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PREPARATION OF POLYURETHANE MICROCAPSULE USING 1,3 PROPANEDIOL AS THE POLYOL COMPONENT

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ABSTRACT

PREPARATION OF POLYURETHANE MICROCAPSULE USING 1,3 PROPANEDIOL AS THE POLYOL COMPONENT. Self-healing property is the ability of a material to heal damages automatically and autonomously. Its application would be ranged from paint coating, anti corrosion coating, space-shuttle material, construction (concrete) and automotive. Extrinsic self healing requires self healing agent preembedded or incorporated into polymer matrix that would be released and close the damage in the polymer system, where the polymer itself is not healable. Healing agents are encapsulated or embedded into the material prior application. Example of monomer encapsulated to give self healing property is isophorone diisocyanate (IPDI) encapsulated in polyurethane shell. In this study, we studied the possibility of 1,3 propanediol, that can be derived from palm oil as polyol monomer for polyurethane microcapsule shell containing IPDI or stannous octoate as a self healing agent. Microcapsule in this study was prepared by interfacial polymerization technique to form IPDI monomer in polyurethane shell. FT-IR analysis show that polyurethane prepolymer produced still have unreacted isocyanate group necessary for interfacial polymerization of polyurethane. Morphological analyses of the microcapsule products show that the products have spherical shapes with smooth surface and some with wrinkled surface. The particle sizes were ranged from 40.29 to 526.80 μm.

Key words : Self healing, Encapsulation, Isocyanate, Polyol, Microcapsule

ABSTRAK

PREPARASI MIKROKAPSUL POLIURETAN MENGGUNAKAN 1,3 PROPANDIOL SEBAGAI KOMPONEN POLIOL. Kemampuan *self healing* adalah kemampuan suatu materi untuk dapat memperbaiki sendiri kerusakan yang terjadi pada materi secara otomatis. Aplikasi materi seperti ini sangat luas dari *coating* cat, *coating* anti karat, bahan pesawat ulang alik, konstruksi (semen) dan otomotif. Sifat *self healing* ekstrinsik didapatkan dengan menambahkan *self healing agent* dengan inkorporasi pada matriks polimer yang nantinya dilepaskan dan kemudian akan menutup kerusakan yang terjadi pada sistem polimer, dimana polimer itu sendiri tidak bersifat *self healing*. Pada aplikasinya, *self healing agent* dienkapsulasi sehingga berada di dalam materi matriks polimer. Contoh monomer yang dienkapsulasi untuk mendapatkan sifat *self healing* adalah *isophorone diisocyanate* (*IPDI*) yang dienkapsulasi dalam cangkang poliuretan. Pada studi ini dipelajari potensi penggunaan 1,3 propandiol, yang dapat dihasilkan dari produk turunan minyak sawit, sebagai monomer poliol untuk cangkang mikrokapsul poliuretan yang berisi *IPDI* atau *stannous octoate* sebagai *self healing agent*. Mikrokapsul pada studi ini dipreparasi dengan teknik polimerisasi antarmuka untuk menghasilkan monomer *IPDI* di dalam cangkang poliuretan. Analisis *FT-IR* menunjukkan bahwa prepolimer poliuretan yang dihasilkan masih memiliki gugus isosianat bebas yang diperlukan untuk polimerisasi antarmuka poliuretan. Analisis morfologi mikrokapsul yang dihasilkan menunjukkan bentuk produk yang sferik dengan permukaan yang halus dan beberapa dengan permukaan berkerut. Ukuran partikel berada dalam kisaran 40,29 μm hingga 526,80 μm.

Kata kunci *: Self healing*, Enkapsulasi, Isosianat, Poliol, Mikrokapsul

INTRODUCTION

The ability of a material to be able to heal damages automatically and autonomously is called self healing property [1]. This material can close the damage within their structure by restoring and maintaining its original mechanical properties. Its application would be ranged from paint coating, anti corrosion coating, space shuttle materials, construction (concrete) and automotive. Examples of

self healing material already in the market are particularly in polymer material such as hydrophobic paint by Nissan Motor Co. that repairs scratches and polyurethane clear coat from Bayer Materials Science [1].

Polymeric coating materials are particularly susceptible to natural or artificial degradation. For its application as structural materials, polymer degradation may come in the formation of microcracking that would reduce materials mechanical properties and shorten its lifetime. This microcracking occurs deep within the polymer matrix and would be difficult to observed and repaired. Thus, it would be beneficial if the materials could be self healed. Engineering self healing property to a material is much inspired from natural process of blood clotting or repairing process in fractured bones. In nature, this process of repairing damage depends on rapid transportation of repair substance to the injured part and reconstruction of the tissues [2].

Incorporation of self healing properties in polymeric materials could be classified into two categories: (i) intrinsic (non-autonomous) self-healing materials that able to heal cracks by the polymers themselves but need external triggering, and (ii) extrinsic (autonomous) in which self healing agent were introduced or preembedded into polymer matrix [1-2]. Intrinsic self healing means that the polymer matrix themselves intrinsically have self healing properties that can heal after damage occur, although it still need external stimulation (thermal, electrical, radiation) [2, 3]. In term of its intrinsic self healing mechanism, certain materials could undergo either physical interaction/rearrangement or chemical interaction where bond rearrangement occurs.

Extrinsic self healing requires self healing agent preembedded or incorporated into polymer matrix that would be released and close the damage in the polymer system, where the polymer itself is not healable. Healing agents are encapsulated or embedded into the material prior application. Beside encapsulation, self healing agent could also loaded in pipeline within the matrix [2]. When crack occurs, mechanical force would destroy the capsule or pipeline and triggers the release of self healing agent. By capillary forces, the self healing agent would reach the site of cracking and interact chemically with polymer matrix to close and heal the crack [4]. Types of self healing agent that can be encapsulated are monomers, dyes, catalysts, and hardener. Those can be encapsulated or embedded into polymeric systems in the mean of microcapsules, hollow fibers, or channels [1].

Microencapsulation enclose particle of solids, droplets of liquids, or gases in an inert shell that act as a protective barrier from external environments [1, 4]. The encapsulation of dicyclopentadiene (DCPD) monomer in microsphere and its application in self-healing polymer composite were extensively studied [4-10]. The chemistry of DCPD monomer was based on ring opening metathesis polymerization when DCPD monomer came in contact with Ruthenium-based Grubbs'catalyst [4]. Self healing property of polymeric composite containing encapsulated DCPD was assessed and applied in polymer system of woven glass fibre matrix [5] and thermosetting matrix (EPON) [4, 6, 9, 10]. Another example of monomer encapsulated to give self healing property is isophorone diisocyanate (IPDI) encapsulated in polyurethane shell [11]. IPDI has the potential to be applied in a free catalyst self-healing system because its reactivity with water. Microcapsule containing catalyst for self-healing polymeric material was also studied, such as microcapsule containing dibutyltin dilaurate (DBTL) catalyst dispersed in polydimethylsiloxane (PDMS) matrix. This work by Cho et al. (2006) based on self-healing reaction of hydroxyl end functionalized PDMS (HOPDMS) and polydiethylsiloxane (PDES) with DBTL catalyst [12]. Mixture of HOPDMS and PDES was phase separated in vinyl ester polymer matrix, while DBTL containing microcapsules were dispersed in the matrix.

Beside already mentioned single capsule system, there was also double capsule system with two type of healing agent encapsulated in a polymeric system. Studied a polymeric system containing encapsulated PDMS resin with Pt catalyst and encapsulated liquid initiator material of hydrosiloxane copolymer dispersed in PDMS elastomeric matrix [13]. Studied epoxy matrix system containing two type of microcapsule within it, which are microcapsule containing bisphenol-A epoxy resin and bisphenol-F epoxy resin [14]. Another way of incorporating self healing agent in polymeric matrix is injecting the self healing agent to microvascular or micropipeline network embedded in the matrix [15,16]. This system also allow two different self healing agents injected in two different microvascular networks so they would not mix to each other before crack occur [16].

Our Research Group of Polymer Laboratory, Indonesian Institute of Sciences, had previously studied the synthesis of palm oil derived polyol to prepare polyurethane [17,18]. An example of palm oil derived polyol is 1,3 propanediol that can be prepared from glycerol, a by product of biodiesel production. In this study, we studied the possibility of 1,3 propanediol as polyol monomer for polyurethane microcapsule shell containing IPDI or stannous octoate as a self healing agent. Stannous octoate can be used as a catalyst in PDMS polymerization.

EXPERIMENTAL METHODE

Prepolymer Preparation

The encapsulated prepolymer was polyurethane prepolymer of toluene diisocyanate and 1,3 propanediol. Toluene diisocyanate was dissolved into cyclohexanone in a three neck flask. The mixture was heated to 80 ^{o}C in an oil bath and stirred with magnetic stirrer. The polyol

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of 1,3 propanediol was then slowly added. The flask was purged with N_2 for an hour and allowed to react for 24 hour. The mixture was then distilled in a vacuum to remove excess reactants. Obtained product was viscous yellow prepolymer. The synthesis of prepolymer was conducted in varied ratio between TDI and 1,3 propanediol (TDI : polyol) of 2 : 1; 2.3 : 1 and 2.5 : 1.

Synthesis of Microcapsules

At room temperature, 30 mL of water and gum arabic (4.5 g) surfactant were mixed in a round bottom flask for 3 hour prior to encapsulation. Meanwhile, the prepolymer (2,9 g) was dissolved in chlorobenzene (4 g) at 68 ^oC. Once the prepolymer was completely dissolved, either IPDI or the stannous octoate catalyst was added to this organic mixture. This mixture was then slowly poured into the gum arabic solution. The water bath was heated to 70 ^oC and 1,3 propanediol as a chain extender was slowly added to this emulsion. The mixture was agitated and reacted for 3 hours. Solid product was filtered and dried in open air for 48 hours prior further analysis.

Characterization

Microcapsule and prepolymer product were anayzed with Fourier Transform Infrared (FT-IR, IRPrestige-21 SHIMADZU). Morphological analysis was conducted with Scanning Electron Microscopy (SEM, JSM-5600LV SEM Instrument, JOEL-Ltd.). Particle size analysis of microcapsule was conducted using Coulter LS Particle Size Analyzer.

RESULT AND DISCUSSION

Microcapsule in this study was prepared by interfacial polymerization technique to form IPDI monomer in polyurethane shell. The polymerization reaction takes place in the interfacial between prepolymer phase in chlorobenzene (oil phase) and water phase containing a polyol chain extender (1,3 propanediol) in an O/W emulsion system. In this study, an emulsion system was prepared with gum arabic surfactant. Encapsulated substance (core material) would be added to the oil phase. This interfacial polymerization, typically condensation polymerization, takes three necessary steps [19-20]. The first step is the formation of isocyanate (-NCO) terminated prepolymer (Figure 1). This prepolymer was prepared by reacting TDI with 1,3 propanediol with certain ratio to form prepolymer with free NCO terminal group. The second step is emulsification of the prepolymer to form O/W emulsion system. Prior to emulsification, IPDI monomer or stannous octoate catalyst to be encapsulated was mixed with the prepolymer as the oil phase. Meanwhile, gum arabic surfactant was dissolved in the water phase. Both

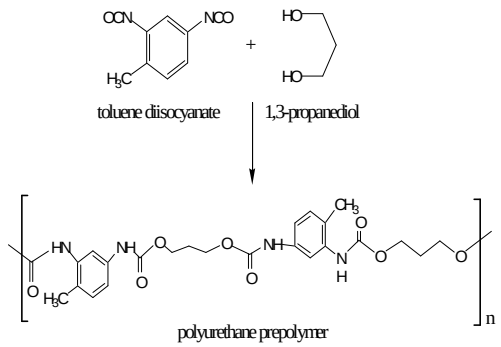

Figure 1. Reaction of polyurethane prepolymer synthesis

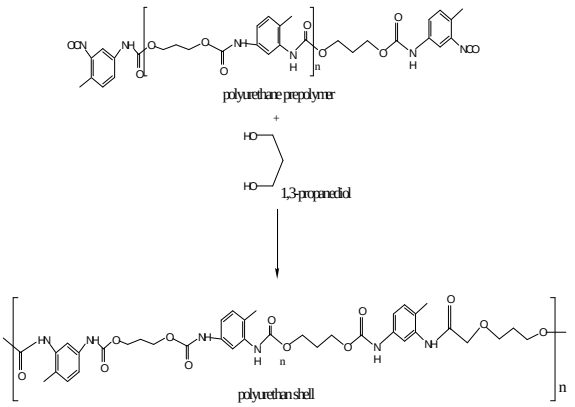

Figure 2. Reaction of polyurethane microcapsule shell

phase were thane mixed and emulsion formation was obtained by mechanical stirring. Polymerization was the last step in this interfacial polymerization. Complementary polyol monomer (1,3 propanediol) was added to the external phase of the emulsion and the polymerization occur in the liquid-liquid emulsion interface between water and oil phase (Figure 2). In the interface, reaction would occur between 1,3 propanediol with isocyanate terminated prepolymer. Meanwhile, the rest of the oil phase that did not make a contact with water phase would kept unreacted.

The first step in interfacial polymerization is synthesis of prepolymer with free isocyanate (-NCO) terminal group. This prepolymer was prepared by reacting TDI with 1,3 propanediol. Isocyanate terminated polyurethane prepolymer could be obtained by reacting the two monomers in certain ratio. To observe the formation of urethane bond and the occurrence of free isocyanate terminal group, FT-IR analysis was conducted to the prepared polymer. The FT-IR spectra of prepared polymer were shown by Figure 3-5. FT-IR spectrum of prepolymer product with TDI : 1,3 propanediol ratio of 2.3 : 1 is shown in Figure 4. In Figure 4, peak in the 2272 cm^{-1} came from isocyanate (-NCO) vibration. We can conclude that the prepolymer still have free unreacted isocyanate groups that are located in the terminal end of polyurethane prepolymer. Peaks in 3302 cm^{-1} from N-H stretching and 1517 cm^{-1} from N-H

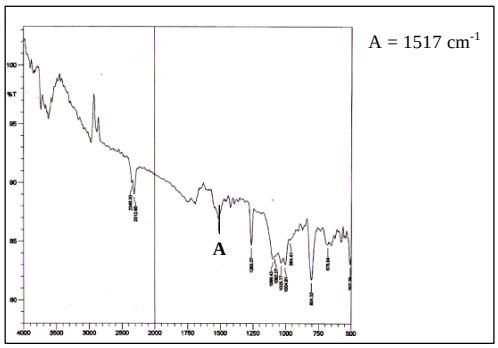

Figure 3. FT-IR spectrum of prepolymer product prepared from TDI : 1,3 propanediol ratio of 2 : 1.

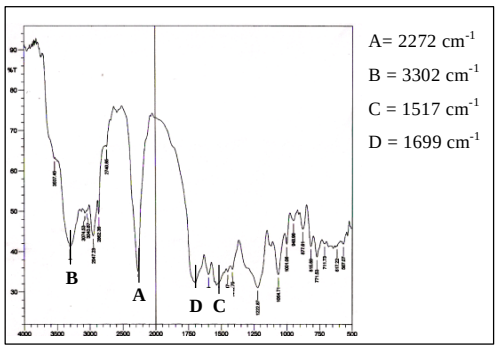

Figure 4. FT-IR spectrum of prepolymer product prepared from TDI : 1,3 propanediol ratio of 2.3 : 1.

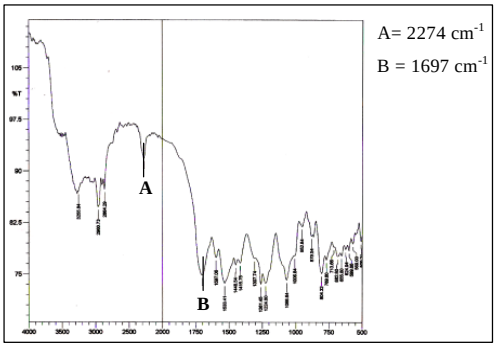

Figure 5. FT-IR spectrum of prepolymer product prepared from TDI : 1,3 propanediol ratio of 2.5 : 1.

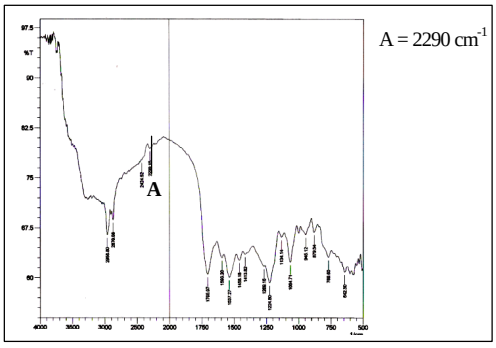

Figure 6. FT-IR spectrum of microcapsule containing stannous octoate healing agent prepared from TDI : 1,3 propanediol prepolymer ratio of 2 : 1.

bending show the formation of urethane linkage. Meanwhile, other peaks in 1699 cm^{-1} from carbonyl –CO of polyurethane and C-O-C of ester from 1000-1200 cm^{-1}

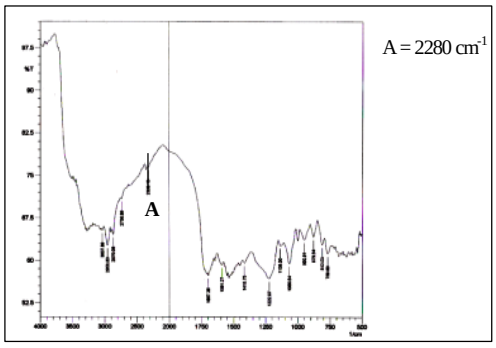

Figure 7. FT-IR spectrum of microcapsule containing stannous octoate healing agent prepared from TDI : 1,3 propanediol prepolymer ratio of 2.3 : 1.

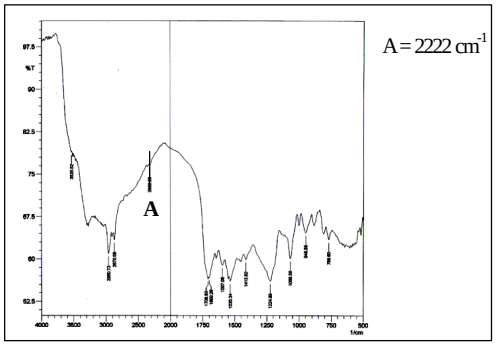

Figure 8. FT-IR spectrum of microcapsule containing stannous octoate healing agent prepared from TDI : 1,3 propanediol prepolymer ratio of 2.5 : 1.

also confirm that urethane linkage had already formed in the prepolymer product. In preparing polyurethane prepolymer, we varied the TDI and 1,3 propanediol ratio from 2 : 1; 2.3 : 1 and 2.5 : 1. FT-IR spectrum of prepolymer with 2 : 1 ratio did not show peak in the area around 2270 cm^{-1} that came from isocyanate group but gave peak at 1517 cm^{-1} that show the formation of urethane linkage. We presume that the product was polyurethane pepolymer with only small amount of unreacted isocyanate group. Meanwhile, both products with TDI and 1,3 propanediol ratio of 2.3 : 1 and 2.5 : 1 gave peak from isocyanate group vibration along with peaks from urethane linkage. Unreacted isocyanate group is necessary in the next step of interfacial polymerization. Isocyanate terminal group would later crosslink with polyol and form polyurethane microcapsule shell by extending the polymer chain.

Figures 6-8 show the FT-IR spectra of microcapsule containing stannous octoate healing agent that were synthesized from already prepared prepolymer. In microcapsule synthesize, 1,3 propanediol was reacted with the already prepared prepolymer and the reaction occur between 1,3 propanediol and free isocyanate of the prepolymer. This reaction occur in the interface between prepolymer as the oil phase and 1,3 propanediol in the water phase. From these spectra, we can see that the intensity of peaks from isocyanate at around 2200 cm^{-1} were decreased significantly compared to their related prepolymer spectra.

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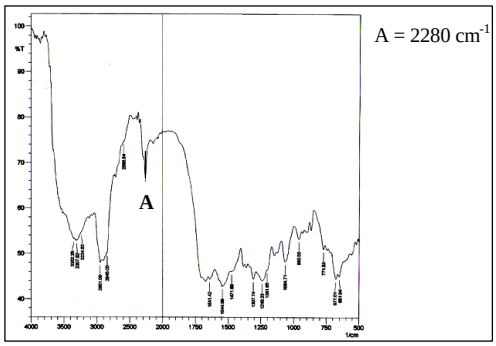

***Figure* 9.** FT-IR spectrum of microcapsule containing IPDI healing agent prepared from TDI : 1,3 propanediol prepolymer ratio of 2 : 1.

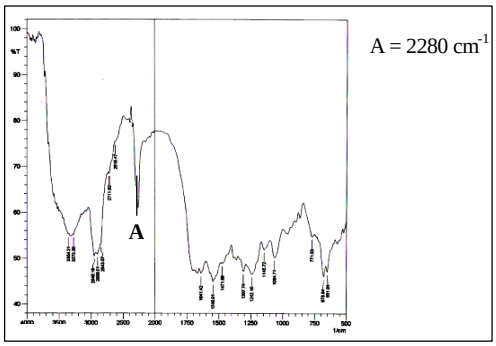

Figure 10. FT-IR spectrum of microcapsule containing IPDI healing agent prepared from TDI : 1,3 propanediol prepolymer ratio of 2.3 : 1.

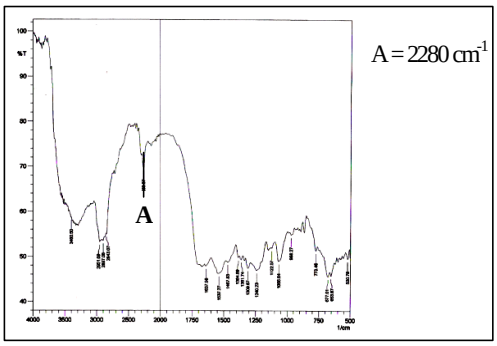

Figure 11. FT-IR spectrum of microcapsule containing IPDI healing agent prepared from TDI : 1,3 propanediol prepolymer ratio of 2.5 : 1.

The FT-IR spectra of microcapsule containing IPDI healing agent were shown in Figure 9-11. FT-IR spectra in Figures 9-11 show free icoyanate group peak at around 2280 cm^{-1}. These peaks may come from the free icoyanate group of IPDI encapsulated in the microcapsule as the self healing agent.

Morphological analysis of the microcapsule product was conducted using scanning electron microscopy (SEM). The microcapsule product gave spherical shape with smooth surface and some with wrinkled surface. Figure 12 shows the example of scanning electron micrograph of microcapsule from TDI : 1,3 propanediol of 2:1 ratio, containing self healing agent of stannous octoate and IPDI. Morphology of the capsule outer surface is resulted from

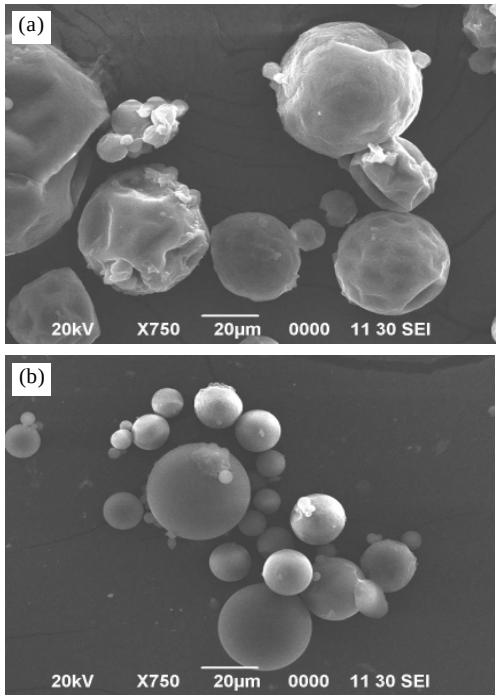

Figure 12. Scanning electron micrograph of polyurethane microcapsule from 2 : 1 prepolymer containing a) stannous octoate and b) IPDI monomer.

Table 1. Size distribution of polyurethane microcapsule containing IPDI or stannous octoate.

Sampel		Microcapsule diameter (µm)				
		% < 10	% < 25	% < 50	% < 75	% < 90
Prepolymer 2:1	IPDI	6.761	21.38	53.84	97.87	137.2
	stannous octoate	1.385	3.150	7.384	13.74	21.33
prepolymer 2.3:1	IPDI	1.13	3.504	14.32	76.9	122.2
	stannous octoate	151.9	340.6	542.6	742.8	858.3
prepolymer 2.5:1	IPDI	2.763	11.20	27.60	64.78	95.38
	stannous octoate	0.979	4.077	78.47	123.4	151.3

the interaction of inhomogeneous reaction kinetics, fluid-induced shear forces, and shell-determined elastic forces [11]. The size of the capsules was not uniform. Microcapsule from prepolymer with 2 : 1 ratio gave particle size of 9.64 ± 8.31 µm and 64.93 ± 53.6 µm for capsule filled with stannous octoate and IPDI respectively. Particle size analysis show that the average size of microcapsule prepared from prepolymer with 2.3 : 1 ratio are 526.8 ± 256 µm and 41.82 ± 48.3 µm for capsule filled with stannous octoate and IPDI respectively. Microcapsule from prepolymer with 2.5 : 1 ratio gave particle size of 74.39 ± 58.2 µm and 40.29 ± 35.8 µm for capsule filled with stannous octoate and IPDI respectively. Table 1 shows the size distribution of polyurethane microcapsule.

CONCLUSION

Polyol monomer of 1,3 propanediol could be used to synthesis the polyurethane prepolymer. This polyol can also act as the chain extender in the polyurethane

microcapsule shell via interfacial polymerization. The microcapsule obtained was in the spherical shape with smooth surface and some with wrinkled surface. The particle sizes were ranged from 9.64 to 526.80 μm.

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