Polyurethane microcapsule with glycerol as the polyol component for encapsulated self healing agent

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***Abstract*— Self healing property is the ability of a material to be able to heal damages automatically and autonomously. It has wide range of application from paint coating, anti-corrosion coating, space-shuttle material, construction (concrete), automotive, etc. Microcapsules containing reactive compound for use in self healing polymers are successfully fabricated via interfacial polymerization of polyurethane (PU). The possibility of glycerol as polyol monomer for polyurethane microcapsule shell in the preparation of PU prepolymer was studied. In this research, we also studied encapsulated self healing agent using IPDI, stannous octoate, dibutyl tin dylaurate. FTIR analysis showed that obtained polyurethane prepolymer still have unreacted isocyanate group necessary for interfacial polymerization of polyurethane. The morphology of polyurethane microcapsules containing IPDI was observed by scanning electron microscopy and shows spherical microcapsule with wrinkled surface but no agglomeration was found. The morphology of polyurethane microcapsules containing stannous octoate was also in spherical form but have a tendency of agglomerating and so were microcapsules containing dibutyl tin dilaurate. The average microcapsule size was 12.33; 28.59; and 25.65 µm for microcapsule containing IPDI, stannous octoate, and dibutyltin dilaurate respectively. The smallest average particles size (12.33 µm) was observed in microcapsules containing IPDI with narrow particle size distribution so the particles were more homogenous than the others.**

I. INTRODUCTION

The ability of a material to be able to heal damages automatically and autonomously is called self-healing property [1]. Polymeric coating materials are particularly susceptible to natural or artificial degradation. For its application as structural material, polymer degradation may come in the formation of microcracking that would reduce material's 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 material 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]. This self-healing material can close the damage within their structure by restoring and maintaining its original mechanical properties. It has wide range of application from paint coating, anti-corrosion coating, space-shuttle material, construction (concrete), automotive, etc. Examples of self-healing material already in the market are particularly in polymer material such as hydrophobic paint by Nissan Motor Co. that would repairs scratches and polyurethane clear coat from Bayer MaterialScience [1].

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 material 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, embedded or loaded in pipeline within the matrix 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].

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]. 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].

Our Research Group of Polymer Laboratory, Indonesian Institute of Sciences, had previously studied the synthesis of palm oil-derived polyol to prepare polyurethane [13-14]. In this study, we studied the possibility of glycerol as polyol monomer for polyurethane microcapsule shell. This research also studied encapsulated self healing agent using IPD, stannous octoate or dibutyl tin dilaurate.

II. MATERIAL AND METHODS

2.1 Preparation of prepolymer varied polyol

Toluene diisocyanate (TDI) and polyol is prepared as a constituent material for microcapsule shell wall. Polyol used in this research was glycerol. Toluene diisocyanate was dissolved into cyclohexanone in three neck flask. The mixture was heated to 80^0C in an oil bath and stirred with magnetic stirrer. The polyol was slowly added. The flask was purged with N_2 for an hour and allowed to react for 24 hours.

The synthesis of prepolymer was conducted in TDI to glycerol ratio of 3:1

2.2 Synthesis of Microcapsules

At room temperature, 30 ml of deionized water and 4.5 g of gum arabic surfactant were mixed in a 100 ml beaker glass. The beaker was suspended in a temperature controlled water bath on a programmable hot plate with an external temperature probe. This solution was agitated with magnetic stirrer for 3 hour prior to encapsulation. Meanwhile, either IPDI, stannous octoate or dibutyiltin dilaurate was added to the prepolymer (2.9 g). This mixture was then slowly poured into the gum arabic solution. The water bath was heated to 70^0C. At 50^0C, polyol as a chain extender was slowly added to this emulsion. Polyol used in this encapsulation step was the same polyol used in prepolymer step. After 45 minutes of agitation, the mixer and hot plate were switched off. After cooled to ambient temperature, the suspension of microcapsules was rinsed with deionized water and vacuum filtered. Microcapsules were air-dried in open air for 48 hours prior further analysis.

2.3 Characterization of Prepolymer and Microcapsules

Fourier Transform Infrared (FTIR). The completion of prepolymer reaction and synthesis of microcapsule was confirmed by Fourier Transform Infrared. FTIR analysis was conducted using IRPrestiged-21 SHIMADZU in Research Center for Chemistry, Indonesian Institute of Sciences.

Scanning Electron Microscopy (SEM). Particle structure of the microcapsule was characterized by using Scanning Electron Microscopy JEOL JSM-5600LV SEM Instrument, in BATAN, Indonesia's National Nuclear Agency.

Particle Size Analyzer (PSA). Particle size analysis of the microcapsule was conducted using Coulter LS Particle Size Analyzer in Research Center for Chemistry, Indonesian Institute of Sciences.

III. RESULT AND DISCUSSION

3.1 Reaction of Prepolymer and microcapsules

Microcapsules in this study was prepared by interfacial polymerization technique to encapsulate self healing agent (IPDI, stannous octoate or dibutyltin dilaurate) in polyurethane shell that use glycerol as polyol. The polymerization reaction takes place in the interfacial between prepolymer phase in cyclohexanone (oil phase) and water phase containing polyol chain extender in oil in water emulsion system. Polyol chain extender used in this study was same as with polyol used in prepolymer process. In this study, an emulsion system was prepared with gum arabic as surfactant. Encapsulated substance (core material) would be added to the oil phase. This interfacial polymerization, typically condensation polymerization, takes three necessary steps [15-16]. The first steps is the formation of isocyanate (-NCO) terminated prepolymer as shown in Fig. 1. This prepolymer was prepared by reacting TDI with glycerol polyol with certain ratio to form prepolymer with free –NCO terminal group. The second steps is emulsification, self-healing agent/catalyst (IPDI, stannous octoate or dibutyltin dilaurate) to be encapsulated were mixed with prepolymer as the oil phase. Meanwhile, gum arabic surfactant was dissolved in the water phase. Both phases were then mixed and emulsion formation was obtained by mechanical stirring. Polymerization was the last steps in this interfacial polymerization. Complementary polyol monomer used glycerol as chain extender was added to external phase of the emulsion and the polymerization occur in the liquid-liquid emulsion interface between water phase and oil phase as shown in Fig.2.

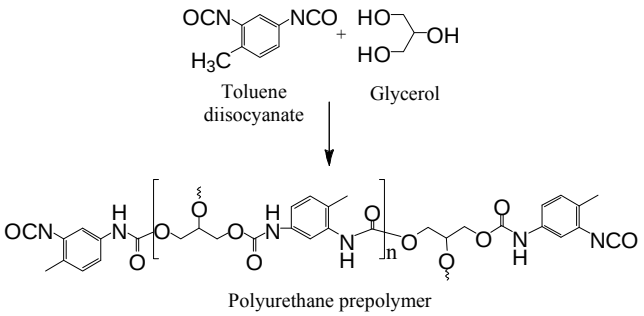


Figure 1. Reaction of polyurethane prepolymer synthesis

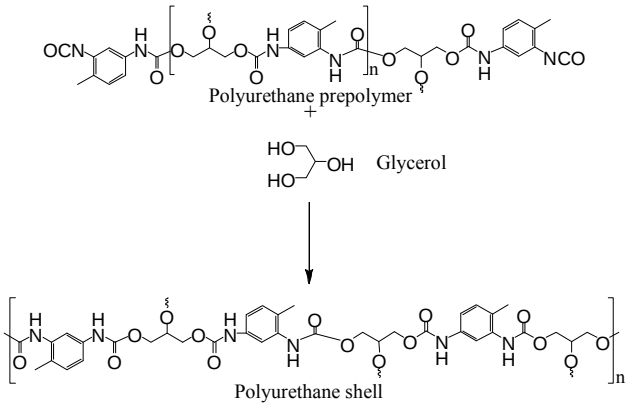


Figure 2. Reaction of polyurethane microcapsule shell.

3.2 Fourier Transform Infrared (FTIR).

Prepolymer Synthesis

The first steps in interfacial polymerization is synthesis of prepolymer with free isocyanate (-NCO) terminal group. In this study, synthesis of prepolymer was conducted by using gylcerol as polyol. FTIR spectrum of prepolymer using gylcerol as polyol can be shown in Fig 3.

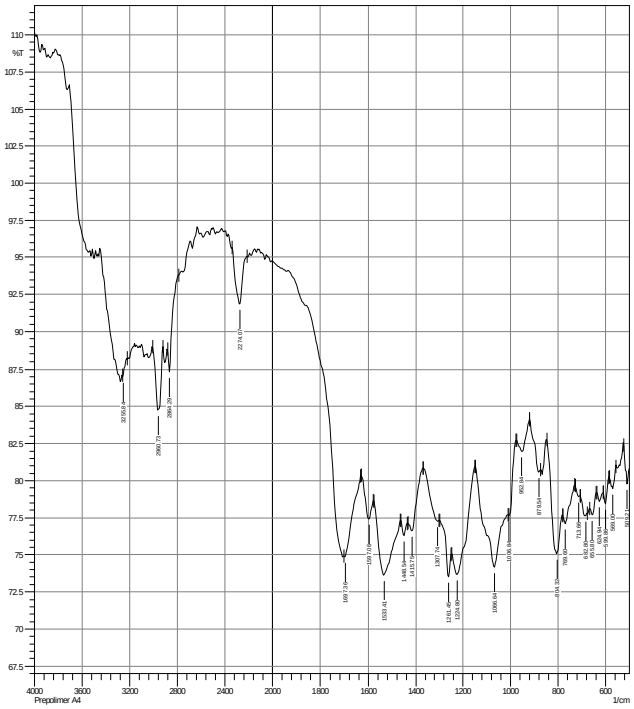


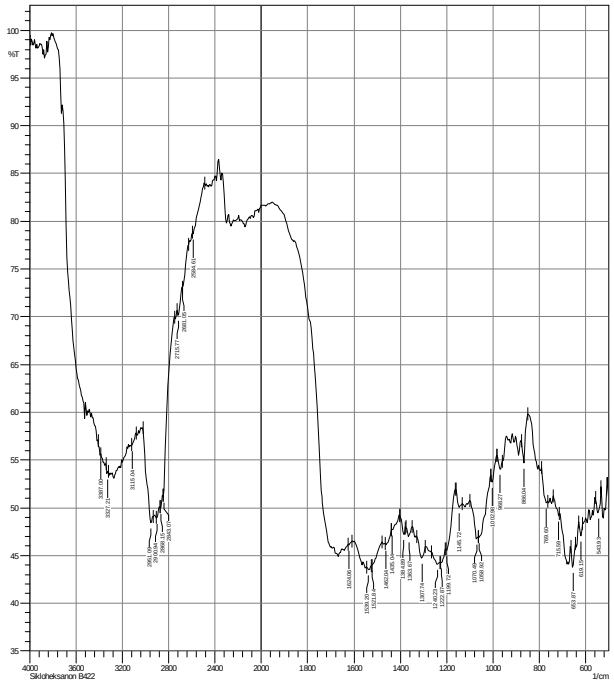
Figure 3. FTIR spectrum of prepolymer using glycerol

FTIR spectrum in Fig 3 showed that peak in the 2274.07 cm^{-1} came from isocyanate (-NCO) strecth vibration in range 2280-2260 cm^{-1}. We can conclude that the prepolymer still have unreacted isocyanate group that are located in the terminal end of polyurethane prepolymer. Peaks in 3255.84 cm^{-1} from N-H stretching (3350-3050 cm^{-1}) and peaks in 1533.41 cm^{-1} from N-H bending show the formation of urethane linkage. Meanwhile, others peaks in 1697.36 cm^{-1} from carbonyl –CO of polyurethane (1870-1650 cm^{-1}) and peak in 1066.54 cm^{-1} C-O-C of ester (1000-1200 cm^{-1}) also confirmed that urethane linkage had already formed in prepolymer product. The unreacted isocyanate group was exactly what we wish due to it necessary for interfacial polymerization. Free isocyanate group would be later crosslink with polyol and form to form polyurethane shell by extending the polymer chain.

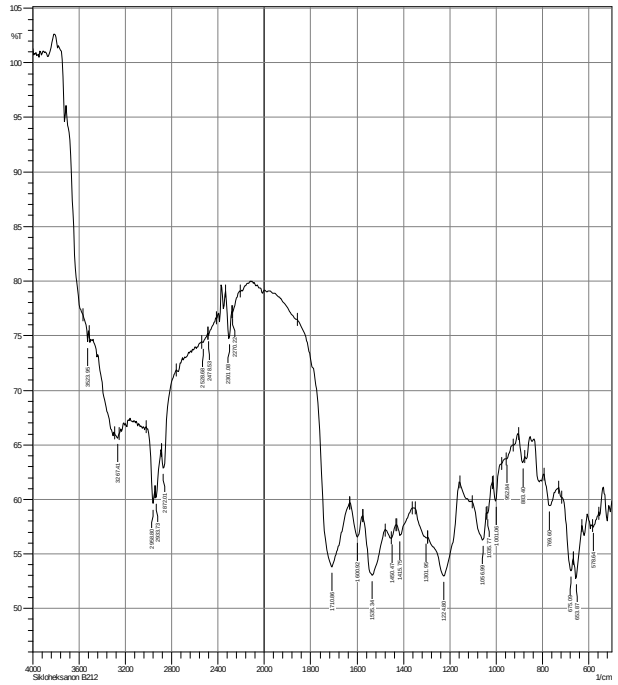
Microcapsule Synthesis

In this study, we used three variation of reactive agent to be encapsulated in polyurethane shell for self healing polymers. The reactive agents used in this study were IPDI, stannous octoate or dibutyltin dilaurate.

FTIR spectrum of microcapsules using varied reactive agent for self healing polymers can be shown in Fig 4.



(a)



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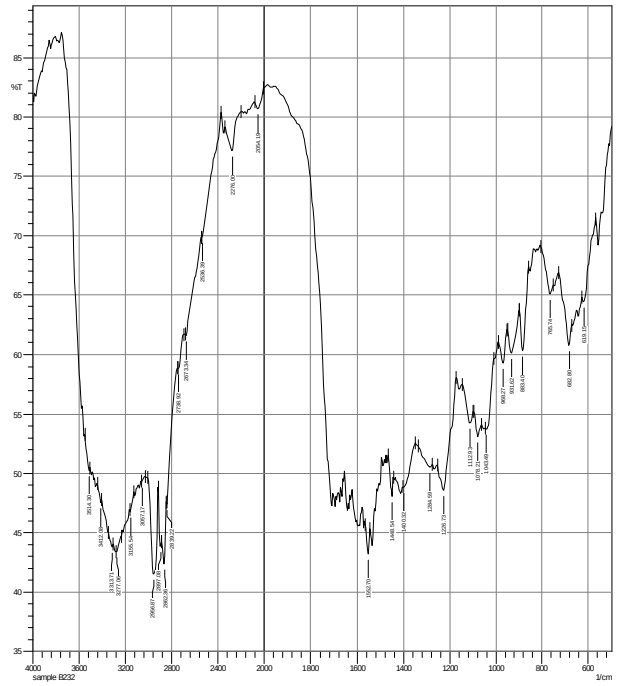


(c)

Figure 4. (a) Spectrum FTIR of microcapsules using IPDI; (b) Spectrum FTIR of microcapsules using stannous octoate; (c) Spectrum FTIR of microcapsules using dibutyltin dilaurate.

Based on FTIR spectrum of microcapsule in the Fig. 4a, the polyurethane shell containing IPDI was formed completely. It can be observed that there was no peaks from isocyanate (-NCO) strecth vibration in 2280-2260 cm^{-1}, peaks from N-H stretching (3350-3050 cm^{-1}) and peaks from N-H bending. However, FTIR spectrum of microcapsule containing stannous octoate and dibutyltin dilaurate shows that peak of isocyanate (-NCO) stretch was still remained but was decreased of its intensity. Presence of isocyanate in small quantaity of polyurethane microcapsule containing stannous octoate and dibutyl tin dilaurate showed that polyurethane shell was not formed completely. Polyurethan microcapsule shell formation also can be revealed with morphology analysis by scanning electron microscopy.

3.3 Microsphere morphology.

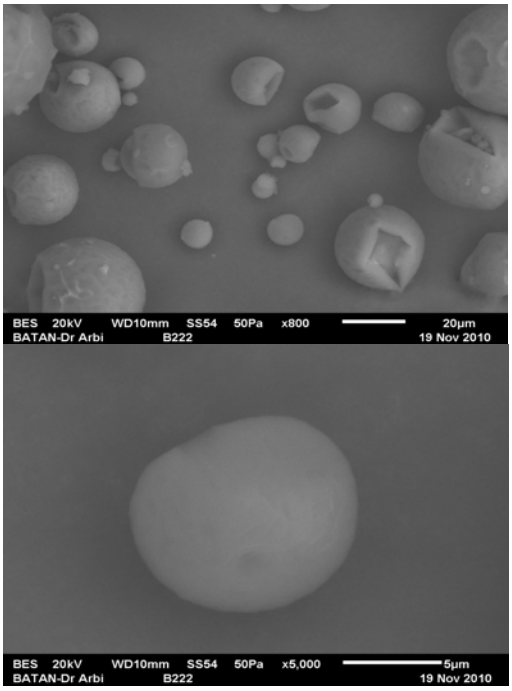


Figure 5. Scanning electron micrograph of polyurethane microcapsule containing IPDI

Morphological analysis of the microcapsule product containing IPDI by Scanning Electron Micrograph was shown in Fig 5. The product gave spherical shape with wrinkled surface. According to Yang et al. (2008), morphology of the capsules outer surface have some wrinkled resulting from the interaction of inhomogeneous reaction kinetics, fluid- induced shear forces, and shell determined elastic forces [17].

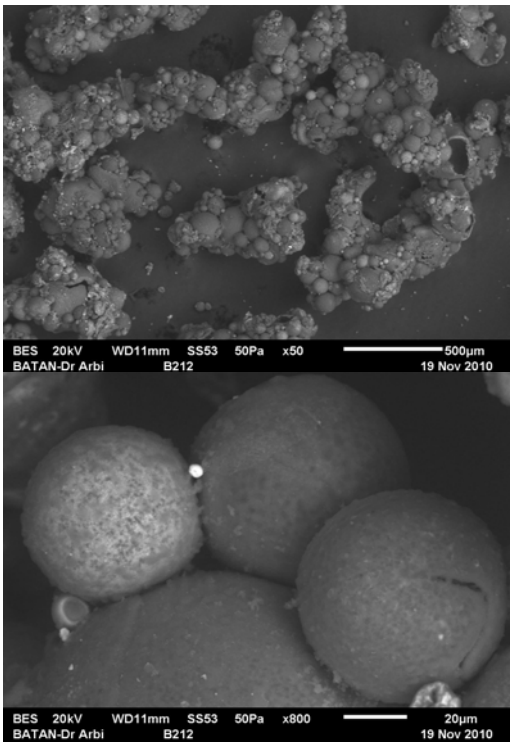


Fig 6. Scanning electron micrograph of polyurethane microcapsule containing stannous octoate.

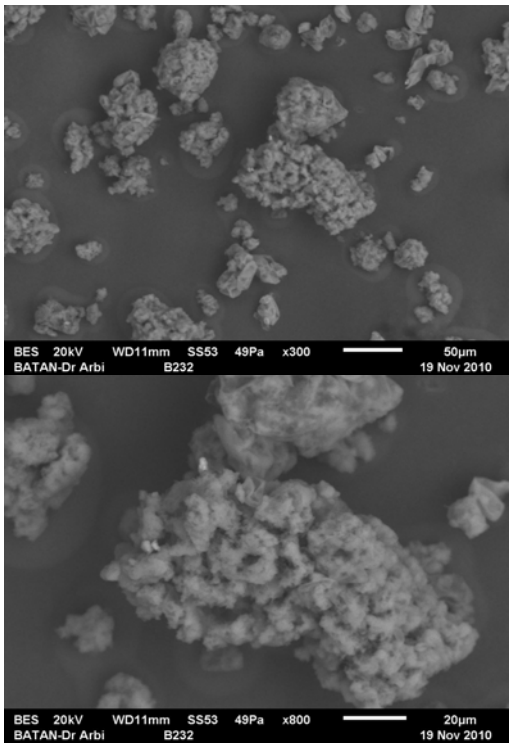


Fig 7. Scanning electron micrograph of polyurethane microcapsule containing dibutyl tin dilaurate

Morphological analysis of the microcapsule product containing stannous octoate by Scanning Electron Microscopy (SEM) was shown in in Fig 6. The product gave spherical shape and tendency of agglomeration. The agglomeration of microcapsule due to presence isocyanate (revealed by FTIR spectrum on fig 4) that was not react completely to form polyurethane shell. During air-dried of microcapsule this unreacted isocyanate might react with air and effecting on microcapsule agglomeration.

Morphological analysis of the microcapsule product containing dibutyltin dilaurate by Scanning Electron Micrograph was shown in in Fig 7. The microcapsule product containing dibutyl tin dilaurate was not formed microcapsules. Free isocyanate group obtained in prepolymer process, hopely would be later crosslink with polyol to form polyurethane shell by extending the polymer chain on microcapsule process. However, free isocyanate obtained in prepolymer process in this case might be not react completely as what we wish and the microcapsule product obtained not formed polyurethane shell.

We can conclude that the different microcapsule result was based on the kind of reactive compound encapsulated used in polyurethane shell, and so will be obtained different emulsion stability.

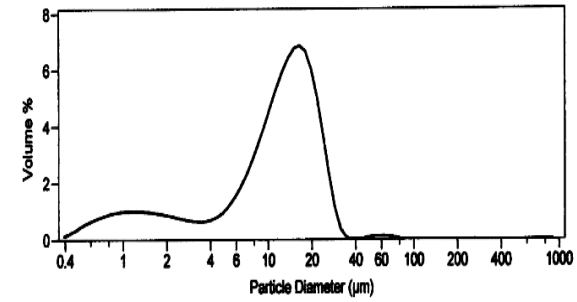
3.4 Particle size analyser

Particle size analysis showed a main mode in intermediate range 10-60 µm. The Particle size analyzer result was given in Fig 8 and table 1 shows the particle size distribution of polyurethane microcapsule containing IPDI, stannous octoate, and dibutyltin dilaurate

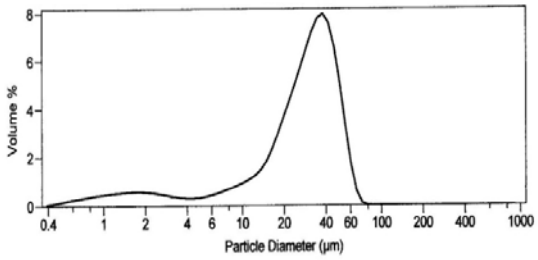
The size of prepared microcapsule was determined by particle size analyser. The average microcapsule size was 12.33; 28.59; and 25.65 µm for microcapsule containing IPDI, stannous octoate, and dibutyltin dilaurate respectively. Figure 8 shows the particle size analysis result of prepared microcapsule, shown as volume distribution.

The smallest particle size was produced by polyurethane microcapsules containing IPDI and the biggest particle size was produced by polyurethane microcapsules containing stannous octoate.

Microcapsules polyurethane containing IPDI showed the narrowest size distribution, exactly what we wish because narrower particle distribution means more homogenous particle. This wall composition particle can obtain better stability and improve release accuracy as their function.



(a)



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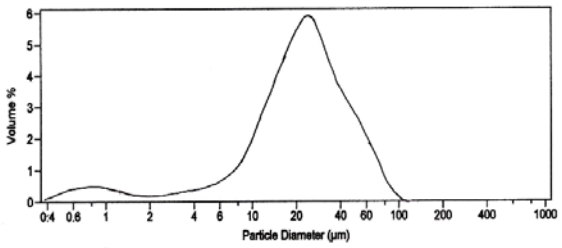

(c)

Figure 8. (a) Particle size analysis of microcapsules with core material of IPDI; (b) Particle size analysis of microcapsules with core material of stannous octoate; (c) Particle size analysis of microcapsules with core material of dibutyltin dilaurate

Table 1. Particle size distribution of polyurethane microcapsule

microcapsules containing of	%< 10	%< 25	%< 50	%< 75	%< 90
IPDI	1.387	6.54	12.19	17.41	22
Stannous octoate	4.24	17.86	29.22	39.76	48.68
dibutyltin dilaurate	6.425	13.66	22.13	33.92	50.57

IV. CONCLUSION

Based on the result obtained in the present study, it can be recommended the utilization of glycerol as polyol monomer for polyurethane microcapsule shell. The polyurethane containing IPDI as reactive agent for self healing polymer was presented best result than those containing stannous octoate and dibutyltin dilaurate. This sample presented the optimum result. It was observed that the morphology of polyurethane microcapsules containing IPDI by scanning electron microscopy was in spherical form and with wrinkled surface but no agglomeration found. The morphology of polyurethane microcapsules containing stannous octoate was also in spherical form but have a tendency of agglomerating and so were microcapsules containing dibutyltin dilaurate.

The average microcapsule size was 12.33; 28.59; and 25.65 µm for microcapsule containing IPDI, stannous octoate, and dibutyltin dilaurate respectively. The microcapsule containing IPDI was also gave narrowest particle size distribution so the particles sizes were more homogenous than the others.

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