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Thermo-Responsive Self-Healing Polycaprolactone Urethane Coatings from Waste Palm Cooking Oil

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Abstract: ***The evolution of responsive polymers has amplified expressively in consequence of the growth of precise polymer architecture with predetermined structure-to-property behavior. In this study, new thermal responsive self-healing polycaprolactone urethane coatings were prepared from waste palm cooking oil. Nine different formulations of coatings with various percentages of ε-caprolactone (ε-CL) were successfully developed and the effect of polycaprolactone network in the polyurethane coating on the self-healing behavior. The remendability of the coatings was studied by using thermal analysis and dynamic mechanical analysis. The PCLU coating with the highest content of PCL network was nearly completely healed after 2 hours at 90ºC. The results were confirmed by scanning electron microscopy before and after healing. The mechanism of scratch closure by thermal stimuli-responsive self-healing was also discussed.***

Index Terms: Waste palm cooking oil, polycaprolactone, polyurethane, coatings, self-healing.

I. INTRODUCTION

The self-healing polymers are a new materials that have the integrated capacity to mending destruction themselves without requiring manual detection or repair in any form. The demand for smart materials is increasing in the era of Industry 4.0 with demand for improvements in performance in challenging applications driving the need for materials with extended lifetimes.

Self-healing technology is designed to provide polymer materials with the ability to seize the propagation of cracks in the early stage and thus prevent catastrophic failures. Nowadays, the range of emerging responsive polymers has grown significantly in virtue of the consistent development of new formulation and polymerization methods with predetermined structure-to-function behavior.

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In recent years, researchers have shown the benefits of focusing on the development of materials with self-healing properties enthused by the self-healing of wounds in biological systems [1, 2]. Other possibilities that have been investigated by the researchers include self-healing materials that facilitate remotely-controlled self-healing after damage to fully restore the mechanical properties of the pristine material and to repair the micron-size cracks or cuts with minimum external intervention [3, 4]. There are two popular strategies to synthesize self-healing materials: (i) the impregnation of catalysts such as in fibers or capsules [5, 6]; and (ii) through the consolidation of dynamic reversible bonds in the polymer matrix, for example crosslink, oligomers, monomers, and so on.

The discovery of shape memory polymers (SMPs) are also extensively discovered in the growth of self-healing materials. This type of polymers tends to undergo phase separation into hard and soft segments owing to thermal mismatches between adjoining segments. The hard segments construct physical crosslinks between urethane networks because of the secondary bonding (polar interaction or hydrogen bonding) [7]. Besides hydrogen bonding between urethane networks, the conformation of phase separation is also reliant on types of polyol used, molecular weight as well as processing. Meanwhile, the soft segments contribute to the elastic properties of a material due to the molecular motion in a rubbery state and influences material performance for instance strength, modulus and rigidity at low temperatures. The SMPs is classified in accordance with the type of stimulus applied to trigger the shape memory effect particularly chemo-responsive, photo-responsive and thermo-responsive SMP. Thermo-responsive SMP is usually triggered by heat, while photo-responsive SMP is induced by light without any heat involved. Chemo-responsive SMP is induced by chemicals for instance ethanol, water etc. [8, 9]. Rodriguez et al. [10] also investigated shape memory in their study by presenting the term of "shape memory assisted self-healing" (SMASH). They heated the damaged polymer above the melting temperature of a linear polycaprolactone. Rivero et al. [11] were able to heal the polyurethane below the melting temperature of PCL by introducing the "Diels-Alder based shape memory assisted self-healing" (DASMASH). However, almost all researches on self-healing polymer based on shape memory have used a commercial PCL diol.

Therefore, this study focuses on the development of thermal stimuli-responsive self-healing polycaprolactone urethane (PCLU) coatings based on waste palm cooking oil (WPCO) with the ε-caprolactone (ε-CL) as a self-healing agent. The effects of different ratios of ε-CL to WPCO-based polyesteramide (PEA) on the self-healing properties of PCLU coatings were investigated. The mechanism of self-healing of PCLU coatings was also investigated and discussed.

II. MATERIALS AND METHODS

A. Materials

ε-caprolactone (high purity), 2-(dimethyamino)-ethanol (DMEA), 1,8-diazabicyclo 5.4.0 undec-7-ene (DBU), isophorone diisocyanate (IPDI) and diethylene glycol (DEG) were purchased from Terra Scientific (M) Sdn. Bhd. WPCO was collected from restaurants in Klang valley, Malaysia.

B. Synthesis of WPCO-based Polycaprolactone Polyol

There are two-steps involved in the synthesis of WPCO based polyol. First step, WPCO based polyol was synthesized by using transesterification process by mixing a polyhydric solution with WPCO and 1,8-diazabicyclo 5.4.0 undec-7-ene (DBU) as a catalyst. The transesterification was performed in a chemical reactor at a temperature of 90°C for about 1 hour under vacuum and inert conditions. In the second step, the synthesis was continued through ring opening polymerization by adding the ε-caprolactone (CL) into the mixture and it was continuously stirred and maintained at the same temperature for another 2 hours. The characteristic of PCL polyol was discussed in our previous report [12].

C. Polycaprolactone urethane coatings preparation

For the preparation of polycaprolactone urethane (PCLU) coatings, PCL polyol based on WPCO was reacted with isophorone diisocyanate (IPDI) with isocyanate to polyol (NCO:OH) ratio is 1:1. Nine types of PCL-U coatings were prepared, which were labeled as PCLU-10, PUCL-20, PCLU-30, PCLU-40, PCLU-50, PCLU-60, PCLU-70, PCLU-80, PCLU-90. The details of the samples are described in Table 1. Prior to the application of coatings, AA 6061, which was used as a substrate, was abraded with 600 grit size sandpaper. The PCL-U coating was applied on the metal surface with a nylon brush and the samples were left at room temperature for 72 hours for complete curing before testing their performance properties.

Table. 1 PCLU Coating Samples

Sample	Polyols Used	Percentage of CL (%) in Polyol
PCLU-10	PCL10	10
PCLU-20	PCL20	20
PCLU-30	PCL30	30
PCLU-40	PCL40	40
PCLU-50	PCL50	50
PCLU-60	PCL60	60
PCLU-70	PCL70	70
PCLU-80	PCL80	80
PCLU-90	PCL90	90

D. Differential Scanning Calorimetry

The DSC test is one of the methods for thermal analyses. This test was performed to determine the glass transition temperature, Tg and melting temperature, Tm of all PCLU coatings produced by a dynamic scan with temperature range of -70 – 300°C and a heating rate of 10 °C min-1 using a DSC823 Mettler Toledo calorimeter. A sample of pure PCL was also scanned for reference.

E. Dynamic Mechanical Analysis

The dynamic mechanical analysis (DMA) measurement was carried out in tensile mode using DMA 2980 at a frequency of 1 Hz and a strain amplitude of 0.2% with a force track of 110%. The samples with a dimension of 3 mm x 20 mm x 1 mm were heated at a rate of 3°C/min from 20 – 120 °C under nitrogen atmosphere.

F. Self-Healing Test

The ability of the PCLU coatings to self-healing was characterized by making a 2 mm through-coating scratch with a sharp razor blade on the coating surface with a dimension of 10 x 10 mm^2. The damaged coatings were heated in an oven at a temperature of 90°C for 2 hours to perceive the self-healing behavior of PCLU coatings. The morphology before and after the healing process was also observed using an optical microscope with 50X and 100X magnifications.

III. RESULTS AND DISCUSSION

A. Thermal Analyses

Glass transition temperatures, T_g, and melting temperatures, T_m, of PCLU coatings are shown in Table 2. The results reveal that the percentage of CL in polyol has a significant effect on the reduction on T_g of PCLU coating. The T_m was also lowered as the percentage of CL increased. The reduction of T_g and T_m values might be due to the long linear chain of PCL in the PU network.

Table. 2 Glass transition and melting temperatures of PCLU coatings

Sample	T_g (°C)	T_m (°C)
PCLU-10	35.27	208.15
PCLU-20	34.04	200.05
PCLU-30	33.57	198.86
PCLU-40	32.94	191.26
PCLU-50	31.56	186.34
PCLU-60	30.05	172.11
PCLU-70	29.57	167.97
PCLU-80	27.23	162.96
PCLU-90	25.93	153.92

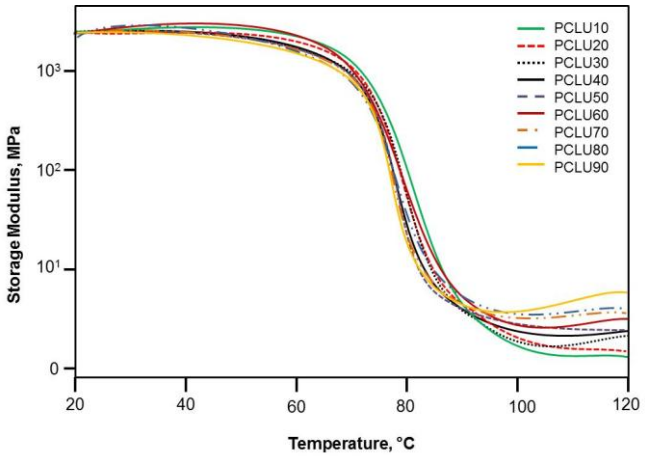
This linear chain is easier to move and break compared to the branched chains from waste cooking oil, which are more complex. In coatings with lower CL content, the branched structures slowed down the segmental mobility of the PCLU coating, which caused to higher T_g and T_m.

Based on these results, the heating condition was set to study the self-healing behavior of PCLU coatings. The shape memory effect is estimated to be initiated under this heating condition and the PCL chain is expected to melt, diffuse into the coating scratch and initiate the closure of the scratch.

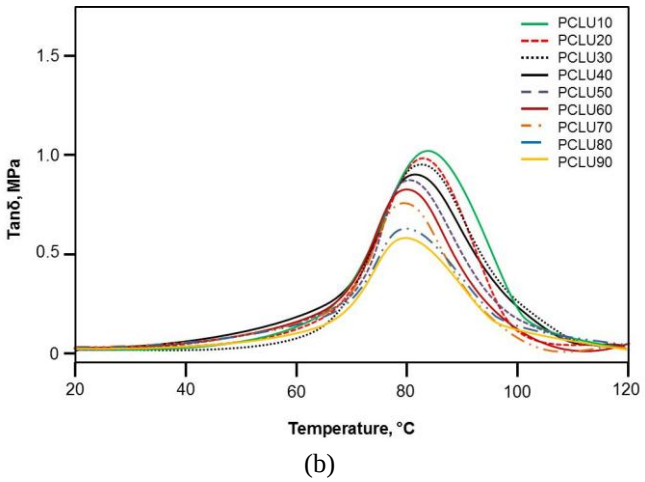
B. Dynamic Mechanic Properties

Fig. 1 represents the tan δ and storage modulus (E') as a function of temperature in tensile mode from DMA measurement.

Well-characterized rubbery levels exhibited by the all coating samples, suggestive of cross-linked structures. The transition of the soft domain/segment (PCL) is observed at a temperature range from 80 – 85°C. The E' is slightly decreased at the higher CL content. It is clearly shown that CL content has a significance effect on viscoelastic of the PCLU coating and contributes to the self-healing behavior of the PCLU coatings. At the point when the coatings is heated at temperatures in the range of 85 - 110°C, the soft segments change from the semi-crystalline to the liquid state [13] and it brings about drop of E'. This phenomenon will drive to the higher mobility that permit the polymer stream and recuperate the defect.



(a)



(b)

Fig. 1 DMA curves of PCLU coatings, (a) Storage modulus, (b) Tan Delta

Tan δ denotes the ratio of the storage modulus to loss modulus. The tan δ peak of PCLU-10 occurred at ~85°C and the peaks shifted towards lower temperatures as the CL content increased which reflects the improvement of the self-healing efficiencies of PCLU coating. The addition of PCL in the PU network allowed considerable latitude in the mobility of the polymer chain. Gu et al. [14] reported that the value of tan δ is related to the dissipated energy as heat in the material. Increasing tan δ indicates that the polymer has more energy dissipation potential so the greater the tan δ, the more dissipative the material is. On the other hand, decreasing tan δ means that the material acts more elastic. It is clearly shown that the tan δ value dropped when adding more CL content in the PU network leading to quick recovery or self-healing process.

C. Self-Healing Behavior

To verify that the self-healing effect definitely caused from CL content in the PU network, the PCLU coatings were further characterized using optical microscope. The micrographs of self-healing behavior in PCLU coatings before and after thermal stimulation at 90ºC can be observed in Fig. 2. The selection of temperature for self-healing test was based on the dynamic mechanic properties of PCLU coating which this temperature (90°C) is expected to be the ideal temperature to trigger the self-healing effect as at this temperature soft segment turned to molten state.

The original scratches in Fig. 2 exhibited a result of plastic deformation significantly induced by the blade. The damage to the coating presented two appearance categories: the shaded zone adjacent to the crack tip which is designated as plastic deformation; and cracks. Even in some cases, some parts of the coating material were enduringly detached from the material [15]. No significant difference was found for PCLU-10 sample before and after 2 hours heating, as is shown in Figure 2 (a). A low percentage of shape recovery might be the reason for this case. Figure 2 (b) demonstrates the healing behavior of the PCLU-50 sample. The image shows that the melted PCL molecules have diffused and filled the gap but it was still not complete, indicating that the shape recovery result was estimated about 60 – 70% only. Additionally, Figure 2 (c) shows that the healing process of melted PCL molecules in the PCLU-90 samples was almost complete with an estimation of 98% recovery.

It is worth to claim that the scratch healing process is more efficient for the samples with higher CL content. It shows that the polymer network containing the highest CL demonstrated nearly complete recovery due to the reconstruction of the polymer network that was triggered when it was exposed to a temperature of 90ºC for 2 hours. This might be due to the longer PCL network in the polymer coating, as the PCL contributes to the soft segments. Huang et al. [5] claim that heating above the T_m of PCL induced the shape memory effect by mitigating the PCL segments. Consequently, the mechanical scratches or damages could be physically closed conceivably reinstate the barrier properties of the coating [16]. Definitely, healing is only effective in PCLU coatings with a higher CL content. In accordance to the observation on PCL recovery, no significant changes were discovered in PCLU coatings with a low CL content.

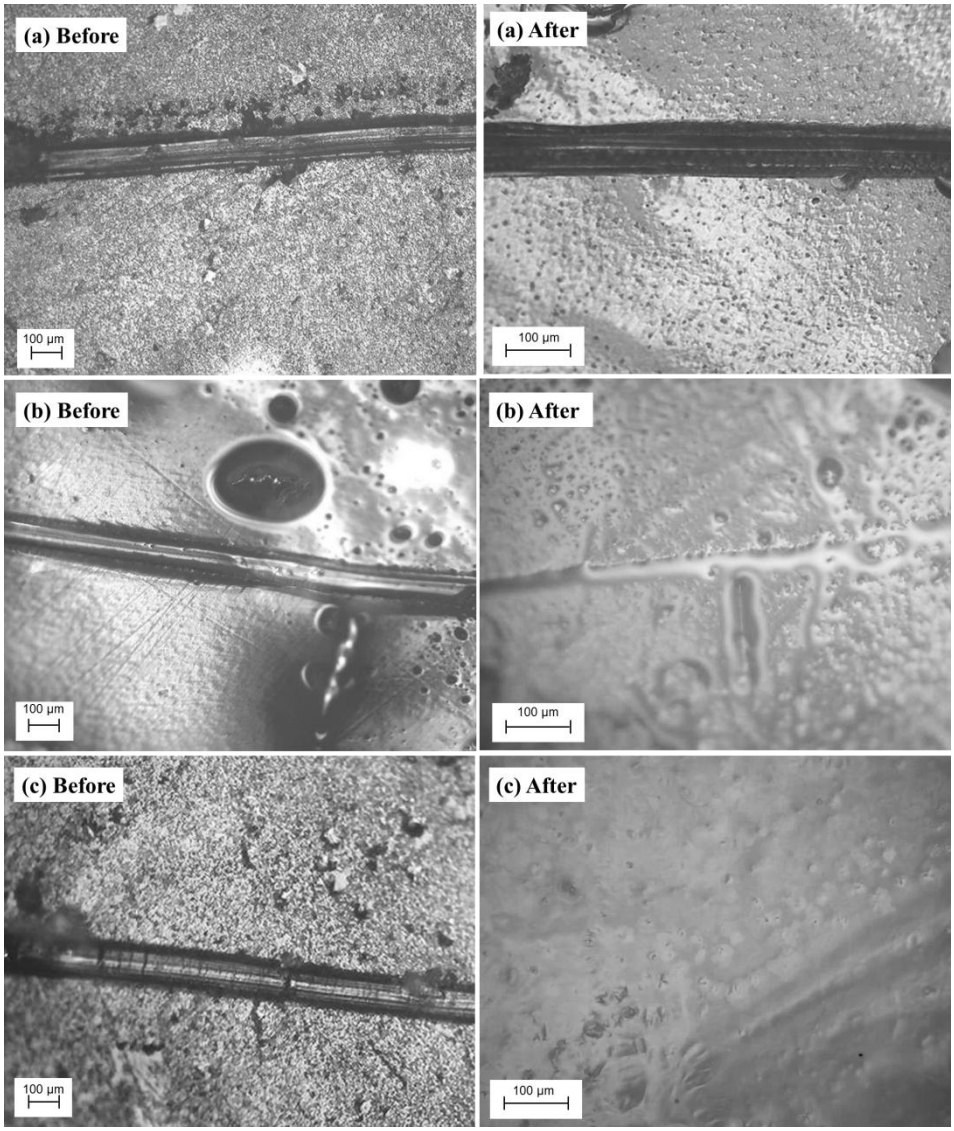


Fig. 2 Micrographs of self-healing behavior of PCLU coatings before and after thermal stimulating at 90ºC , (a) PCLU-10, (b) PCLU-50, and (c) PCLU-90

D.Mechanism of Scratch Closure by Self-Healing

The mechanism of scratch closure can be well explained by the schematic self-healing process of PCLU coating with a macro-scratch shown in Figure 3. The healing process comprises of two-steps. Generally, in the initial step, self-healing of polymer is stimulated by applying a heat on the scratched coating with a temperature above than the melting temperature of the PCL in PU networks to trigger the thermal-induced shape memory behavior of PCL. The PCL molecules then melt and diffuse into the tapering flaw by capillary force [1. In the second step, the diffused PCL forms a physical entanglement within the PU matrix and fills the scratch when the sample is cooled down. Therefore, the higher CL content will develop the proficiency of self-healing process.

Throughout the mechanism of self-healing, the separation of the crosslinks temporarily improves the movement of the polymer chains. It also lead to increase the diffusion close to the defect area, trailed by the arrangement of new bonds that result in the repair of the system [17] and recuperation of the mechanical properties. Subsequently, the optimization of free volume is a significant factor to accomplish the ideal portability of the chains, which can likewise be constrained by external stimuli. The self-healing properties also pledge the degradation through the incorporation of a repair mechanism which reacts to the micro-damage of a material.

IV. CONCLUSION

A thermal stimuli-responsive self-healing polycaprolact one urethane coating was developed from waste palm cooking oil. Based on the experimental results, it is concluded that knowledge on the structure–property relationships is crucial in improving material design and enhancing its functional and mechanical performances.

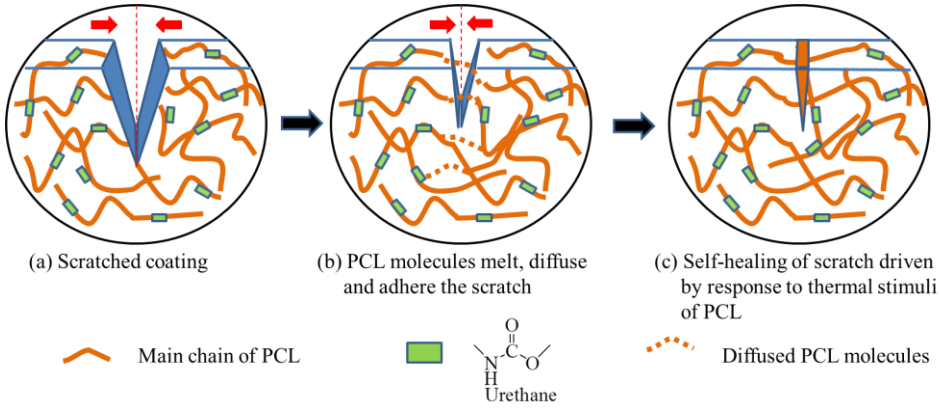


Fig. 3 Schematic depiction of thermal responsive self-healing mechanism of PCLU coatings

It is believed that PCL structure in the PCL polyol based on waste palm cooking oil represented the main contribution in the development of the self-healing polyurethane coating, which estimated to contribute up to 98% of shape recovery by thermal stimulation. The effect of shape memory is more significant to the crack closure at a temperature above the melting point of PCL. However, to verify the functional performance of the PCLU coating, further studies should be made, especially on the mechanical aspects of recovery.

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