

# Application of advanced polymeric materials for controlled release pesticides

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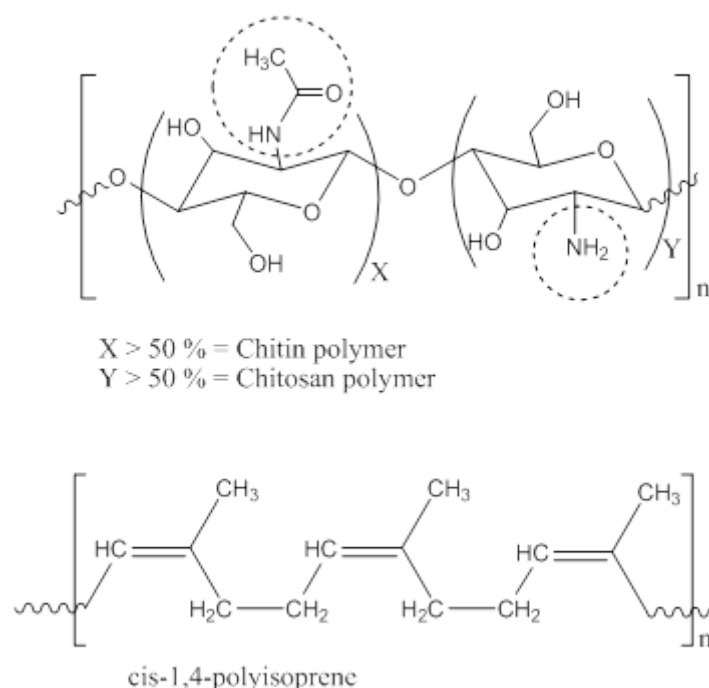
**Abstract.** The objective of this work was to study the capability of advanced polymeric material constituted by chitosan and natural rubber matrices for controlled release of pesticides (1-hydroxynaphthalene and 2-hydroxynaphthalene) in aqueous solution. The released amount of pesticides was measured spectrophotometrically from the absorbance spectra applying a standardized curve. The release of the pesticides was studied into refreshing and non-refreshing neutral aqueous media. Interestingly, formulation successfully indicated a consistent, controlled and prolonged release of pesticides over a period of 35 days.

## 1. Introduction

Pesticides are increasingly used over the past 60 years for the yield improvement of agricultural production [1]. However, each year 30,00,000 metric tons of pesticides have been applied, Worldwide [2] while 90 % of the applied conventional pesticides are lost in the environment leading to high cost and severe environmental pollution particularly surface and groundwater contamination [3]. According to a survey, three million pesticide poisoning cases occur every year with 220000 deaths, Worldwide [4]. Controlled release formulations (CRFs) can significantly protect the food crops damage and number of applications [5]. The superior advantages of CRFs are safe handling and less human toxicity [6].

Recently, the researchers have been focused to formulate a CRF system in order to produce the pesticide active ingredients over a long period. The application of CRF can minimize the spreading of pesticides residues into natural environment [7]. Therefore, the use of biodegradable and eco-friendly materials is of great interest for the development of CRF. In addition, several materials have been used as controlled-release carriers. However, natural, bio degradable, nontoxic and environmental friendly materials are strongly recommended [8]. Therefore, in the present study, concentration was focused on advanced materials comprising of chitosan encapsulated in natural rubber matrices.





**Figure 1.** Chemical structure of chitin, chitosan and natural rubber

## 2. Preparation of advanced polymeric materials

Chitosan was dissolved in 2 % acetic acid containing selected pesticides such as 1-hydroxynaphthalene or 2-hydroxynaphthalene. The mixture was stirred for 1 hour using mechanical stirrer to prepare a gel. Natural rubber latex with known amount of curing ingredients as specified in Table 1 were mixed. The advanced polymeric material (APM) was prepared through encapsulation of the chitosan gel by natural rubber matrices. The resulting capsules were isolated and dried in oven at 60 °C for 48 hours.

**Table 1.** Chemical composition of curing ingredients

S.No.	Curing Ingredients	Amount (phr <sup>a</sup> )
1	Natural rubber	100
2	Chitosan	28
3	Sulphur	1.5
4	Zinc-oxide active	1.8
5	ZDEC (Zinc diethyldithiocarbamate)	1.0
6	Antioxidant[2,2'-methylene-bis(6-tert-butyl-4-methylphenol)]	1.0

<sup>a</sup>phr: Parts per hundred of rubber

### 2.3. Characterization

The APMs were characterized by Fourier Transform Infrared Spectroscopy (FT-IR) and Thermogravimetric Analysis (TGA).

### 2.4. Release study

In order to study APMs for slow release of pesticides, the materials were studied under two different ways “without refresh” and “with refresh”. First (without refresh), known amount of the APMs was immersed in 50 mL of distilled water and the bottles were closed with screw caps and protected from light in order to prevent photo degradation of active ingredients. After the selected time intervals, the

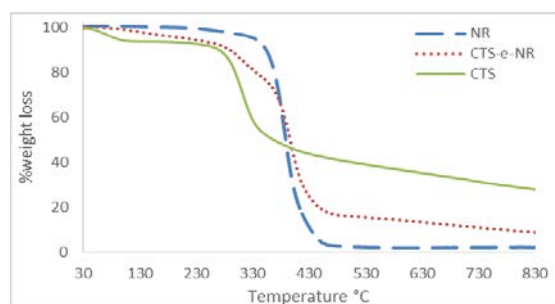
pesticide concentration was monitored by UV-VIS spectrophotometer. The experiment was continued upto 35 days.

Second (with refresh), the APMs were also studied with refreshing the release medium after each 24 hours. The known amount of APMs was submerged in 50 mL of distilled water, after each 24 hours the concentration of released compounds was monitored and the medium was refreshed by 50 mL fresh distilled water. The “with refresh” study was also continued for 35 days.

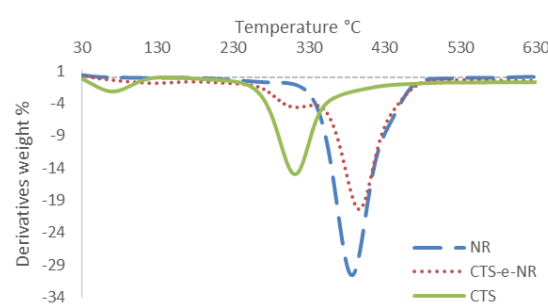
### 3. Results and discussion

APMs were prepared, characterized and successfully used for the controlled release of pesticides. The TGA and derivative thermo gravimetric (DTG) thermograms of partially cross linked natural rubber (NR), chitosan (CTS) and APM have been shown in Figure 3 and 4, respectively. Chitosan indicated two-step decomposition process, first step decomposition of 6.2 % indicates the liberation of volatile compounds and bound water molecules. The second stage rapid decomposition (weight loss of 58.1 %) shows thermal cleavage and chain scission of C—C and C—O bonds indicating main degradation temperature of 309.26 °C as shown in DTG thermogram [9-10].

Natural rubber matrices indicate single step degradation with rapid weight loss of 97.3 %, and the main decomposition temperature was observed 383.68 °C, as shown in the DTG curve. APM shows two step thermal decomposition, the first step decomposition of 8.4 % and the second decomposition of 83.4 % was due to bound water and thermal cleavage of cis-1,4-polyisoprenes, respectively.

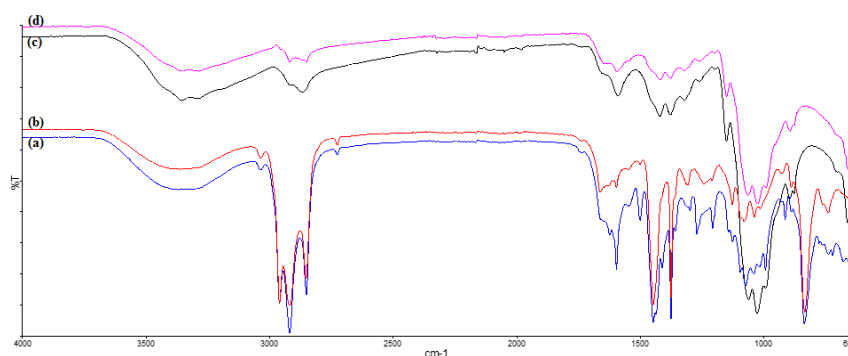


**Figure 3.** TG thermograms of CTS, NR and CTS-e-NR



**Figure 4.** DTG curves of CTS, NR and CTS-e-NR

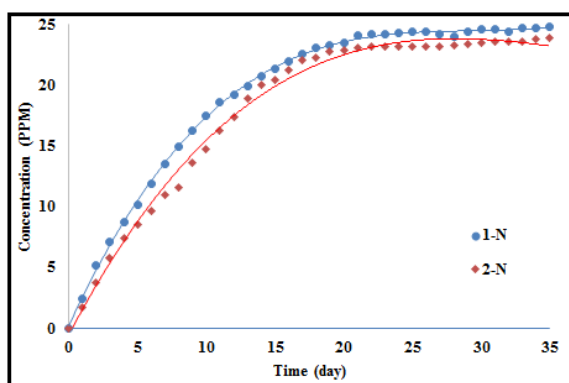
The FTIR spectra of chitosan, partially cross-linked natural rubber (CNR) and APMs have been shown in Figure 5. The FTIR spectrum of the APMs indicate that there is no alteration of the existing peaks and production of no new peaks. The spectra indicate that the interaction between chitosan and natural rubber matrices are totally physical.



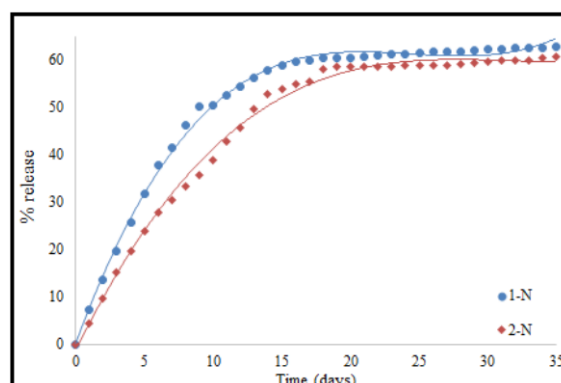
**Figure 5.** FT-IR spectra; (a). NR, (b). bicomposite outer surface, (c). CTS and (d). biocomposite internal surface

### 3.1. Pesticide release study

The objective of this work was to study the capability of APMs constituted by chitosan and natural rubber matrices for controlled release of pesticides in aqueous solution. Therefore, the APMs were studied for the release behaviour of 1- and 2-hydroxynaphthalene. The with-out-refresh results indicate that pesticides release gradually, and effective concentration of the pesticides was observed upto 20 days, as shown in Figure 6. With-refresh, the effective amount was released upto 16 days. In a conclusion, the release profile of the pesticides from APMs was found satisfactory: a lower pesticides release was observed at the early stage of the release experiments that lasted for 35 days, as presented in Figure 7.



**Figure 6.** The release behaviour of naphthol compounds (without refresh)



**Figure 7.** Accumulative % release of naphthol compounds (with refresh)

## 4. Conclusion

A polymeric advanced material consist of chitosan encapsulated in natural rubber matrix was prepared and characterized by FT-IR and TGA. The APMs were studied for the controlled release of pesticides such as 1-hydroxynaphthalene and 2-hydroxynaphthalene. The release of pesticides were found controlled, consistent and prolonged over a prolonged period of 35 days. Therefore, the formulation was strongly recommended for the controlled-release of pesticides on industrial scale.

## 5. Acknowledgement

The authors would like to appreciate Universiti Sains Malaysia (grant no. 1001/PKIMIA/814124) and TWAS (The World Academy of Sciences) and Universiti Sains Malaysia for providing TWAS-USM Fellowship.

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