate and Percentage of Relatively Large Particles of Physical Blowing Microcapsules Prepared

Acid value of polyconsendate (mgKOH/g)	Percentage of relatively big particle (%)
75.7	1.7
104.0	4.2
136.6	5.1
150.1	27.2
186.0	49.6

3. Particle Size and Size Distribution of the Physical Blowing Microcapsules as a Function of the Polycondensate's Acid Value

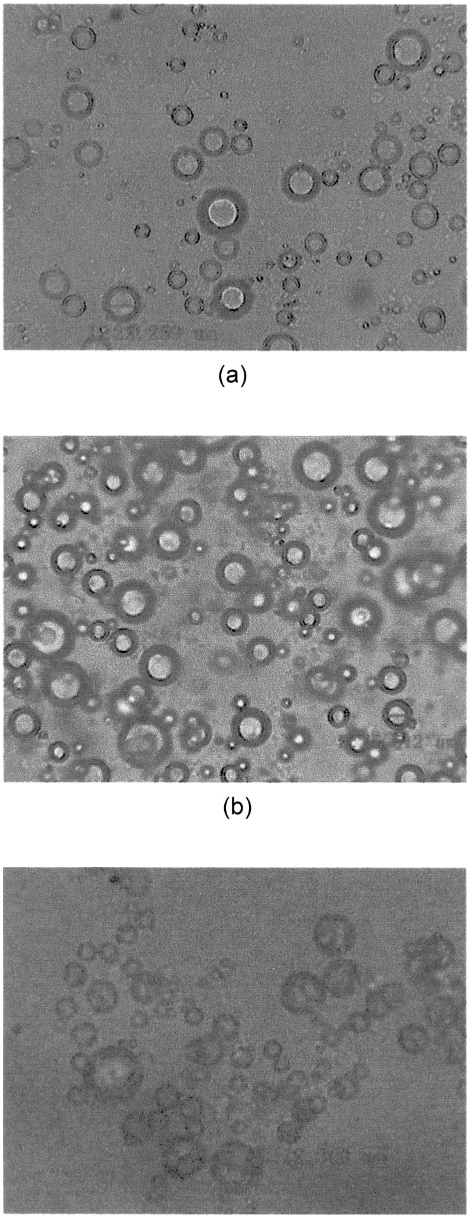
As a dispersant, the acid value of polycondensate, which implied the dispersing performance, undoubtedly possessed a certain effect on the size of microcapsules prepared. In order to observe such an effect, the microcapsules prepared with polycondensate as a dispersant were filtered by screen with 120 pore/cm^2. Small particles passed through the screen, and relatively large particles remained on it. The relative amounts in percentage were determined. Table 7 shows the results. When the acid value of polycondensate was as high as 150.1 mgKOH/g, the perentage of the large particle would be over 25%.

Table 8 shows the average particle size and particle structure as content of single-cored microcapsules subjectively estimated in relationship of the acid value of polycondensate as a dispersant.

Table 8 and Figure 1 indicate that the particle size and appearance (single- or multi-cored) of microcapsules were good, the particles appeared relatively homogeneous when acid values of the polycondensate were from 75.7 to 104.0. As the acid value of the polycondensate reached 186.0, most of the microcapsules had poor

TABLE 8 The Relationship Between Acid Value of Polycondensate and Average Particle Size and Appearance of Physical Blowing Microcapsules

Acid value of polycondensate (mgKOH/g)	Average particle size (μm)	Appearance of microcapsules
75.7	9.6	Most single-cored
104.0	10.9	Most single-cored
136.6	18.5	Average
186.0	46.1	Most multi-cored

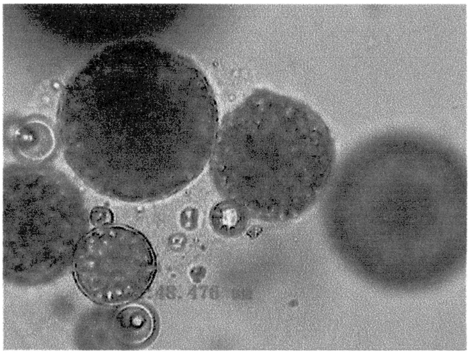


(a)

(b)

(c)

FIGURE 1 Microscope photos of physical blowing microcapsules prepared with different acid values (mgKOH/g; a: 75.7, b: 104.0, c: 136.6, d: 186.0) of polycondensates as dispersant. (a) Microcapsules prepared with 75.7 acid value of polycondensate, (b) microcapsules prepared with 104.0 acid value of polycondensate, (c) microcapsules prepared with 136.6 acid value of polycondensate, (d) microcapsules prepared wtih 186.0 acid value of polycondensate. (Continued).



(d)

FIGURE 1 (*Continued*).

structure are appeared mainly as multi-cored with large size differences. As far as the particle size of microcapsules is concerned, the acid value of polycondensate used in preparing the physical blowing microcapsules better be from 75.7 to 104.0 mgKOH/g.

Moreover, a size distribution of the physical blowing microcapsules prepared with such a polycondensate (acid value 75.7 mgKOH/g) was obtained by XSP-BM microscope and Panasonic photographic finder with digital picture analysis system. The result is shown in Figure 2. Figure 2 shows that the particle size distribution concentrated at

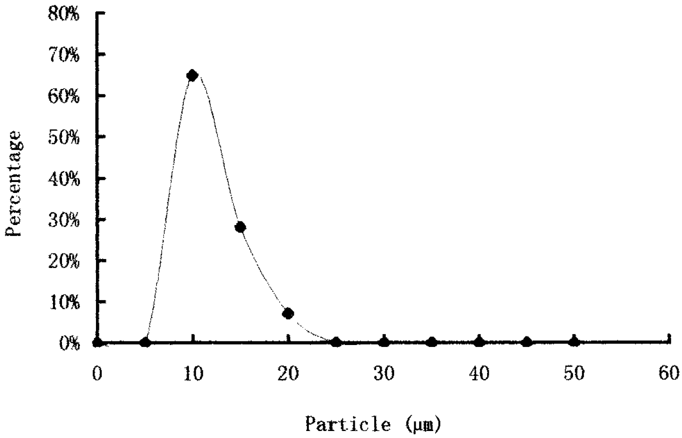


FIGURE 2 The size distribution of the microcapsules prepared with acid value 75.7(mgKOH/g) polycondensate as a dispersant.

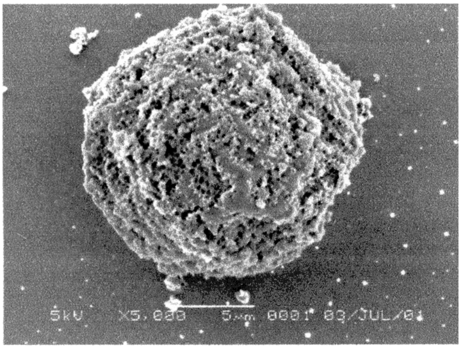


FIGURE 3 An SEM photo of the high-temperature blowing microcapsules prepared with acid value 75.7(mgKOH/g) polycondensate as a dispersant (145–155°C).

10–15 μm, which could meet the demands of applications in cubic pigment printing.

4. Surface Morphological Structure of Physical Blowing Microcapsules

The electron microscope photos of physical blowing microcapsules prepared with polycondensate of 75.7 (mgKOH/g) acid value acting as a dispersant are shown in Figure 3 and Figure 4.

It is obvious from Figure 3 and Figure 4 that the physical blowing microcapsules, no matter whether they were high-temperature or low-

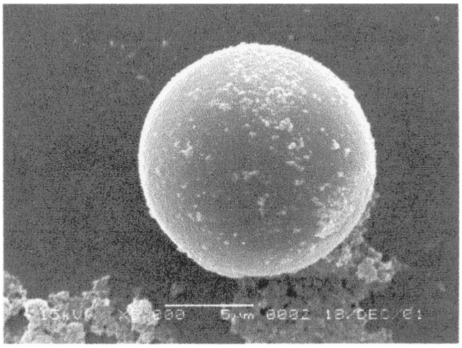


FIGURE 4 An SEM photo of the low-temperature blowing microcapsules prepared with acid value 75.7(mgKOH/g) polycondensate as a dispersant (90–100°C).

temperature blowing, all possessed single-cored spherical shape if they were prepared with 75.7 (mgKOH/g) acid value polycondensate as a dispersant.

CONCLUSIONS

(1) The factors influence the acid value of polycondensate from strong to weak were the temperature, time, type of vacuum supply and the quantity of p-toluene sulfonic acid.
(2) The acid value of polycondensate decreased as the reaction temperature was raised.
(3) At 120°C, the acid value of polycondensate decreased very slowly as the reaction time prolonged, while at 160°C the acid value of polycondensate decreased rapidly with the prolongation of reaction time and finally the system gelled.
(4) Vacuum supply promoted the polycondensation substantially, and the acid value of polycondensate fell quickly under vacuum.
(5) Polycondensate with an acid value of 75.7 mgKOH/g possesses an outstanding emulsifying property, even better than that of PVP.
(6) The range of acid value of polycondensate suitable for dispersant in preparing physical blowing microcapsule should be 75.7 to 104.0 mgKOH/g.

REFERENCES

[1] Morehouse, Jr. et al. (1971). US Patent 3,615,972.
[2] Lin, Jin, Wang, Lanzhi. (1999). *Journal of Liao Ning Chemical Engineering* **28**, 294–295.
[3] Kida, et al. (1999). US Patent 5,536,756.
[4] Xu, Muqing. (1985). *Test & Identification in Dyeing and Printing*, Textile Industry Press, Beijing, 1st ed., Chap. 1, p. 147.
[5] Pan, Zuren. (1986). *Macromol. Chem.*, Chemistry Industry Press, Beijing, 1st ed., Chap. 7, pp. 218–219.