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Effects of shell crosslinking on polyurea microcapsules containing a free-radical initiator

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ABSTRACT: Microencapsulation of a material is often used when a controlled release of a substance is desired. This study examines the effects of crosslinking in polyurea microcapsule shells on stability of microcapsules containing the free-radical initiator cumene hydroperoxide (CHP). Crosslinking of polyurea shells was varied by using amine monomers containing different amine functionalities, and/or changing the isocyanate/primary amine ratio. Thermogravimetric analysis was performed to determine thermal properties of these microcapsules, and the pot lives of monomer systems containing these microcapsules were measured. Thermal stability is greater with a moderate degree of crosslinking from a trifunctional amine, and decreases when crosslinking is increased through use of higher amine functionality. Stability in monomer media generally increases with increased crosslinking through higher amine functionality, but is less predictable due to crosslinks formed between capsules. Generally, increasing crosslinking through altering the isocyanate to primary amine ratio decreases capsule stability in both dry and monomer storage. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42408.

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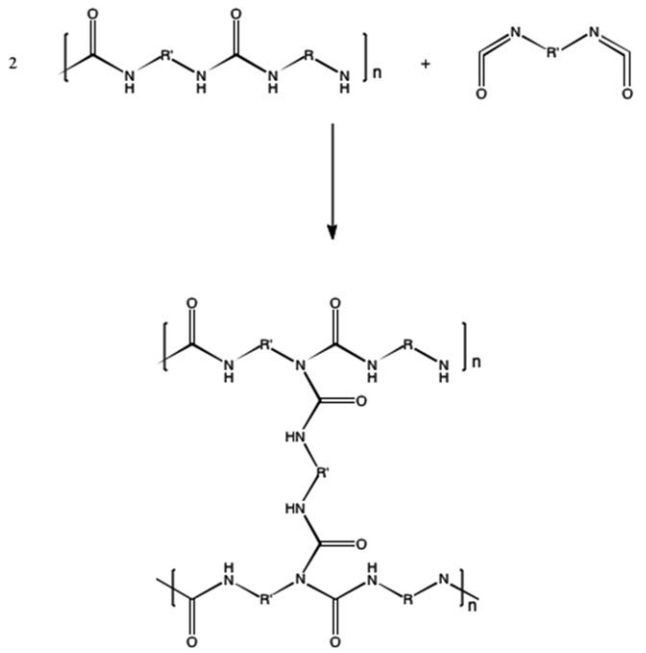
INTRODUCTION

Microencapsulation of an active core material within an external shell is a widely used technique for separation of components of a mixture until a desired release is triggered. Common applications in which microencapsulated components are used include but are not limited to pharmaceutical delivery,[1,2] cosmetics,[3] flavor enhancement of foods,[4] carbonless carbon paper,[5] pesticides,[6] and dyes[7]; common methods of release include pH changes,[8] melting of the shell,[9] and mechanical stress.[10] Either aqueous or nonaqueous cores can be microencapsulated.[11] Another application of particular interest is the use of microencapsulated components of reactive polymeric systems, often to increase the pot life of the system until a desired moment of curing.[12] It has been demonstrated that various components of these systems can be microencapsulated, including monomers,[13] initiators,[12,14] and catalysts.[10]

Frontal polymerization is a specialized polymeric system in which a monomer is converted into a polymer via a localized reaction front that propagates through the monomer, converting it into polymer as it passes.[15] This method of polymerization has been demonstrated with several different mechanisms of reaction, including free-radical polymerization,[12,14–17] anionic polymerization,[18] ring-opening polymerization,[19] step-growth polymerizations,[20,21] thiol-ene polymerizations,[22] and curing of epoxides.[23] One problem that has been observed with some frontal polymerization systems is an insufficient pot life when components are mixed and stored; often, these systems will spontaneously polymerize upon storage due to reaction of the monomer with other species stored in the system, such as initiators.[12] We have determined through previous experimentation that it is possible to microencapsulate the free-radical initiator cumene hydroperoxide (CHP) via synthesis of a polyurea shell produced from interfacial polymerization of a multifunctional isocyanate with a multifunctional amine.[12,14] It was observed that these microcapsules could be ruptured thermally by heating a portion of the reaction system with an external heat source; the release occurred when the microcapsules burst open due to internal pressure from gaseous byproducts produced during CHP decomposition. When this initiator was released, the subsequent polymerization was sufficiently exothermic to burst more capsules, and thus sustained a propagating front throughout the system. The pot lives of frontal polymerization systems with microencapsulated CHP increased with respect to systems with dissolved CHP, and further characteristics of these systems (such as front velocity, effects of cobalt naphthenate accelerator, and mechanical properties of produced polymers) were studied.



Scheme 1. Formation of a biuret linkage between two linear polyurea chains, forming a crosslink.

During formation of the polyurea shell, the primary initial reaction is between isocyanate groups and primary amine groups of the respective monomers to form a linear polyurea chain.[24–27] These chains can then be crosslinked by reaction of a secondary amine group within the chain with another isocyanate molecule to form a biuret linkage (Scheme 1).[28] The degree to which this crosslinking occurs is an important factor in the overall quality of the microcapsules. If there is a low degree of crosslinking, the microcapsules can be soft, with thin, porous walls through which the core material can easily escape. Even if initial leakage does not occur through pores, the thin walls can make handling of the capsules (and mixing of them into polymerization systems) much more difficult due to an increased chance of accidental mechanical rupture. Because of these factors, it is a natural assumption that one would want a very large degree of crosslinking. However, this can also pose a problem; if there are too many reactive isocyanate groups in the system relative to primary amine groups, it could be possible for the microcapsules to form crosslinked bridges to each other at the surface of the shells, resulting in small clusters rather than individual microcapsules. Attempting to mechanically separate the individual microcapsules within a cluster will most often result in stress to the shells, causing cracks to form, which in turn allow leakage of the core material.

Because of its importance in overall microcapsule quality, we investigated the effects of varying degrees of crosslinking in two ways. First, an investigation of the effects of amine functionality was conducted by making respective microcapsule samples using a diamine, a triamine, a tetramine, and a pentamine. These amines are listed in ascending order of secondary amine functionality. Increasing secondary amine functionality was hypothesized to lead to an increased number of crosslinking sites within each polyurea chain. Second, a series of microcapsule samples were prepared using varying amounts of identical amine monomers. By varying the amounts of amine monomer used, we altered the ratio of isocyanate to primary amine groups within the system. It was hypothesized that increasing the number of primary amine groups would lead to a higher degree of linear polyurea formation, reducing the overall number of isocyanate groups available for crosslinking. Overall effects of degree of crosslinking were analyzed using thermal analysis and observation of frontal polymerization system pot lives.

EXPERIMENTAL

Materials

Diethylenetriamine (99%) (DETA), ethylenediamine (99%) (EDA), tetraethylenepentamine (89.7%) (TEPA), triethylenetetramine (60%) (TETA), poly(vinyl alcohol) (87−89% hydrolyzed), cobalt naphthenate in mineral spirits (8% cobalt) and cumene hydroperoxide (88%) (CHP) were obtained from Sigma Aldrich and used as received. The remaining 12% of the CHP solution was inert with the rest of our reagents, and therefore not problematic. Mondur MRS (a polymeric isocyanate based on 4,4'-diphenylmethane diisocyanate) was obtained from Bayer Corp. and used as received. 1,6-hexanediol diacrylate (99%) was obtained from UCB and used as received.

Preparation of Microcapsules and Determination of Core-Loading Percentage

Microcapsules containing a CHP core were prepared through interfacial polymerization of a polyurea shell around dispersed CHP droplets. The core solution for each batch of microcapsules(nonaqueous) was prepared by dissolving 80 mL of CHP in 10 mL of Mondur MRS. This solution was then dispersed using an IKA stir motor (fitted with a stainless steel, 2" 3-pitch-bladed impeller) mixing at 230 rpm into 250 mL of a 1.2% (w/w) aqueous solution of PVA that had previously been heated to

Table I. Formulations of Microcapsule Shells Produced

Amine used	mL amine used	Isocyanate : primary amine ratio
DETA	5.90	0.86 : 1
DETA	4.83	1.05 : 1
DETA	4.37	1.16 : 1
DETA	3.50	1.45 : 1
DETA	2.63	1.93 : 1
TETA	13.00	0.86 : 1
TETA	11.00	1.05 : 1
TETA	10.00	1.16 : 1
TETA	8.00	1.45 : 1
TETA	6.00	1.93 : 1
TEPA	11.43	0.86 : 1
TEPA	9.36	1.05 : 1
TEPA	8.48	1.16 : 1
TEPA	6.78	1.45 : 1
TEPA	5.10	1.93 : 1

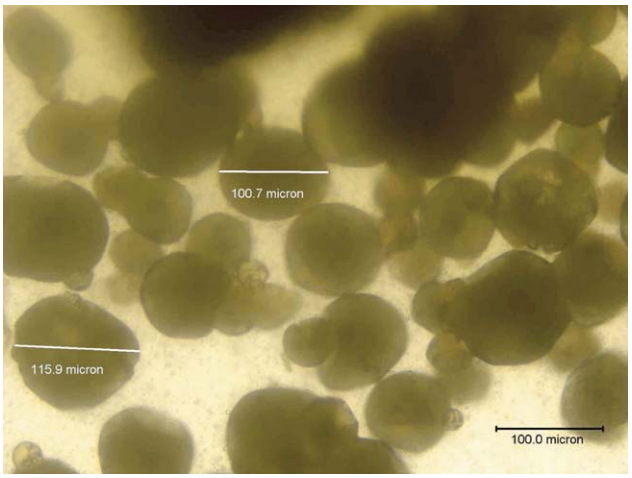


Figure 1. Polyurea microcapsules containing a CHP core, prepared via interfacial polymerization using TETA as the amine monomer. The microcapsules are roughly spherical, with slight wrinkling (evidenced by small light spots at the edges of the microcapsules). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

50°C. Droplet sizes were measured using light microscopy; once the dispersed droplets had sizes in the desirable range (100−400 μm), an aqueous solution containing between 3.0 and 13.0 mL of a multifunctional amine (either TETA, TEPA, or DETA) dissolved in 20 mL of water was added (the exact volumes used, corresponding with resulting isocyanate:primary amine ratios, are summarized in Table I). The mixture was then heated at 50°C for 4 h with continuous mixing at 230 rpm. After 4 h, the microcapsules were vacuum-filtered, separated with the aid of fumed silica, and were then allowed to air-dry overnight. Each batch of microcapsules was ∼80% by mass, and contained capsules ranging from 100 to 400 μm. Dried microcapsules were rinsed with heptane prior to use in order to ensure removal of trace amounts of CHP from the outer portion of the shells. To determine core-loading percentage, a known mass of capsules was crushed and stored in methanol overnight to ensure complete removal of the CHP core. The next day the empty shells were filtered, dried, and reweighed, allowing determination of overall percentage of CHP and overall percentage of polyurea shell in the microcapsules.

Analysis of Thermal Properties of Microcapsules

Thermogravimetric analysis was performed on a TGA 2050 thermogravimetric analyzer from TA Instruments. Samples of 5−15 mg were analyzed in a nitrogen atmosphere. Samples were analyzed using a 20°C/min ramp up to 300°C and isothermally at 50 and 85°C.

To determine the physical mode of core release, microcapsules were examined by light microscopy while they were heated to 300°C using a 20°C/min ramp on a Mettler Toledo FP82HT heated microscope stage. The heating rate was controlled by a Mettler Toledo FP90 central processor.

Determination of Pot Lives of Monomer-Initiator Systems

Pot lives of systems containing a crosslinking monomer (HDDA) and initiator (either dissolved or microencapsulated CHP) were determined by adding a known percentage (2%) of CHP to the monomer, and examining the mixture for an increase in opacity, which would indicate a bulk polymerization of the monomer. Microencapsulated CHP was suspended in the monomer with fumed silica (4% w/v) (for consistency, the same amount of silica was also added to mixtures containing dissolved CHP). The systems were either stored at room temperature containing 0.04% (v/v), cobalt naphthenate accelerator or at 50°C without the presence of the accelerator.

RESULTS AND DISCUSSION

Microcapsule Formation and Core-Loading Percentage

The microcapsules that were produced by this method using DETA or TETA as the amine monomer in general were roughly spherical in nature, with some surface wrinkles; they had diameters ranging from approximately 30−400 μm in diameter. Figure 1 shows the general appearance of the microcapsules when viewed by light microscopy. The contour of each individual microcapsule was observed to contain some areas of wrinkling of the shell, as evidenced by the existence of small light spots on the edge of each microcapsule. However, the microcapsules produced did not exhibit additional leakage or wrinkling over time when analyzed by light microscopy. Figure 1 also shows that the exterior of the capsules contained no apparent cracks or crevices that would give an indication of leakage of the core material. Although some of the microcapsules appear to cluster together, they separated easily when gently agitated with a small probe, and also easily separated during the drying stage; this indicated that discrete, individual microcapsules had been produced.

Microcapsules produced by using TEPA as the amine monomer had a different appearance to those produced using DETA or TETA. The capsules were similar in size to previous samples, but the wrinkling of each capsule shell was more pronounced—

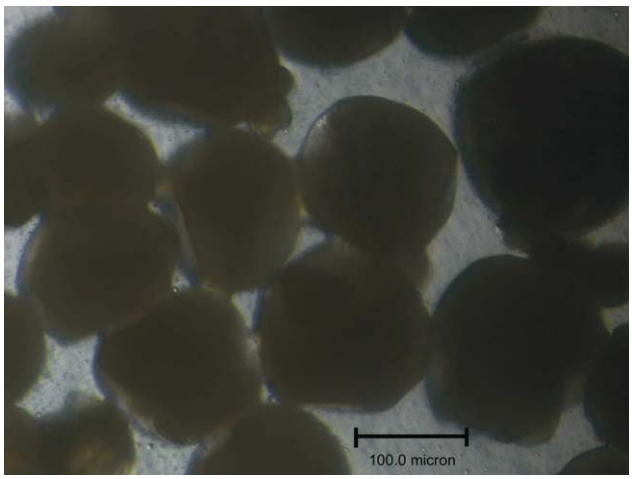


Figure 2. Polyurea microcapsules containing a CHP core, prepared via interfacial polymerization, using TEPA as the amine monomer. These capsules have a more dimpled appearance (evidenced by the large concave light spots at the edges of the microcapsules), with fusion of capsules visible in the center. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

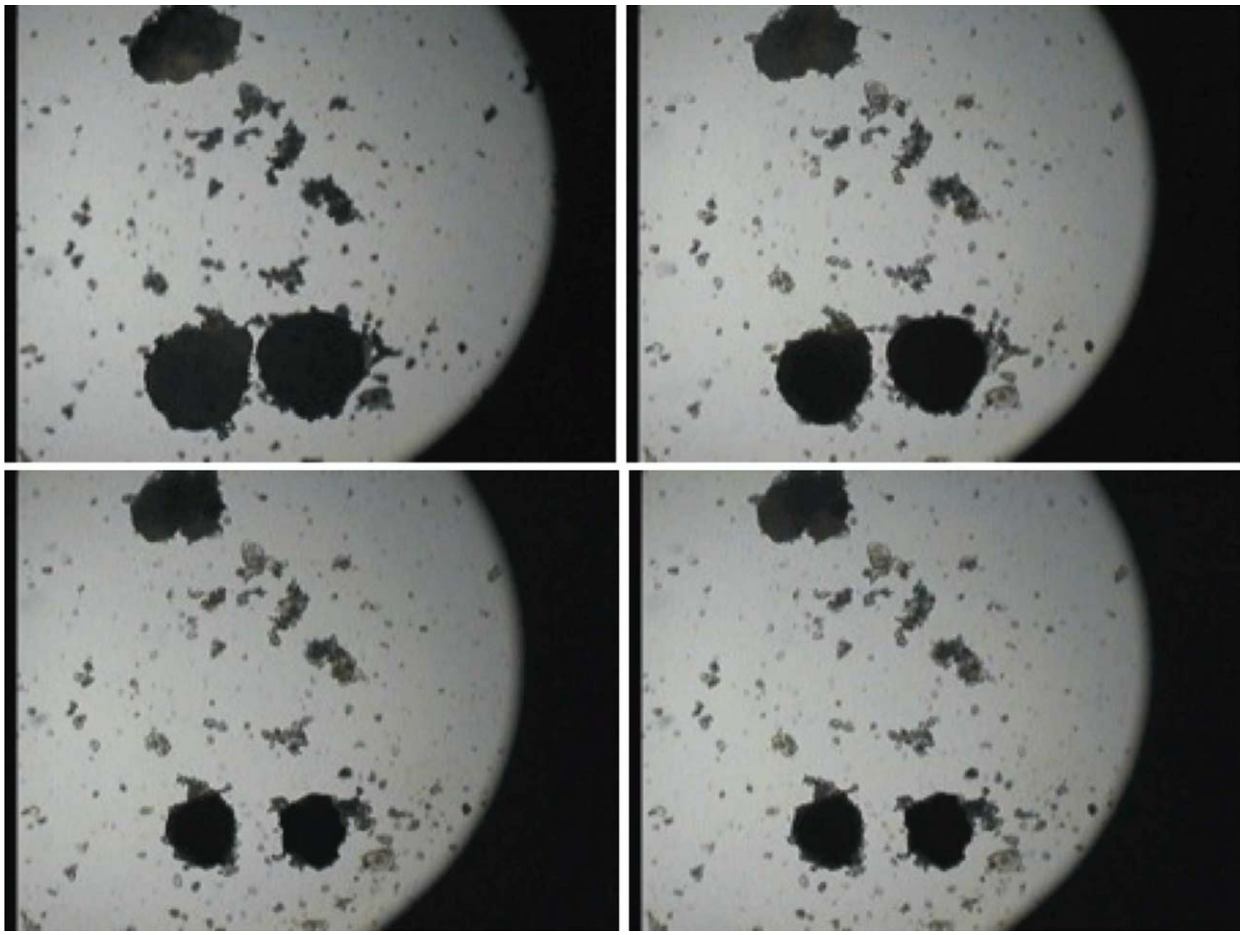


Figure 3. Polyurea microcapsules containing a CHP core, viewed by light microscopy while heated. Images are listed sequentially beginning in the upper left, and following a clockwise pattern. It was observed that the microcapsules experienced a buildup of internal pressure when heated, causing a gradual leakage of core as the temperature increased. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

large concave dimples were present on the edge of each microcapsule, rather than slight wrinkling (Figure 2). Also, evidence of fusions formed between capsules (rather than just within individual capsule shells) was also observed. This is undesirable, as these fusions cause brittle surface imperfections, as well as limiting the ability to harvest and separate individual, free-rolling capsules that can be easily dispersed. It is suspected that these fusions may be caused by crosslinking between the surfaces of multiple capsule shells, due to the higher concentration of secondary amine groups present.

The core loading percentage (weight percentage of capsule that is composed of the core material) for capsules made with DETA ranged from 75 to 85%. Capsules made with TETA and with TEPA, respectively, also had core-loading percentages of 75−80%. Capsules made with EDA had core-loading percentages of 25−30%, and when viewed by light microscopy these capsules had irregular shapes that were not consistent with the spherical nature of the other microcapsules samples. Because of this evidence, capsules produced with EDA were deemed to have insufficient crosslinking to produce quality capsules, so no further experiments were conducted with these. Further experiments were conducted with the other capsules.

Thermal Stability of Microcapsules

To determine the feasibility of using the initiator-core microcapsules in frontal polymerization reactions, an examination of the thermal stability of the microcapsules was necessary. A typical polymerization front in a multifunctional acrylate propagates with a temperature on the order of 250°C; in order to be effective, the microcapsules must release the core initiator either partially or completely at the front temperature. However, the microcapsules must have a thermal stability to resist excessive leakage at slightly elevated temperatures in order to maintain a sufficient pot life when used in certain situations (e.g., at a construction site on a hot summer day).

A microcapsule sample was examined by heated-stage microscopy in order to visually observe the reaction of the microcapsules to an increase in temperature; the temperature was ramped at a rate of 20°C/min, starting at a temperature of 30°C. The appearance of the capsules changed as the temperature increased, as illustrated in Figure 3. The microcapsules initially underwent a slight swelling, and then gradually began to shrink in volume, with the size of the capsules becoming smaller than the initial size at ~160°C. The shrinking of the individual capsules can be easily seen by observing the change

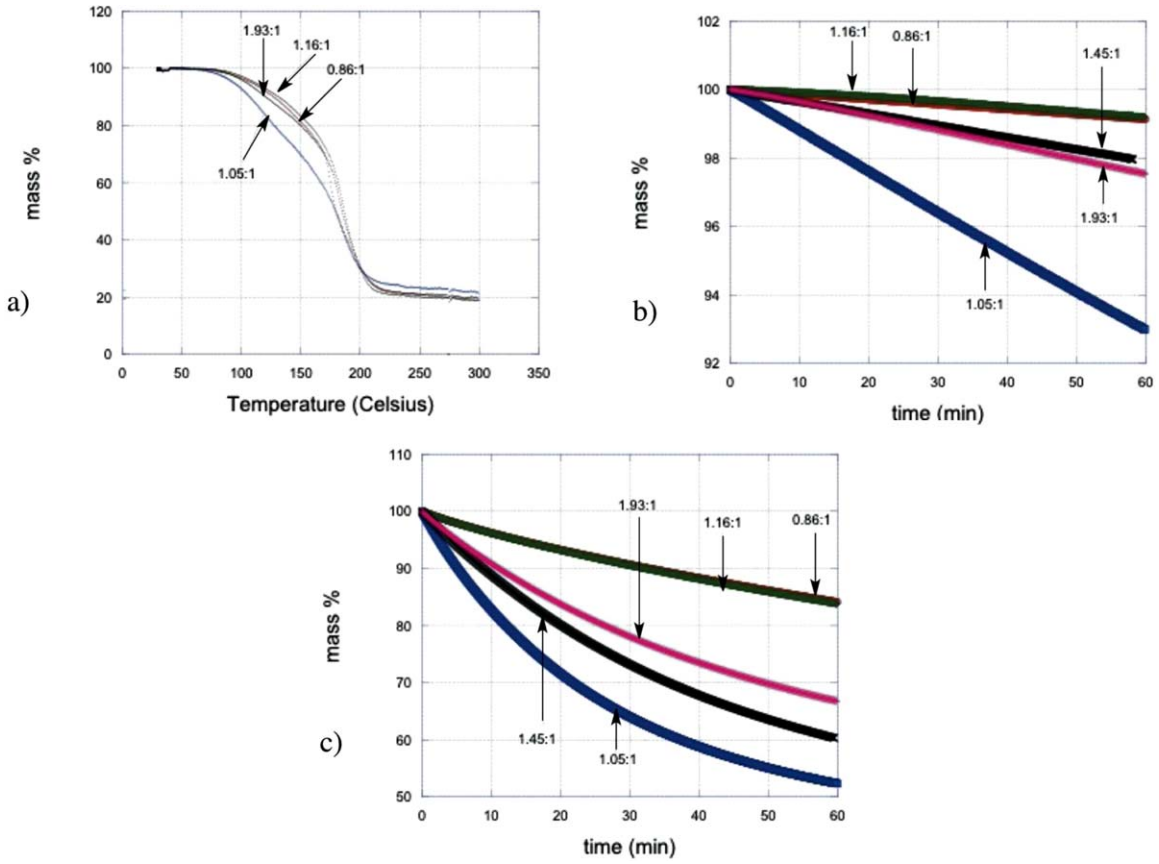


Figure 4. (a) TGA analysis of CHP-core microcapsules prepared with varying amounts of TETA as a shell component, ramped 20°C/min. The isocyanate to primary amine ratios are shown and matched with corresponding curves with arrows. Microcapsules made with an isocyanate to primary amine ratio of 1.45 : 1 were not tested. (b) TGA analysis of these microcapsules, held isothermally at 50°C for 1 h. (c) TGA analysis of these capsules, held isothermally at 85°C for 1 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

in proximity of the capsules to each other. The capsules appeared to release the core fairly rapidly after this point, but still as a steady leak and not a sudden "pop" of the capsules. By the time the capsules reached a temperature of 200°C, the capsules were quite shriveled, and apparently had released all of the core material. This is shown by the fact that there was no further shriveling as the temperature was increased above 200°C.

Visual examination of the microcapsules through heated-stage microscopy indicated that they would sufficiently release the core initiator at the temperature of a typical polymerization front. A more definitive analysis of the thermal release properties was needed, so the microcapsules were tested by thermogravimetric analysis (TGA).

It was hypothesized that changing the crosslinking of the shells could possibly affect various properties of the microcapsules. One of these properties was the thermal stability of the capsules. There were two methods proposed earlier in which crosslinking could be affected: (1) Using amines of varying secondary amine functionality, and (2) Varying the ratio of isocyanate groups to primary amine groups during the microencapsulation process. Microcapsules were prepared using a triamine, tetramine, and a pentamine as respective monomers; the effect of varying the ratio of isocyanate to primary amine groups was tested with capsules prepared from each type of amine.

The first microcapsule batches were made using triethylenetetramine (TETA) as the amine monomer. The isocyanate to primary amine ratios tested were 0.86 : 1, 1.05 : 1, 1.16 : 1, 1.45 : 1, and 1.93 : 1. It was hypothesized that too low of a ratio could result in insufficient crosslinking in the capsule shell, but that too high of a ratio could result in intercapsule crosslinking that could result in surface imperfections that could negatively affect the thermal stability of the capsule. A rapid 20°C/min ramp of these capsules is shown in Figure 4(a). It is seen that the general trend within all the capsule sets was to exhibit noticeable loss in mass at ~100°C, and to undergo a gradual complete release of core CHP over a 125° range until the core was completely released at ~225°C.

The microcapsules were then tested by holding isothermally at 50°C for 1 h. Figure 4(b) shows the results of these tests. Capsules prepared with ratios of 0.86 : 1 and 1.16 : 1 proved to be the most stable, losing ~1.5% total mass, followed by capsules prepared with 1.45 : 1 (2% mass loss), 1.93 : 1 (2.5% mass loss), and 1.05 : 1 (7.0% mass loss). With the exception of capsules prepared with a 1.05 : 1 ratio, capsules seemed to be slightly more stable when prepared with a lower isocyanate to primary amine ratio.

Figure 4(c) shows a comparison of these capsule samples held at 85°C. The samples made with ratios of 0.86 : 1 and 1.16 : 1

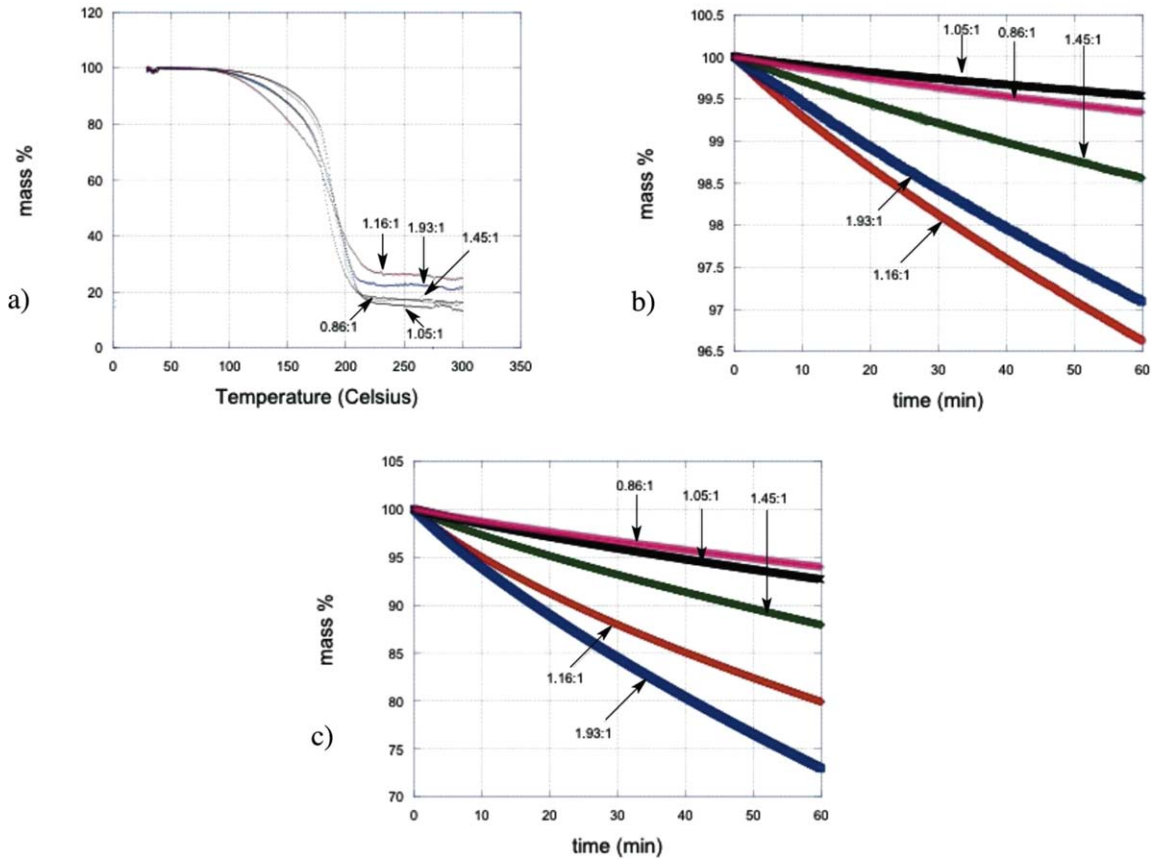


Figure 5. (a)TGA analysis of CHP-core microcapsules prepared with varying amounts of DETA as a shell component, ramped 20°C/min. (b) TGA analysis of these microcapsules, held isothermally at 50°C for 1 h. (c) TGA analysis of these microcapsules, held isothermally at 85°C for 1 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

again show the greatest thermal stability; however, in this case capsules prepared with a 1.93 : 1 ratio showed a greater stability than those prepared with a 1.45 : 1 ratio. Capsules prepared with a 1.05 : 1 ratio again showed the least stability.

Microcapsule batches were made using diethylenetriamine (DETA) as the amine monomer, at the same isocyanate to primary amine ratios that were used to make the previous capsules. Figure 5(a) shows a comparison of each sample as they underwent a rapid ramp of 20°C/min. Each sample showed noticeable major release of the core beginning at ~125°C and continuing over about a 100° range until ~225°C, when all the core had apparently been released.

The microcapsules were then tested by holding isothermally at 50°C for 1 h. The results of these tests can be seen in Figure 5(b). The capsules are seen to be quite stable, losing a range of ~0.5% (in capsules prepared with an isocyanate to primary amine ratio of 1.05 : 1) to 3.3% (1.16 : 1 ratio). Microcapsules made with the two lowest ratios proved to be the most stable, but no definitive trend could be seen in the stability as the ratio of reactants ascended or descended.

These capsules were also tested isothermally at 85°C for 1 h; the results can be seen in Figure 5(c). In this case, a more definitive trend is seen: with the exception of the 1.16 : 1 ratio, the microcapsules showed greater thermal stability as the isocyanate to primary amine ratio decreases. The most stable capsules were made from a ratio of 0.86 : 1 (6.0% total mass loss), and the least stable were made from a ratio of 1.93 : 1 (27.0% total mass loss).

The last batches of microcapsules were prepared using tetraethylenepentamine (TEPA) as the amine monomer. The same isocyanate to primary amine ratios were tested. Figure 6(a) shows the results for a rapid ramp of 20°C on these samples. The capsules made with the pentamine showed less stability at all ratios, tending to show major leakage starting at ~75°C and continuing over a 125° range to 200°C.

The microcapsules were then tested isothermally at 50°C for 1 h, and the results are shown in Figure 6(b). Overall, the capsules were less stable than capsules made with the triamine and tetramine, as the mass loss ranged from 7% (using a 0.86 : 1 isocyanate to primary amine ratio) to 16.3% (using a 1.05 : 1 ratio). Although once again capsules made from the lowest ratio seemed to be the most stable overall, no discernible trend could be seen as the ratio increased or decreased.

Figure 6(c) shows the results when the microcapsules prepared with TEPA were tested isothermally at 85°C. Again there was no noticeable trend in thermal stability among variations in the

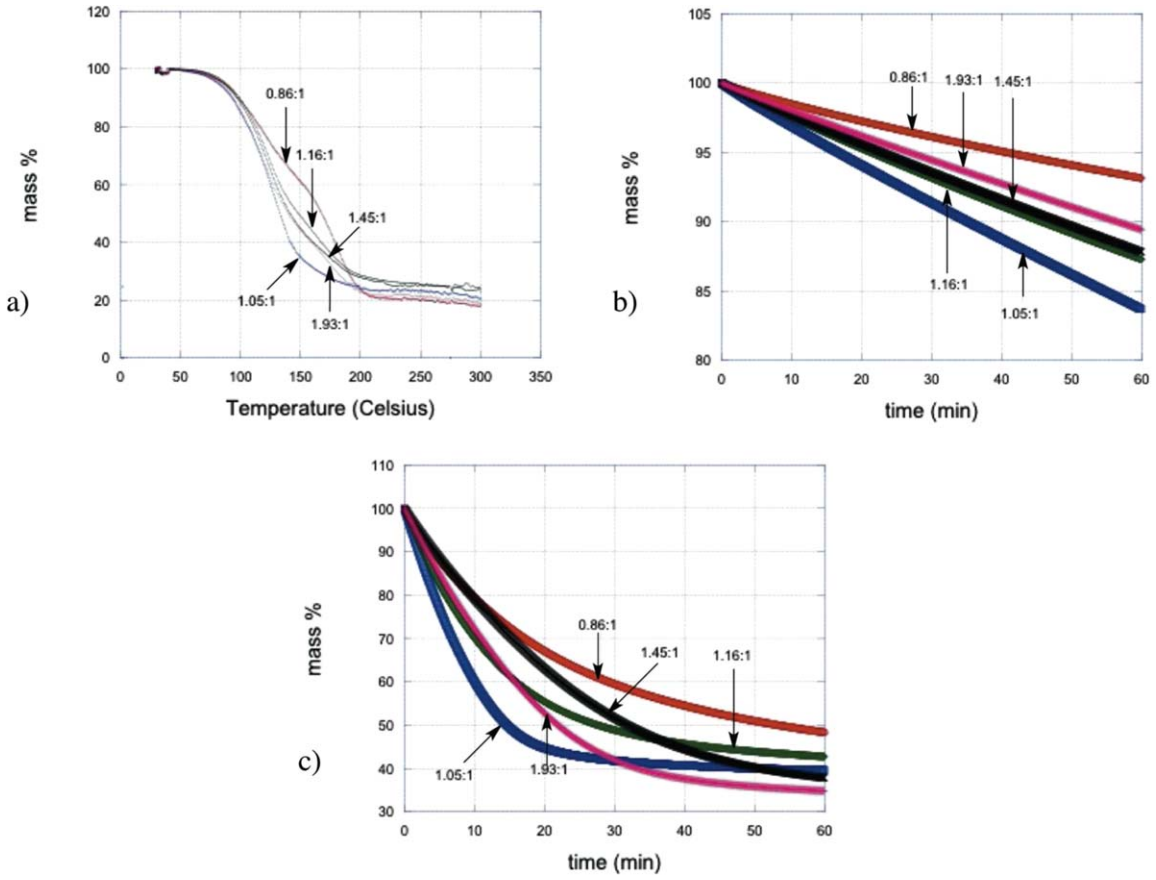


Figure 6. (a) TGA analysis of CHP-core microcapsules prepared with varying amounts of TEPA as a shell component, ramped 20°C/min. (b) TGA analysis of these microcapsules, held isothermally at 50°C for one hour. (c) TGA analysis of these microcapsules, held isothermally at 85°C for 1 h. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

isocyanate to primary amine group ratio. The most stable capsules at 85°C were made with the 0.86 : 1 and 1.16 : 1 ratios, the least stable with the 1.05 : 1 ratio. There was a wide range in stability among the different capsules tested, with the most stable samples losing ~16% of total mass and the least stable losing ~48% of its mass.

Table II. Capsule Mass Loss, at 50°C for 1 h

Isocyanate : primary amine (amine used)	Percent mass lost
0.86 (DETA)	0.7%
1.05 (DETA)	0.5%
1.16 (DETA)	3.4%
1.45 (DETA)	1.4%
1.93 (DETA)	2.9%
0.86 (TETA)	0.9%
1.05 (TETA)	7.0%
1.16 (TETA)	0.8%
1.45 (TETA)	2.0%
1.93 (TETA)	2.4%
0.86 (TEPA)	6.8%
1.05 (TEPA)	15.9%
1.16 (TEPA)	12.7%
1.45 (TEPA)	12.3%
1.93 (TEPA)	10.6%

Table III. Capsule Mass Loss, at 85°C for 1 h

Isocyanate : primary amine (amine used)	Percent mass lost
0.86 (DETA)	6.0%
1.05 (DETA)	6.8%
1.16 (DETA)	20.0%
1.45 (DETA)	12.2%
1.93 (DETA)	27.2%
0.86 (TETA)	16.9%
1.05 (TETA)	47.5%
1.16 (TETA)	17.0%
1.45 (TETA)	39.0%
1.93 (TETA)	33.5%
0.86 (TEPA)	51.7%
1.05 (TEPA)	59.5%
1.16 (TEPA)	57.0%
1.45 (TEPA)	60.9%
1.93 (TEPA)	65.0%

Table IV. Average Mass Loss of Microcapsules in Isothermal TGA Measurements

Amine monomer used to make shells	Average mass loss, 50°C for 1 h	Average mass loss, 85°C for 1 h
DETA	1.8%	14.4%
TETA	2.6%	30.8%
TEPA	11.7%	58.8%

A summary of the isothermal TGA data can be seen in Tables (II–IV). Overall, TGA showed that microcapsules made with TETA and DETA showed the best thermal stability. Contrary to what was originally hypothesized, the microcapsules made with the triamine appeared to be slightly more stable than the microcapsules with the tetramine; the ramp results show that the DETA capsules began to show major loss of mass at a temperature of 125°C as opposed to 100°C for the TETA capsules. DETA and TETA-component capsules seemed to show similar

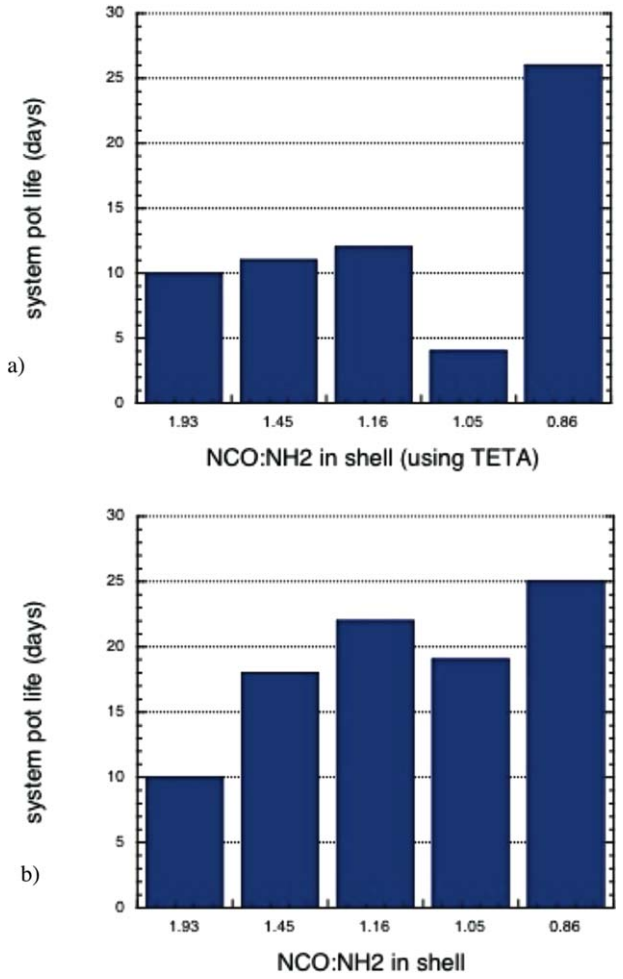


Figure 7. Pot lives of HDDA systems containing: (a) 2% CHP (encapsulated) and 0.04% cobalt naphthenate at room temperature. (b) 2% CHP (encapsulated) stored at 50°C. Capsules were made with TETA using different isocyanate to primary amine ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

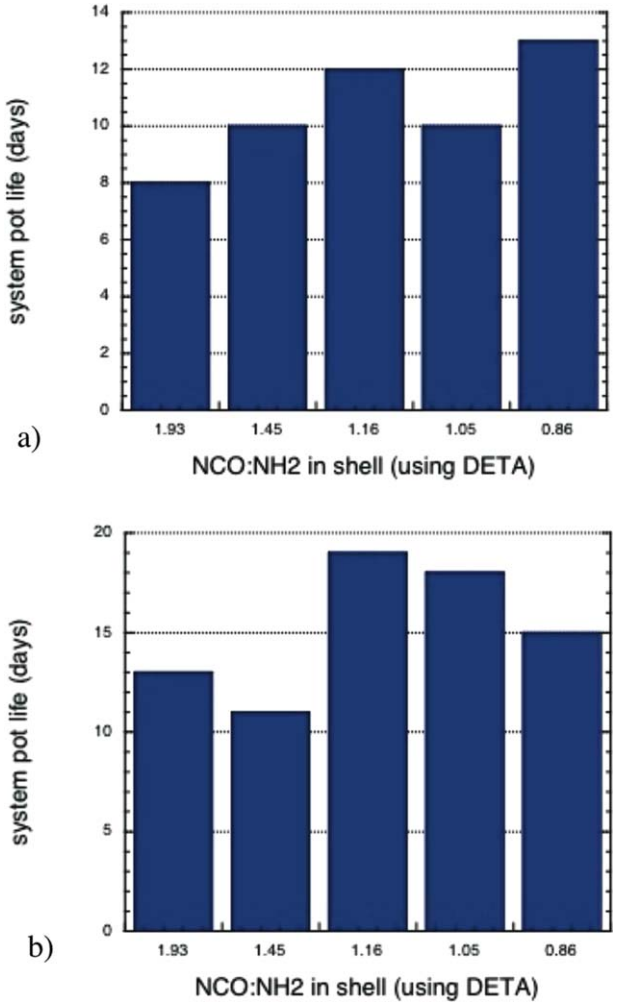


Figure 8. Pot lives of HDDA systems containing: (a) 2% CHP (encapsulated) and 0.04% cobalt naphthenate at room temperature. (b) 2% CHP (encapsulated) at 50°C. Capsules were made with DETA using different isocyanate to primary amine ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stabilities during isothermal testing at 50°C (with the exception of the TETA capsules made with a 1.05 : 1 isocyanate to primary amine ratio); all batches except one in these two sets lost less than 3.5% of total mass. A larger difference can be seen, however, in the isothermal runs held at 85°C. Capsules made with DETA showed a mass loss ranging from approximately 6−27% and an average mass loss of 14.4%, while capsules made with TETA showed a mass loss ranging from approximately 16−48% and an average mass loss of 30.8%. This indicates that the shells prepared using amines of lower secondary amine functionality (which had fewer reactive spots to form crosslinks) had a higher thermal stability; this could possibly be due to intercapsule crosslinks that formed when using the higher functionality amine, causing surface imperfections when broken apart during the drying process.

This trend was further evidenced when examining thermal properties of the capsules made using TEPA (the pentamine). This was the highest functionality amine that was tested, and it

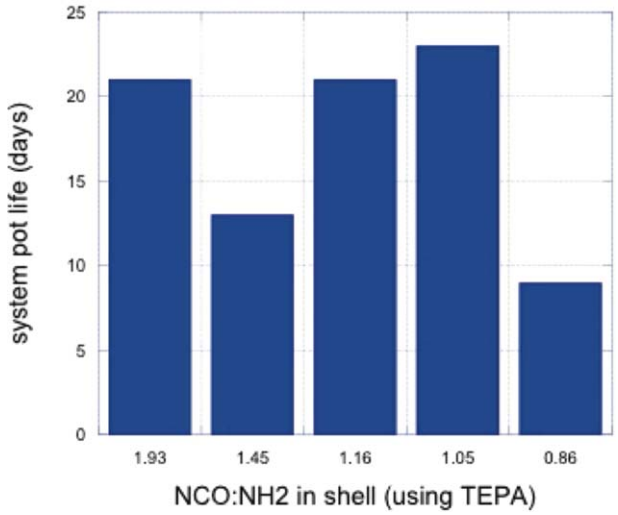


Figure 9. Pot lives of HDDA systems containing 2% CHP (encapsulated) stored at 50°C. Capsules were made with TEPA at different isocyanate to primary amine ratios. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

produced the capsules with the poorest thermal properties. The capsules began to show major mass loss at ~75°C during the rapid ramp, a temperature considerably lower than seen in the ramps of capsules prepared with TETA and DETA. Isothermal tests at 50°C and 85°C showed a loss of core material that was considerably higher than in capsules prepared with TETA and DETA (especially at 85°C, where an average mass loss of 58.8% was observed.

Overall, the trend observed when measuring thermal stabilities of the microcapsules was that DETA > TETA > TEPA when selecting amine monomers that produced more thermally stable microcapsules. DETA had the lowest secondary amine functionality of these monomers, and TEPA had the highest; this indicates that in dry storage, these microcapsules exhibit a larger degree of thermal stability with a moderate degree of crosslinking as opposed to a heavier degree.

In general, there were no definite trends regarding the change in isocyanate to primary amine ratio. In each of the isothermal tests the lowest ratio (0.86 : 1) seems to be the most stable, but the other ratios were not consistent in showing thermal stability trends. It seems that although changing the ratio of reactants can have some effect on the thermal stability, a more dependable result can be reached by changing the functionality of the amine instead.

Pot Lives of Monomer-Initiator Systems

One of the primary purposes for conducting this research was to increase the pot lives of monomer systems that are used in frontal polymerization. Previously, it was demonstrated that the pot lives of common thermosetting monomers were quite limited in systems that contained unencapsulated CHP.[12] These pot lives were tested in two sets of conditions that could accelerate polymerization of the monomer: (1) storage at an elevated temperature (50°C), and (2) storage at room temperature, in the presence of a species that accelerates peroxide decomposition (cobalt naphthenate).[29] These pot life tests were replicated using the thermosetting monomer HDDA and microencapsulated CHP. Again, the effects of different degrees of capsule shell crosslinking were examined.

Table V. Pot Lives of HDDA Systems with 2% Encapsulated CHP and 0.04% Cobalt Naphthenate, Stored at Room Temperature

Isocyanate : primary amine (amine used)	Pot life (days)
0.86 (DETA)	13
1.05 (DETA)	10
1.16 (DETA)	12
1.45 (DETA)	10
1.93 (DETA)	8
0.86 (TETA)	26
1.05 (TETA)	4
1.16 (TETA)	12
1.45 (TETA)	11
1.93 (TETA)	10
0.86 (TEPA)	<1
1.05 (TEPA)	<1
1.16 (TEPA)	<1
1.45 (TEPA)	<1
1.93 (TEPA)	<1

Figure 7(a) shows the pot lives of accelerated HDDA systems stored at room temperature containing CHP-core microcapsules produced with TETA as a shell component. Capsules produced with different isocyanate to primary amine ratios were tested in the systems. It was observed that the pot life of the HDDA system containing the capsules with the highest ratio had a pot life of 10 days, and the pot life gradually increased with decreasing ratio. The 1.05 : 1 ratio had the shortest pot life at 4 days, but

Table VI. Pot Lives of HDDA Systems with 2% Encapsulated CHP, Stored at 50°C

Isocyanate : primary amine (amine used)	Pot life (days)
0.86 (DETA)	15
1.05 (DETA)	18
1.16 (DETA)	19
1.45 (DETA)	11
1.93 (DETA)	13
0.86 (TETA)	25
1.05 (TETA)	19
1.16 (TETA)	22
1.45 (TETA)	18
1.93 (TETA)	10
0.86 (TEPA)	9
1.05 (TEPA)	23
1.16 (TEPA)	21
1.45 (TEPA)	13
1.93 (TEPA)	21

Table VII. Average Pot Lives of HDDA Systems Tested

Amine monomer used to make shells	Average pot lives of systems containing 2% encapsulated CHP, 0.04% cobalt naphthenate, room temperature	Average pot lives of systems containing 2% encapsulated CHP, 50°C
DETA	10.6 days	15.2 days
TETA	12.6 days	18.8 days
TEPA	<1 day	17.4 days

the capsules produced with the lowest ratio (0.86 : 1) had the longest pot life at 26 days.

Figure 7(b) shows the pot lives of unaccelerated HDDA systems stored at 50°C containing CHP-core microcapsules produced with TETA as a shell component; capsules with shells prepared from different isocyanate to primary amine ratios were once again tested. The longest pot life was observed using capsules produced with the lowest ratio (0.86 : 1), but no discernible trend was observed with the other ratios.

The same tests were conducted with microcapsules made with DETA as the amine monomer. Figure 8(a) shows the pot life in accelerated HDDA systems. The pot life using capsules made from the highest ratio exhibited a pot life of 8 days, and the pot life increased gradually as the ratio was decreased, with the exception of the 1.05 : 1 ratio. This was consistent with the trends shown in the system pot lives in which TETA capsules were used. When tested in unaccelerated systems at room temperature [Figure 8(b)], a slightly different trend was observed. Optimal pot life (19 days) occurred at capsules made from the middle ratio (1.16 : 1), with a slight decrease in pot life when the crosslinking in the capsules was reduced. However, the capsules prepared with the highest isocyanate to primary amine ratios (1.93 : 1 and 1.45 : 1) again exhibited the lowest pot life stability.

Microcapsules produced with TEPA were also tested. Each set of microcapsules prepared from TETA resulted in a very poor pot life for the respective accelerated HDDA systems in which they were tested. Each accelerated system polymerized within one day of storage. The microcapsules produced considerably longer pot lives when stored in unaccelerated systems at 50°C (Figure 9); no discernible trend in the system pot lives was observed when using capsules prepared from varying reactant ratios. The shortest pot life occurred when using capsules made with the lowest ratio, but there was no consistent pattern of increase or decrease in pot life as the ratio increased. The longest pot life was 23 days, using capsules produced with the second-lowest isocyanate to primary amine ratio (1.05:1). The lack of a trend as the ratio was changed was not really a surprise, however; when using TEPA the capsules tended to stick to each other so much that they were quite difficult to separate into individually capsules, regardless of the ratio of reactants used. Because of the difficulty in separation, large inhomogeneities in capsule surface imperfections could have resulted from batch to batch.

A summary of the pot life data can be seen in Tables (V–VII). On average, microcapsules produced with TETA provided the HDDA systems with the greatest pot life stability in both accelerated systems stored at room temperature and in unaccelerated systems stored at slightly elevated temperatures. The pot lives provided by these capsules were slightly higher than those prepared with DETA in accelerated systems, while the capsules prepared with TEPA provided very short pot lives. However, microcapsules produced with TEPA led to, on average, longer pot lives in accelerated HDDA systems at room temperature than capsules produced with DETA (but slightly shorter than when using capsules produced with TETA. One interesting observation was that although capsules produced with DETA were the most thermally stable according to TGA analysis, they provided the shortest overall pot life when tested in HDDA systems of elevated temperature. The capsules could possibly have a shell structure that results in higher temperature stability in dry storage, but is more permeable to penetration by the monomer storage medium than the other shells. The opposite could be said for the TEPA capsules, which exhibited the poorest thermal stability but exhibited surprisingly long HDDA pot life stability at an elevated temperature. The TEPA capsules were very sensitive to the presence of cobalt naphthenate, as those systems polymerized within a day; the surface imperfections present in these capsules could have made them particularly vulnerable to penetration by the promoter. Capsules produced using TETA and DETA also demonstrated sensitivity to the presence of cobalt naphthenate, but a much lower degree of sensitivity than demonstrated using capsules produced with TEPA.

In capsules produced with DETA and TETA, there is some indication that the shells produced with the highest isocyanate to primary amine ratio were generally the least stable, as pot lives tended to trend downward as this ratio increases. However, as with the TGA data, there is a lack of consistency from the lowest ratio to the highest ratio, so there is no evidence to suggest that varying crosslinking by changing the ratio of isocyanate to primary amine in microcapsule production has an effect on capsule stability in monomer storage.

CONCLUSIONS

Thermogravimetric analysis indicated that the microcapsule shell helped to prevent the loss of CHP upon heating, both in rapid ramps and in isothermal runs. It was found that microcapsules produced with DETA were the most thermally stable in dry storage, followed closely by those made with TETA. Capsules produced with TEPA were considerably less thermally stable. Variation of the isocyanate to primary amine ratio when making the capsules appeared to possibly have an effect in thermal stability, as the lowest ratio (0.86 : 1) was the most thermally

stable in the TETA, DETA, and TEPA capsules at higher (85°C) temperatures. This could have been due to a reduction in intercapsule crosslinking; however, there was sufficient variation in the rest of the measurements to bring the importance of isocyanate to primary amine ratio into question.

The use of encapsulated CHP in place of dissolved CHP proved to greatly improve the pot lives of frontal polymerization systems in HDDA. The pot lives of accelerated systems improved from hours to anywhere from 10 to 25 days in HDDA, and unaccelerated systems held at 50°C experienced pot lives up to four times as long as when using dissolved CHP. Capsules made with different amine monomers and made with different reaction ratios were tested. It was found that capsules made with TETA provided the best overall pot life. Capsules produced with DETA improved the pot life, but not as much; these shells, although more temperature stable in dry storage, may be more prone to penetration by the monomer media. Capsules made with TEPA showed very poor stability in promoted systems, possibly due to added vulnerability to attack by cobalt naphthenate due to surface imperfections caused by intercapsule crosslinking. Although it was found in multiple cases that capsules made with the smallest (0.86 : 1) isocyanate to primary amine ratios provided the greatest pot life stability, no discernible trends relating pot life to isocyanate:primary amine ratio were observed.

In summary, an investigation was made into how variation of crosslinking of polyurea shells containing a free-radical initiator would affect stability and performance of the capsules. Variation was achieved by either: (1) using amine monomers of differing secondary amine functionalities, or (2) altering the ratio of primary amine to isocyanate groups in the shell materials. From the data gathered, it is evident that amine monomers containing different secondary amine functionalities do affect the performance of microcapsules produced, both in dry storage and in monomer storage. However, it is also evident that, although there is some indication that lower ratios of primary amine to isocyanate in shell production could produce higher performance microcapsules, there is a lack of consistent evidence that suggests altering this ratio has an overall effect on the performance of these microcapsules. As there is a range of particle size distribution, future work will include determination of these discrete particle size ranges, and any possible effects particle size may have on the quality of the microcapsules.

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