Inverse Suspension Polymerization of Partially Neutralized and Lightly Cross-Linked Acrylic Acid: Effect of Reaction Parameters

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Summary: An inverse suspension polymerization was carried out in laboratory in one Liter Buchi glass reactor to produce superabsorbent polymers (SAPs) based on acrylic monomers for hygiene applications. Strongly water absorbing polymers, based on acrylic acid, sodium acrylate were prepared by copolymerization using potassium per sulfate as initiator and N-N′ methylene-bisacrylamide (MBA) as crosslinking agent. The effect of varying monomer, crosslinker, initiator, dispersant concentration, time of reaction and degree of neutralization, on absorption capacities was investigated. In the present studies, the continuous hydrocarbon phase was taken as 50:50 mixture of n-heptane and cyclohexane (aliphatic-alicyclic) because the availability of crosslinker in the aqueous phase is controlled by the partition coefficient of the crosslinker between the aqueous phase and the continuous hydrocarbon phase. The SAPs were evaluated for their free absorption capacities in distilled water, saline (0.9% NaCl), and also absorption under load (AUL). The experimental results show that these SAPs have good absorbency both in water and NaCl solutions. It was observed that SAP synthesized from acrylic acid with about 70% degree of neutralization, containing 1% cross-linker, and 0.5–1.0% initiator concentration with 10% dispersant exhibited absorption capacities in water, saline and AUL as 220 g/g, 70 g/g and 27 g/g respectively.

Keywords: cross-linked acrylic acid; hygiene applications; molecular weight distribution; superabsorbent polymers; swelling

Introduction

Superabsorbents are lightly, crosslinked polymers, which can absorb huge amounts of water.[1] They are used mainly as absorbents in healthcare and agricultural applications and are commonly based on acrylic monomers such as acrylamide, acrylic acid and salts of the acid.[2,3] The monomers can be polymerized both by solution as well as inverse suspension/emulsion techniques,[4] but the former is preferred industrially for its simplicity and economics.

The main advantage of inverse emulsion polymerization over other polymerization methods is that it enables both to reach high molecular weights and high reaction rates during polymerization. Inverse emulsion polymerization has been far less investigated than conventional emulsion polymerization and it seems that application of the theories, which were developed for conventional emulsion polymerization, cannot be easily extended to inverse emulsion polymerization.

Apparently the inverse emulsion polymerization initiated by water soluble initiators is a solution polymerization in the microparticles[5,6] while when the oil soluble initiator is used the micellar model is valid in some cases.[7] It has been reported in literature[8] that the swelling rate of a

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superabsorbent prepared by suspension process is twelve times faster than prepared by solution process. Studies have also revealed that increasing amount of cross-linker reduced the ultimate swelling capacity but speeded up the rate of swelling for products made by both processes.[9,10]

The key properties such as swelling capacity and gel modulus are primarily controlled by the choice and amount of crosslinker. Compounds such as methylene-bisacrylamide and trimethylpropanetriacrylate are most widely used crosslinkers. The particle size of the product from inverse emulsion process is primarily controlled by the choice of suspending agent or the dispersant.

In the present studies we report the dependence of swelling characteristics of the end product on the degree of neutralization of acrylic acid and also on the concentration of crosslinker, initiator, dispersant added during polymerization.

Experimental Part

Materials

Cyclohexane, n-heptane, methanol, acetone, sodium hydroxide were used as such (Ranbaxy Laboratories, Bombay). Potassium persulfate (Merck), N-N′ methylene-bisacrylamide and Sorbitan monostearate (SP-60) both analytical grade >98% (Fluka Chemie AG, Switzerland) was used as such. Acrylic acid (glacial) LR was procured from Mayfair and Croydon laboratories Manchester, England.

Process Description

A combination of orientation experiments, trials and careful evaluation of literature led to the following:

Preparation of a Continuous Phase

A mixture of Cyclohexane/n-heptane (50:50 v/v) was selected as an organic phase. The organic phase containing an appropriate amount of (water in oil surfactant SPAN-60 sorbitan monostearate) was heated to 55°C while nitrogen was purged into the liquid medium over a 15 to 20 minutes period.

Preparation of a Dispersed Phase

A predetermined amount of acrylic acid was carefully added (dropwise under cooling) to sodium hydroxide solution in order to obtain a partial neutralization degree. Later on, a defined amount of water-soluble initiator (potassium persulfate) and a cross-linking agent (N-N′ methylenebisacrylamide) was dissolved in the above mentioned monomer solution under nitrogen bubbling until a clear mixture was obtained.

Polymerization

The monomer blend (“*dispersed phase b*” *above*) was added dropwise at a predetermined flow rate to the continuous phase while the agitation speed was set at around 400 rpm. The reaction mass was held as such under agitation for ~2 h at 80 °C to ensure full consumption of the remaining monomers. The polymer was then filtered washed with methanol and dried at 50 °C in vacuum for 3 to 4 h.

Characterization

Absorption Capacity

0.2 g of a superabsorbent resin (coarse powder) was dispersed into 300 mL of doubled distilled water/saline (0.9% NaCl) separately and allowed to swell sufficiently under moderate agitation at ambient temperature (27 °C). The amount of water absorbed by the resin was determined gravimetrically after the swelling equilibrium had been reached (30 minutes). Thereafter dispersion was filtered through a 100-mesh wire sieve, surface dried with a piece of filter paper and weighed. (Since equilibrium is reached within 30 minute and beyond this time no significant absorption takes place. Hence 30 minutes were taken as optimum time to attain the equilibrium. This time period of 30 minutes to attain the equilibrium is an important attribute of commercially available SAPs. Please also refer to the European Disposables and Nonwovens Associations (EDANA) standard test method 400.1–99. The equilibrium absorption capacity expressed as grams of fluid absorbed per gram of dry polymer was calculated as follows:

Equilibrium absorption capacity EAC (g/g)

$$EAC = \frac{w_{sg} - w_{dg}}{w_{dg}}$$

W_{sg} = Weight of the swollen gel
W_{dg} = Weight of the dry gel

Absorbency Under Load (AUL)

The absorbency under load test measures the swelling capacity of the polymer while an external pressure is applied to the gel.

Procedure

A porous filter plate was placed in a petri dish and 0.9% NaCl solution was added till the liquid level was equal to the tip of the filter plate. A filter paper was placed on the filter plate and allowed to wet with saline solution. 0.6–0.8 g. of superabsorbent polymer (SAP) was carefully scattered onto the filter screen test device a plexiglass cylinder with 400 mesh SS cloth at button + a piston assembly including additional weight to achieve a load of 0.3–0.7 psi was placed on to top of SAP. After weighing the device, it was placed on the filter plate and absorption was all for 1 h. After 1 h the entire device was reweighed and AUL was calculated as follows:

$$AUL(g/g) = \frac{W_b - W_a}{W_{sa}}$$

W_a = dry cylinder group mass in g
W_b = mass of cylinder group after suction in g
W_{sa} = initial mass of the test portion in g

Results and Discussion

As has been mentioned in the introductory part of this paper the absorption characteristics of these polymers depend largely on a number of factors such as degree of neutralization, concentration of crosslinker, initiator and dispersant. In the following section the effect of these factors will be discussed separately.

Degree of Neutralization

In inverse suspension polymerization processes neutralization of the monomer is required due to appreciable solubility of acrylic acid in hydrocarbons (continuous phase). The degree of neutralization of acrylic acid has an important bearing on the rate of polymerization. The rate of polymerization of sodium acrylate and acrylic acid depends on the reactivity ratios of individual monomers, which is reported to be proportional to 3/2 power of acrylic acid concentration. This indicates that higher degrees of neutralization would be preferred in order to have a controlled polymerization kinetics array. In addition, the pH of an aqueous solution containing the swollen gel is directly related to the degree of neutralization. A pH between 5.5 and 6.5 is desired for use in applications where the product may come into contact with human skin. These factors practically restrict the degree of neutralization to 60–80 mol %.

The degree of neutralization was varied from 45% to 100% in the present investigations and the results are shown in (Table 1). Higher degree of neutralization increases the concentration of acrylic acid (in the form of salt) in the aqueous phase but simultaneously decrease the solubility of the crosslinker in the aqueous phase. This is reflected by the results given in (Table 1). As the percentage of neutralization is

Table 1.
Effect of degree of neutralization of acrylic acid on Absorption characteristics of SAPs.

Neutralization (%)	Abs.H_2O g/g	Abs.sal. g/g	Ab.AUL g/g
45	200	50	26
54	182	61	26
63	190	64	27
70	194	64	27
72	200	61	26
90	247	83	22
100	246	83	22

KPS = 1.2%, MBA = 0.998%, SP-60 = 9.98% contiuous phase (cyclohexane + n-heptane 50:50, 340 mL) acrylic acid = 35.32% water for dissolution of initiator, crosslinker and NaOH = 35 mL reaction temperature = 80°C, Time = 2 h.

increased from 72–90% there is a remarkable decrease in the AUL values from 26 to 22. The foregoing results indicate that 70–72% neutralization of acrylic acid is necessary to get desired absorption characteristics of the SAPs.

Please note that in literature these values are always expressed as g/g. Please refer to the standard test methods used for evaluation of SAPs (European Disposables and Nonwovens Associations EDANA).

Effect of Crosslinker

In an inverse emulsion polymerization process the availability of crosslinker in the aqueous phase will be controlled by the partition coefficient of the cross-linker between the aqueous phase and the hydrocarbon continuous phase. The partition coefficient will depend on the extent of neutralization and on the nature of the hydrocarbon (e.g. whether aromatic or aliphatic). For this purpose in the present studies the continuous phase was taken as a 50:50 mixture of n-heptane and cyclohexane (aliphatic-alicyclic).

As reported in literature,[11] the choice and amount of crosslinker plays a vital role in determining the ultimate swelling characteristics of the superabsorbent polymers. Therefore, solubility, reactivity, hydrolytic stability in alkaline medium, concentration and steric factors must be considered before choosing a particular crosslinker for a specific polymerization system during synthesis of superabsorbents. The crosslinker should have moderate reactivity and it must homogeneously react with the growing polymer till the end of the reaction. Otherwise if it is highly reactive it will deplete in the beginning of the polymerization reaction and polymer chains formed later will not have crosslinks, which may result in more soluble polymer. The allyl group shows only a low-to-moderate reactivity to acrylic acid. Crosslinkers containing such allylic groups, therefore, are incorporated more randomly during the polymerization. After screening a number of crosslinkers, N-N′ methylene bis acrylamide (MBA) was chosen as the suitable candidate for the present investigations, because MBA gave the highest absorption values.

The effect of increasing concentration of MBA on the absorption characteristics was studied. The results of these findings are shown (Table 2) It was observed that with the increase in crosslinker concentration the absorption capacity for water and saline is reduced while AUL increases up to $\sim$ 1.0% MBA concentration (AbsH_2O = 200 g/g, Abs.sal = 61 g/g, AUL = 26 g/g), beyond which the overall absorption capacities start reducing, because of very rigid SAPs formed at higher crosslinker concentrations. Also at high crosslinker concentrations, cyclic structures (extractable by water) are formed, rather than being incorporated into the three-dimensional network of SAPs. This also accounts for decrease in overall absorption capacities

Please note that in literature these values are always expressed as g/g. Please refer to the standards used for evaluation of SAPs (European Disposable Non-Woven Association, EDNA).

Effect of Initiator

For inverse emulsion polymerization, water-soluble initiators such as potassium persulfate (KPS) are generally preferred. Most, if not all, the commercial processes use KPS salts as one of the initiators. In this case, the kinetics of polymerization is proportional to 3/2 power of the acrylic acid concentration and to square root of the concentration of persulfate. These initiators affect overall rate of polymerization

Table 2.
Effect of N-N′ methylenebisacrylamide cross-linker on absorption characteristics of SAPs.

Ser.No.	MBA (%)	Abs.H_2O g/g	Abs.sal. g/g	Abs.AUL g/g
1	0.249	624	96.5	10.5
2	0.499	400	88	21.5
3	0.998	200	61	26
4	1.497	162	64	25
5	1.997	122	55.5	24

Degree of neutralization = 72%, MBA = variable. Rest is same as in Table 1.

Table 3.
Effect of potasium per sulphate (KPS) initiator on absorption characteristics of SAPs.

Ser.No.	KPS (%)	Abs.H_2O g/g	Abs.sal. g/g	Abs.AUL g/g
1	0.249	222	66	27.6
2	0.499	209	67	28
3	1.218	200	61	26
4	1.747	218	75	26

Degree of neutralization = 72%, KPS = variable.
Rest same as in Table 1.

thereby changing the conversion and consequently the molecular weight of the end product. The sudden temperature rise caused by the exothermal polymerization increases the rate of decomposition of initiator, thereby reducing the weight average molecular weight of the resin and broadening its molecular weight distribution (MWD).

In the current studies (Table 3) a KPS concentration of 0.25–0.5% (wrt monomer concentration) seems to be optimum for desired swelling capacities. Too high initiator concentration is not desirable as it results in short polymer strands, which are not cross linked and can be extracted by water. In addition to initiating the polymerization reaction, initiators are also a factor in reducing the levels of unreacted monomer during the drying step,[12] and can contribute to undesirable chain cleavage reactions that occur when the gel is handled at higher temperatures. For example, higher content of soluble polymer is found when the sodium polyacrylate gels made with ammonium persulfate initiator are dried in a hot oven.[13]

Effect of Dispersant Concentration and Reaction Time

Acrylic acid and sodium acrylate are polymerized in the presence of surfactants having hydrophilic-lipophilic balance (HLB) values between 7 and 18 and in this case surfactant renders the crosslinking agent water compatible. For inverse suspension polymerization involving hydrocarbons as a continuous phase the non-ionic dispersants of low HLB values are preferred. Sorbitan monostearate a non-ionic surfactant (SP-60, of lower HLB value 2–6) was taken and the concentration was varied between 10–20%. It was found that SP-60 concentration of $\sim$15% was optimum to obtain a superabsorbent polymer with a balance in absorption characteristics for water, saline and AUL (Table 4).

Table 4.
Effect of dispersant SP-60, on absorption characteristics of SAPs.

Ser.No.	SP-60 (%)	Abs.H_2O g/g	Abs.sal. g/g	Abs.AUL g/g
1	9.98	200	61	26
2	14.9	223	81.9	27.9
3	19.97	227	67.5	25

Degree of neutralization = 72%, SP-60 = variable.
Rest is same as in Table 1.

Table 5.
Effect of reaction time on the absorption characteristics of SAPs.

Ser No.	Time (hrs)	Abs.H_2O g/g	Abs.sal. g/g	Abs.AUL g/g
1	2	200	61	26
2	3	220	70	27
3	4	222	69	26

KPS = 1.218%, MBA = 0.998%, SP-60 = 9.98%.
Degree of neutralization = 72%, Time = variable.
Rest is same as in Table 1.

The inverse suspension polymerization was carried out for a period of two, three and four hours respectively. It was observed (Table 5) that 3 h was the optimum reaction time at which the ultimate absorption characteristics of the polymer attain a maximum value and level off. With further increase in reaction time the value for saline absorption and AUL start decreasing (Table 5). Longer reaction times approximately 3 h are generally preferred so that the residual monomer and soluble fraction are minimal.

Conclusions

To obtain superabsorbents with a high absorption capacity for water and saline solution some optimizations chiefly on neutralization degree, amount of cross-linker initiator and surfactant must be done. In the present studies SAPs prepared by inverse suspension polymerization of acrylic acid had absorption capacities as 220 g/g, 70 g/g and 27 g/g in water, saline and under load respectively.

Acknowledgements: The author is sincerely grateful to Dr. Shashikant Sharma for useful technical discussions and suggestions at various aspects of preparation of this manuscript. The author is also thankful to Dr. Sudhakar Padmanabhan for meticulous edition of the manuscript in the required template. My sincere thanks to the Management of Reliance Industries for their permission to present this paper at the Polychar-16, (World Forum on Advanced Materials) held on from 17th–21st Feb. 2008 at the World Unity Convention Centre, Lucknow, India.

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