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

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Abstract

The development of responsive polymers has expanded significantly owing to the development of well-defined polymer architechture with predictable 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 self-healing ability of the coatings was studied by using thermal analysis and Atomic Force Microscopy (AFM). The PCLU coating with the highest content of PCL network nearly complete healed at 90ºC after 2 hours. 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.

Keywords: *Waste palm cooking oil, polycaprolactone, polyurethane, coatings, self-healing.*

1. Introduction

The self-healing polymers are a new classification of smart materials that have the ability to repair themselves when damaged without requiring for detection or repair manually in any form. The demand for smart materials is increasing in the era of Industry 4.0 with improve performance in challenging applications which drive the need for materials with extended lifetimes.

Self-healing technology is designed to provide the ability of polymer materials to seize the propagation of cracks in the early stage and thus prevent catastrophic failures. Nowadays, the emerging responsive polymers has amplified significantly owing to the consistent development of new chemistries and controlled polymerization methods with predictable structure-to-function behavior. In recent years, researchers have shown their significant efforts by focusing on the development of materials with self-healing properties inspired by the self-healing of wounds in biological systems [1, 2]. Other possibilities that have been focused by the researchers are to develop self-healing materials to facilitate remotely controlled self-healing properties upon damage or fracture that fully restore the mechanical properties of 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.e. (i) through the impregranation of catalysts in the form of capsules or fibres [5, 6] and (ii) through the incorporation of dynamic reversible bonds in the polymer matrix either in the form of crosslink points or as (hetero-)bifunctional building blocks for instance; monomers, oligomers and etc.

Moreover, shape memory polymers (SMPs) are also widely explored in the development of self-healing materials. Due to thermal mismatch between two different segments, this type of polymers tends to form phase separation i.e. soft and hard segments. The soft segments subsidizes to the elastic properties of materials due to the molecular motion in a rubbery state and influences material performances such as rigidity, strength and modulus at low temperatures. Meanwhile, the hard segments construct physical crosslinks between urethane networks because of the secondary bonding (hydrogen bonding or polar interaction) or crystallization in the hard domains [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. Almost all existing SMPs fall into three major categories depending to the type of stimulus applied to trigger the shape memory effect i.e. thermo-responsive, photo-responsive and chemo-responsive SMP. Thermo-responsive SMP is normally triggered by means of heating. Meanwhile, photo-responsive SMP is induced by light with different wavelengths without any heat involved. Chemo-responsive SMP involves chemicals such as water, ethanol and etc. [8, 9].

Rodriguez et al. [10] also used the shape memory concept in their study. They have introduced the term ‘shape memory assisted self-healing’ (SMASH). They reported that the damage of polymer was healed by heating the polymer above the melting temperature of the linear PCL. Rivero et al. [11] managed to heal the polyurethane at below than 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 concept were used a commercial PCL diol.

Therefore, in this work, we report on the development of thermal stimuli responsive self-healing polycaprolactone urethane

(PCLU) coatings based on waste palm cooking oil 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.

2. Materials and Methods

2.1. 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. Waste palm cooking oil (WPCO) was collected from restaurants in Klang valley, Malaysia.

2.2. Synthesis of Waste Palm Cooking Oil (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 condition. In the second step, the synthesis was continued by using the 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].

2.3. 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, 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 is described in Table 1. Prior to the coatings application, AA 6061 which was used as a substrate was abraded with abrasive paper grits 600. The PCL-U coating was applied on the metal surface by using nylon brush and the samples were left at room temperature for complete curing (72 hours) 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

2.4. Differential Scanning Calorimetry

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

2.5. Self-Healing Test

Self-healing ability of the coatings 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 damage coatings were heated in an oven at a temperature of 90°C for 2 hours to observe the self-healing behaviour of PCLU coatings. The height profile of PCLU coatings before and after heating, were measured using Atomic Force Microscopy (AFM). In this study, the maximum peak to valley height roughness of both (before, R_{tb} and after heating, R_{ta}) samples were used to calculate the shape recovery, R_t (%) of PCLU coatings by using a formula in Equation 1.

$$R_t(\%) = \frac{R_{ta} - R_{tb}}{R_{tb}} \times 100\% \quad (1)$$

The morphology before and after the healing process were also observed using an optical microscope with 50X and 100X magnifications.

3. Results and Discussion

3.1. Thermal Analyses

Glass transition temperatures, T_g and melting temperatures, T_m of PCLU coatings are shown in Table 2. The results reveal that percentage of CL in polyol is significant to 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. This linear chain is easier to move and break compared to the branched chains from waste cooking oil which is more complex. In coatings with lower CL content, the branched structures hindered the segmental mobility of the PCLU coating which led to higher T_g and T_m. Based on this results, the heating condition was set to study the self-healing behaviour of PCLU coatings. The shape memory effect is expected to be triggered under this heating condition and the PCL chain are expected to melt, diffuse into coating scratch and initiate the closure of the scratch.

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

3.2. Self-Healing Behaviour

Fig.1 signifies the effect of CL content on shape recovery of PCLU coatings. It is clearly shown that CL content gives a significance effect on the self-healing behavior on PCLU coating. As the CL content increased the shape recovery is also improved. PCLU10 with 10% CL shows the lowest result on the shape recovery which is 8.4% only. The percentage of shape recovery were slightly higher as the CL content is higher, which reflects the improvement of the self-healing efficiencies of PCLU coating. The scratch healing process is more efficient for the samples with higher CL content. It shows that the polymer network which contain the highest CL revealed nearly complete recovery due to the reconstruction of the polymer network that was triggered at 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 soft segment.

Huang et al. [5] claimed that heating above the melting temperature (T_m) of PCL softened the PCL segments and induced the shape memory effect. As a result, damage to the coating, such as mechanical scratches, could be physically closed to partially restore the barrier properties of the coating [13]. Indeed, healing was only effective in PCLU coating with higher CL content. It is worth noting that no appreciable differences was detected in PCLU coating with a low CL content, in accordance with the observed PCL recovery in the PCLU coating.

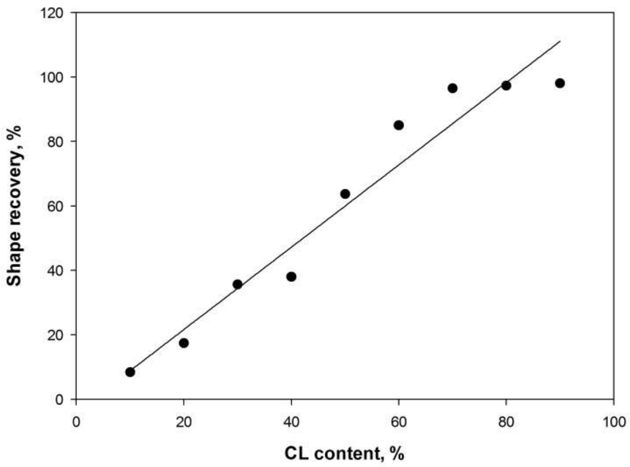

Fig. 1: Effect of CL content on shape recovery of PCLU coating

To confirm that self-healing effect indeed resulted from PCL content in the PU network, the PCLU coatings were further characterized using optical microscope. The micrographs of self-healing behavior on PCLU coatings before and after thermal stimulating at 90ºC can be observed in Fig.2. The original scratches in the figure showed an effect as a consequence of plastic deformation induced by the blade. The damage to the coating contains two forms i.e. plastic/permanent deformation, indicated as the shaded area surrounding the crack tip; and cracks involving the creation of free surfaces. In severe cases, some portions of the material may even be permanently removed from the coating, leaving voided space [14]. No significant different was found for PCLU10 sample before and after 2 hours heating which is shown in Fig.2 (a). A low percentage of shape recovery might be the reason for this case. Fig.2 (b) shows the behavior of PCLU50 sample. The image shows that the melted PCL molecules have diffused and filled the gap but it was still not complete, ascertained the shape recovery result which is only 63.7%. Meanwhile, Fig.2 (c) shows the healing process melted PCL molecules in PCLU90 samples was almost complete, supports the result obtained which was recorded 98% recovery.

The results presented so far have revealed encouraging self-healing of the PCLU coating. This effectively brings the separated crack/scratch surfaces in spatial proximity to facilitate crack/scratch rebonding by the molten PCL.

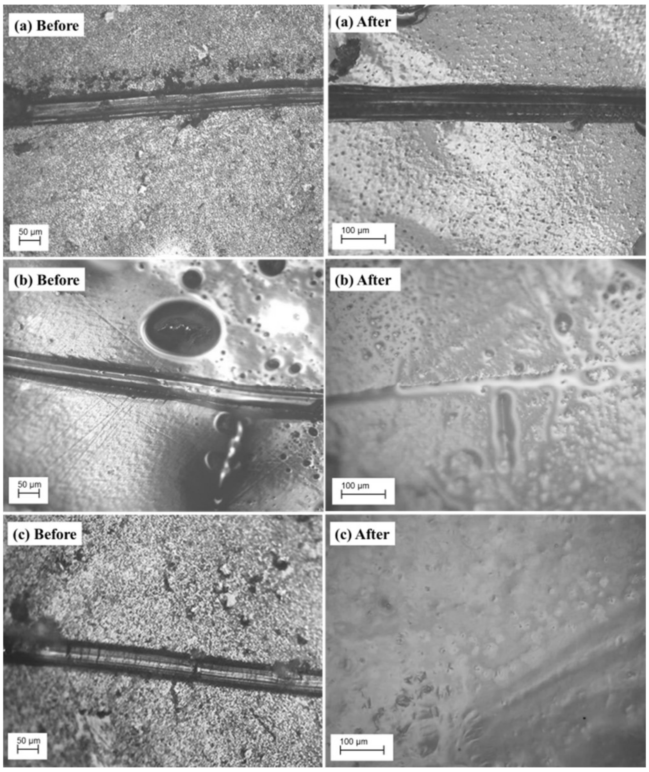

Fig. 2: Micrographs of self-healing behavior of PCLU coatings before and after thermal stimulating at 90ºC , (a) PCLU10, (b) PCLU50, and (c) PCLU90.

3.3. Mechanism of Scratch Closure by Self-Healing

Self-healing is initiated by heating the damaged coating to a temperature higher than both the liquefying temperature of the fibers (in this case, melting temperature or T_m) as well as the transition temperature (glass transition temperature or T_g) of the SMP matrix. The mechanism of scratch closure can be well explained by the schematic self-healing process of PCLU coating with a macro-scratch shown in Fig.3. The healing process consists of two-steps. In the first step, the damaged sample is heated to a temperature above the melting temperature of PCL to trigger the thermal-induced shape memory behavior of PCL. The PCL molecules melt and diffuse into the narrowed crack by capillary force [1]. In the second step, the diffused PCL forms physical entanglement in the PU matrix and bridge the scratch with a solid wedge when the sample is cooled down. Therefore, the higher CL content will improve the efficiencies of self-healing process.

During the repairing mechanism, the dissociation of the cross-links temporarily enhances the mobility of the polymer chains and the diffusion near the damaged area, following the formation of new bonds that results in the repair of the network and recovery of the mechanical properties [15]. Thus, the optimization of free volume is an important factor to achieve the desirable mobility of the chains, which can also be controlled by external stimuli.

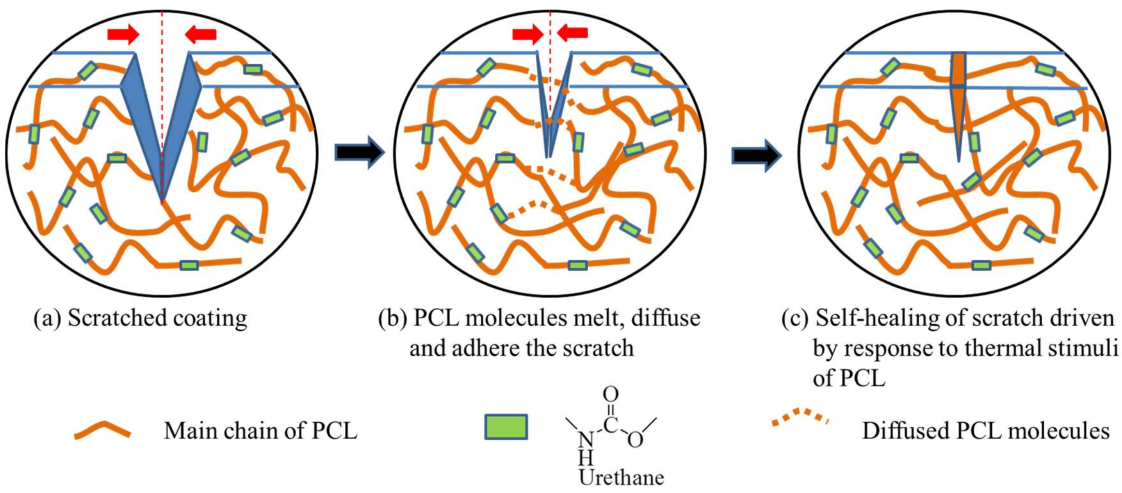

Fig. 3: Schematic depiction of thermal responsive self-healing mechanism of PCLU coatings.

4. Conclusion

A thermal stimuli responsive self-healing polycaprolactone urethane coating was developed from waste palm cooking oil. Based on the results, it is concluded that the knowledge on the structure – property relationships is the key to improve the material design for enhancing the functional performance. It is believed that PCL structure in the PCL polyol based on waste palm cooking oil signified the main contribution in the development of self-healing polyurethane coating which is contributed up to 98% of shape recovery by thermal stimulating. The shape memory effect favors the crack closure at temperature above the melting point of PCL. However, to verify the functional performance of PCLU coating, further studies should be made especially on the recovery from the mechanical aspects.

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