Synthesis and Characterisation of Copoly-(Eugenol-*N,N′*-Methylene Bis(Acrylamide))

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ABSTRACT: *Solvent-free cationic copolymerisation of eugenol and N,N′-methylene bis(acrylamide) (MBA) was conducted with different MBA compositions, i.e., 2%, 4% and 6%. The copolymerisation was performed using an H_2SO_4 initiator in a nitrogen atmosphere at room temperature (28°C–30°C). The structure of the obtained product, copoly-(eugenol−N,N'-methylene bis(acrylamide)) or PEMBA, was identified by Fourier transform infrared (FTIR) and ^1H NMR spectroscopy. The average relative molecular mass (M_v) of PEMBA was determined by viscometer tools at a constant temperature (28°C). The morphology of PEMBA was characterised by scanning electron microscopy (SEM). The thermal properties of PEMBA were analysed using differential scanning calorimetry (DSC). A comparative analysis of the FTIR spectra of PEMBA with eugenol and MBA demonstrated the loss of absorption characteristics of the vinyl group around 995 c^{-1}. It was strengthened by the loss of the ^1H NMR signal for the vinyl proton at δ = 5.5–7.0 ppm and the appearance of a proton signal from the Csp^3 bond at δ = 0.7–1.3 ppm. Based on the viscosity calculation, it was found that the M_v of PEMBA 2%, 4% and 6% were 23543 g mol^{-1}, 19098 g mol^{-1} and 12904 g mol^{-1}, respectively. An SEM examination of PEMBA showed amorphous chunks of irregular shapes and sizes. Thermal analysis showed that the glass transition temperature (T_g) of PEMBA tended to decrease with an increase in the MBA concentration, but on the other hand, both the melting point (T_m) and the crystallisation temperature (T_c) shifted to higher temperatures.*

Keywords: Copoly-(eugenol−*N,N′*-methylene bis(acrylamide)), copolymerisation, eugenol, *N,N′*-methylene bis(acrylamide), cationic copolymerisation

1.   INTRODUCTION

Dye wastes are an environmental problem since these wastes persist in the environment for a long period of time due to their high photo and thermal stability, making them resistant to biodegradation.[1] Various methods for dye waste treatment have been used, such as dye adsorption. Activated carbon is one type of adsorbent, and is currently widely used for adsorption, including dye. The application of activated carbon as an adsorbent presents some practical problems such as the high cost of regeneration, rapidly decreased adsorption ability, and lack of selectivity.[2] To overcome these problems, it is necessary to find new materials having good absorbency properties, i.e., polymers. Diverse polymers have been studied and successfully applied as adsorbents.[2–6]

Nowadays, research interest in the synthesis of polymers is focusing on employing bio-based monomers. There are various classes of bio-based monomers such as phenylpropane, terpene, steroid, fatty acid derivatives, etc.[7–10] One bio-based starting material which has the potential to be utilised as a monomer is eugenol.[7,11–13] Eugenol is an aromatic and/or phenolic compound which is the main volatile component of clove oil (ca. 78%).[14] According to the Indonesian technical Requirements Information System (INATRIMS), clove oils are the most abundant essential oil in Indonesia, with approximately 26000 tons produced annually. More than 70% of global eugenol consumption is supplied from Indonesia.[15]

Eugenol has a reactive hydroxyl group and vinyl group which can be modified into new materials.[7] The polymerisation of eugenol on their vinyl group could afford polymeric materials which have many hydroxyl and aromatic groups. As an active group, hydroxyl and aromatic can interact with dye; thus, the dye can be absorbed by eugenol-based polymers. The polymerisation of eugenol and its derivatives could be done through cationic polymerisation with Brønsted acids, such as sulphuric acid and nitric acid, or Lewis acids such as boron trifluoride.[7,11,16–18] Cationic polymerisation of styrene derivatives, including phenolic compounds, could be carried out directly into living polymers without phenolic group protection. This cationic polymerisation can be performed by an alcohol/boron trifluoride etherate system as the initiator. However, Lewis acids such as BF_3 are less stable in the presence of oxygen and water. As an alternative, sulphuric acid can be chosen as the initiator for the cationic polymerisation of eugenol.[16,17,19]

The introduction of new functional groups into the polymer chain usually leads to a polymer exhibiting desirable properties. Thus, in order to obtain material having good properties in term of selectivity in adsorption processes, polymer can be modified, for example, by transformation of the existing functional group on the polymer chain or grafting onto a new functional group.[20–22] One of the common

modification methods of the polymer chain is to add a crosslinker on the active side of the polymer chain.[12,23,24] In this research, solvent-free cationic copolymerisation of eugenol and N,N'-methylene bis(acrylamide) (MBA) has been studied. MBA has two amide groups which can interact with dye, so that crosslinked polymer eugenol and MBA, copoly-(eugenol−N,N'-methylene bis(acrylamide)) (PEMBA), could have a more active side. Thus, the obtained PEMBA could be more reactive, and thus has the potential to be applied as a dye adsorbent. Also, in this research, the synthesised PEMBA was characterised in detail, including its thermal properties, and a morphological analysis was conducted.

2. EXPERIMENTAL

2.1 Materials

All materials (pro-analysis grade) used were without further purification, such as eugenol (PT. Indesso Aroma), N,N'-methylene bis(acrylamide) (Sigma Aldrich), methanol (Merck), sulfuric acid (H_2SO_4) (Merck), chloroform (Merck), anhydrous sodium sulphate (Na_2SO_4) (Merck), sodium chloride (NaCl) (Merck), and ethanol (Malinckordt Chemicals).

2.2 Instrumentation

Fourier-transform infrared (FTIR) spectra were obtained from a Shimadzu FTIR Prestige-21 spectrophotometer. ^{1}H NMR spectra were recorded on an Agilent V NMR 400 MHz spectrometer. Chemical shifts (δ) are reported in ppm relative to the internal standard tetramethylsilane (TMS, δ = 0.00 ppm). Scanning electron microscopy (SEM) was imaged in 250X magnification using a SEM FEI Inspect-S50 EDAX. Differential scanning calorimetry (DSC) experiments were performed with a DSC, Linsesis PT 1600 type, in a nitrogen atmosphere, at a heating rate of $10°C \times min^{-1}$ up to a temperature of 600°C, and using a sample mass of approximately 2.8–3.6 g. The glass transition temperature, T_g is reported to be the midpoint of the heat capacity change. The melting temperature, T_m, is recorded as the minimum (exothermic transitions are represented upwards) of the endothermic melting peak.

2.3 Experimental Method

2.3.1 Synthesis of PEMBA

Three copolymers were obtained by mixing eugenol (5 g) and MBA at various weights, i.e., 2%, 4% and 6% (percentage by weight of eugenol) in a flask.

The copolymerisation was performed in a nitrogen atmosphere at room temperature (28°C–30°C) without solvent, and magnetically stirred while initiated by adding 1 ml H_2SO_4 (4 × 0.25 ml per h). Reaction was carried out for 4 h and terminated by adding 1 ml of methanol. A violet-black gel was obtained and dissolved in chloroform then washed with deionised water until pH = 7. Anhydrous Na_2SO_4 was added to the organic layer, followed by solvent evaporation. The obtained residue was dried in desiccators. The average molecular weight of viscosity (M_v) from PEMBA was determined using a viscometer at constant temperature 28°C. The morphology and thermal properties of PEMBA were determined by SEM and DSC, respectively.

3.   DISCUSSION

3.1   Synthesis of PEMBA

The vinyl group of eugenol was copolymerised with two vinyl groups of MBA to obtain crosslinked polymer (PEMBA). The copolymer products for the various compositions of MBA were dried-solid. The average relative molecular mass of PEMBA was decreased by increasing the composition of MBA, as shown in Table 1. It might be possible that increasing MBA as a crosslinking agent could lead to a bulky structure in the propagation step and the monomer could not interact to make a longer chain.

Table 1: Result of synthesis of PEMBA.

Copolymer	Initial weight (g)		Product weight (g)	Yield (%)	M_v (g mole^{-1})
	Eugenol	MBA			
PEMBA 2%	5.195	0.103	4.524	85	23543
PEMBA 4%	5.308	0.224	4.880	88	19098
PEMBA 6%	5.176	0.310	4.271	77	12904

3.2   Copolymerisation Reaction

Cationic copolymerisation of eugenol and MBA was performed through conducting copolymerisation under solvent-free conditions. Copolymerisation without solvent (bulk polymerisation) was chosen since it could reduce the risk of contamination of the reaction processes and the obtained product could be easily separated.[25] The addition of H_2SO_4 as an initiator gave a violet-black colour during the initiation step, which was possibly caused by the existence of carbocation during the polymerisation reaction. Carbocation was produced by the addition of the vinyl

group (of eugenol or MBA) with an acid initiator. The possibility of an initiation reaction is shown in Figure 1.
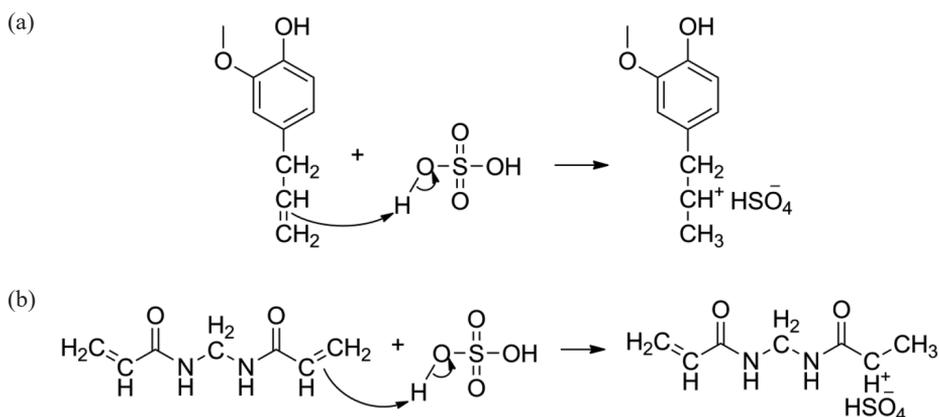
(a)

(b)

Figure 1: Initiation by sulfuric acid in vinyl groups of (a) eugenol, and (b) MBA.

Carbocation produced by the addition of the acid initiator was secondary carbocation since this type of carbocation is more stable than the primary one.[26] Thus, the intermediate carbocation that usually occurs during a cationic polymerisation is the most stable form of carbocation.[27] The formed carbocation then propagates during the polymerisation reaction to form a long chain of polymer. During the propagation step, the vinyl group from other monomers share their lone pair electron with the carbocation, leading to new carbocation (Figure 2). These steps are repeated until the reactions are terminated.

The copolymerisation reaction was then terminated by the addition of methanol as a nucleophile reactant. Methanol has an oxygen atom which is electronegative and can share its lone pair electron. The shared lone pair electron from methanol causes the carbocation to become inactive and the copolymerisation was stopped. The termination step is depicted in Figure 3.
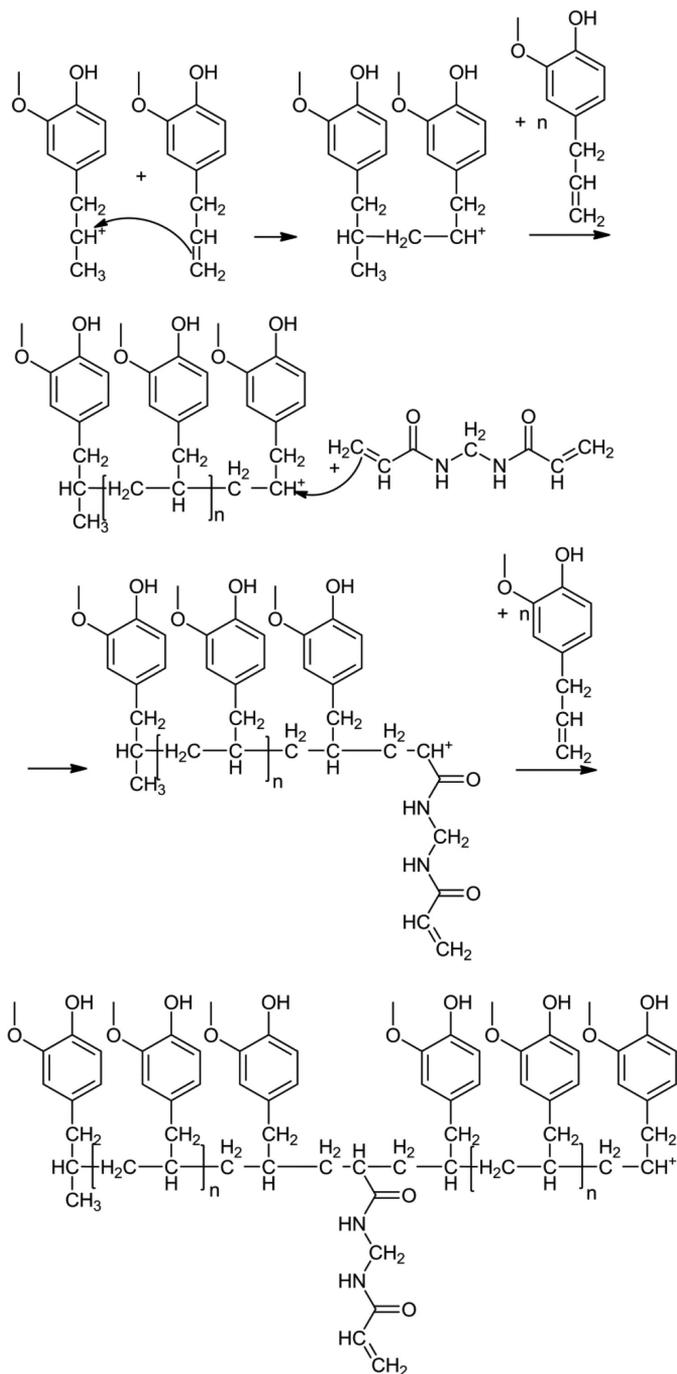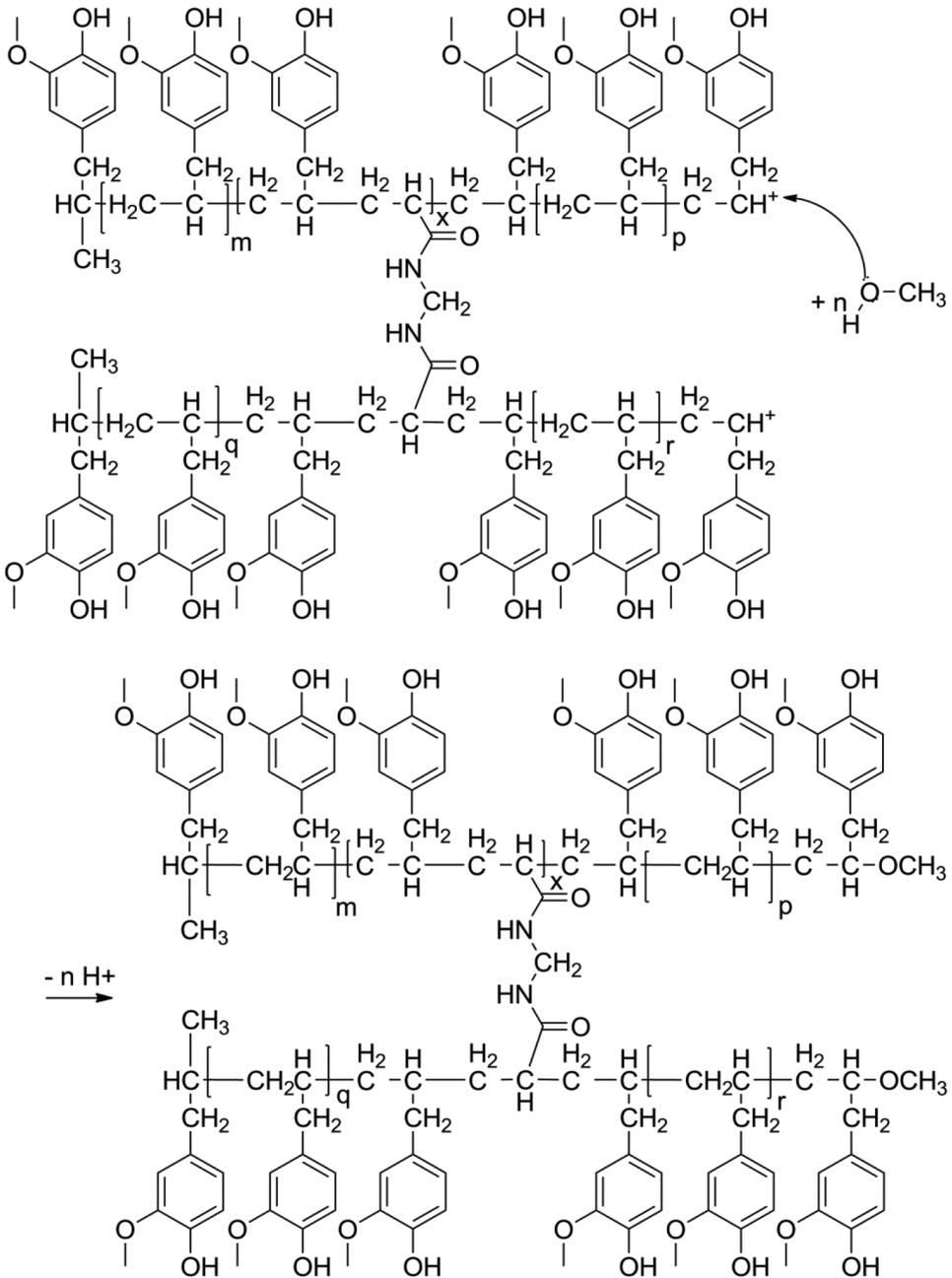
Figure 2: Propagation step of the synthesis of PEMBA.

Figure 3: Termination step of the synthesis of PEMBA.

3.3 Characterisation of PEMBA

Quantitative analysis using FTIR was conducted in the wave number range 4000–400 cm^{-1}. Figure 4 shows a comparison of eugenol, MBA and PEMBA spectra. Both eugenol and MBA had characteristic bands of vinyl groups (–CH=CH$_2$) at 996–992 cm^{-1}. Otherwise, in the spectra of all PEMBA the characteristic band of vinyl groups disappeared. This was possibly because the vinyl groups of both eugenol and MBA successfully reacted via the polymerisation addition reaction.
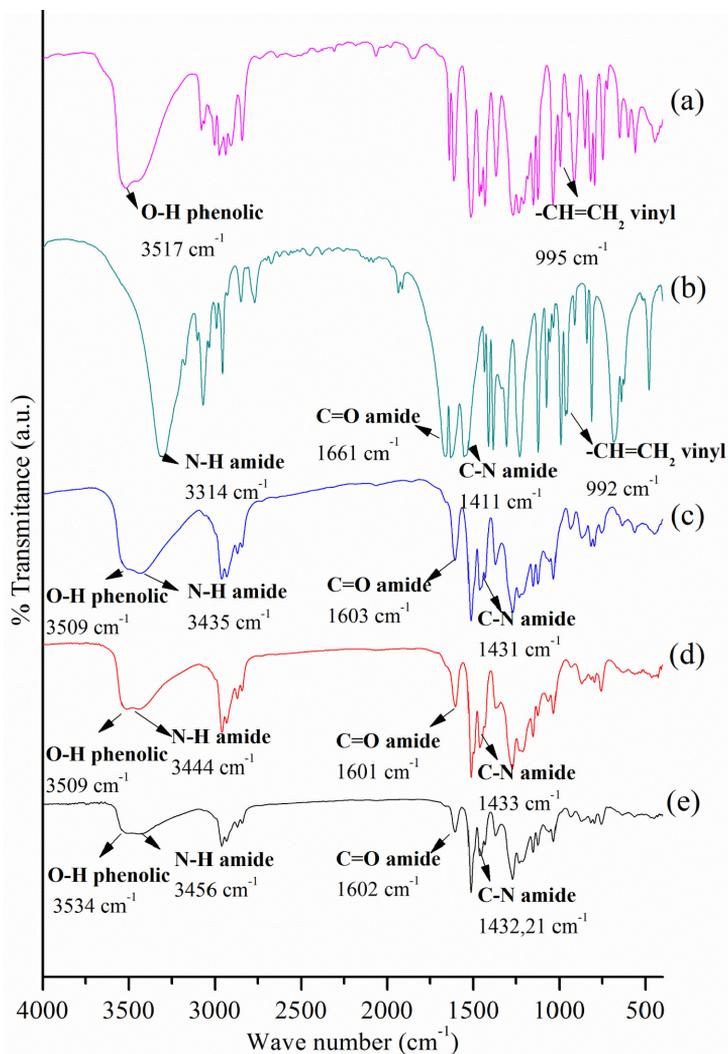

Figure 4: Spectra comparison of (a) eugenol, (b) MBA, (c) PEMBA 2%, (d) PEMBA 4%, and (e) PEMBA 6%.

All products of PEMBA had some resembling characteristic bands with eugenol and MBA. Hydroxyl groups of PEMBA appeared as the O-H stretching band at 3450–3300 cm⁻¹ and overlapped with the N-H stretching band of amide groups. Carbonyl groups of amide appeared as the C=O stretching band at 1600–1605 cm⁻¹ and as the C-N vibration band at 1410–1420 cm⁻¹.

Analysis using ¹H NMR was used to identify protons in eugenol, MBA and PEMBA. In this study, PEMBA 2% was used as the sample for ¹H NMR analysis. Figure 5 shows a comparison of ¹H NMR spectra between eugenol, MBA and PEMBA 2% with a detailed chemical shift as seen in Table 2 (eugenol) and Table 3 (MBA).
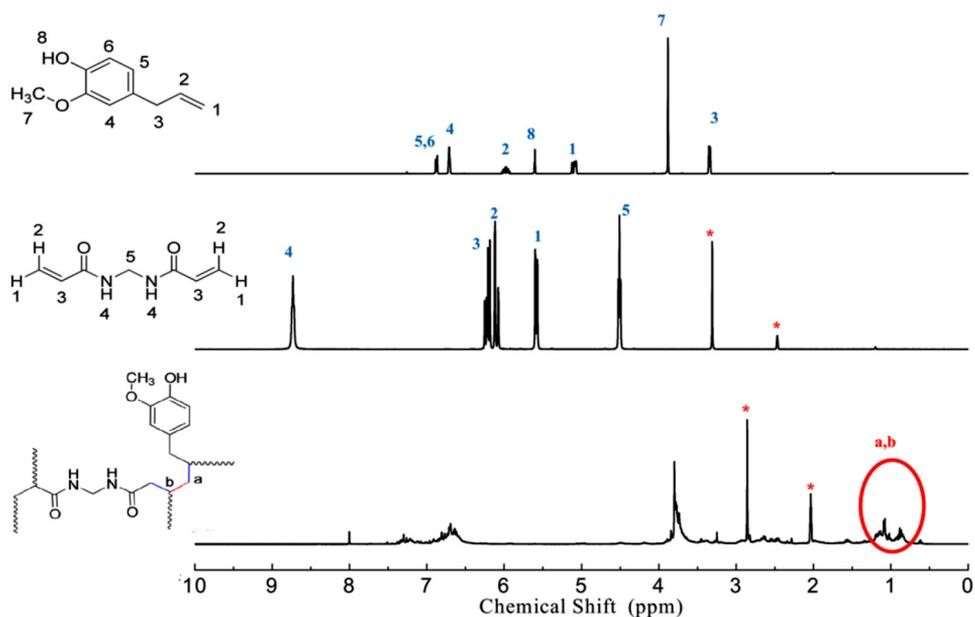

Figure 5: ¹H NMR spectra comparison of eugenol (CDCl3) for (a), MBA (DMSO), and (b) PEMBA 2% (Aseton D6), 400 MHz (* denoting solvent residues).

Table 2: Chemical shift of 1H NMR spectra of eugenol.

Proton	Multiplicity	Chemical shift, δ (ppm)
H(3)	doublet (d),2H	3.35
H(7)	singlet (s), 3H	3.88
H(1)	doublet of doublet (dd), 2H	5.07–5.12
H(8)	singlet (s),1H	5.60
H(2)	multiplet (m), 1H	5.93–6.03
H(4)	singlet (s), 1H	6.89
H(5)	doublet (d), 1H	6.70
H(6)	doublet (d), 1H	6.87

Table 3: Chemical shift of ^{1}H NMR spectra of MBA.

Proton	Multiplicity	Chemical shift, δ (ppm)
H(5)	triplet (t), 2H	4.49–4.52
H(1)	doublet of doublet (dd), 1H	5.57–5.60
H(2)	doublet of doublet (dd), 1H	6.07–6.12
H(3)	doublet of doublet (dd), 1H	6.18–6.25
H(4)	triplet (t), 1H	8.72–8.75

The proton signal of vinyl of eugenol and MBA was in the range of 5 ppm to 7 ppm. Otherwise, that chemical shift disappeared in the PEMBA spectra. The data from the FTIR spectra showed that vinyl groups of eugenol and MBA had successfully reacted in a cationic addition polymerisation reaction and the appearance of proton absorption from sp^3 carbon bond (H a,b) at 0.7 ppm to 1.3 ppm that was produced by the addition reaction. A proton chemical shift of PEMBA 2% at 0.9–1.2 ppm was overlapped. It was possibly caused by polydispersity of the synthesised polymer.[28]

Further characterisation was done by studying the morphology of PEMBA. SEM imaging is shown in Figure 6. At 250X magnification, for all variations of PEMBA, the SEM images showed amorphous chunks of irregular shapes and sizes. Increasing in MBA composition influenced the chunk particle size. It is shown in Figure 6 in the SEM image of the composition of PEMBA 2%, that there are more chunk particles of larger size. On the other hand, there are more small chunk particles observed in the composition of PEMBA 6%.

Differential scanning calorimetric analysis was used to investigate the thermal properties of PEMBA. Thus, the T_g, T_m and T_c were briefly investigated. A thermograph of the DSC analysis is shown in Figure 7 and result of the analysis study is shown in Table 4.
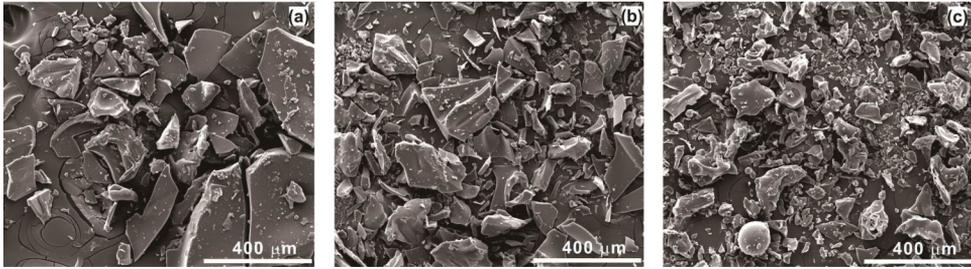
Figure 6:   SEM imaging of (a) PEMBA 2%, (b) PEMBA 4%, and (c) PEMBA 6% (250X magnification).
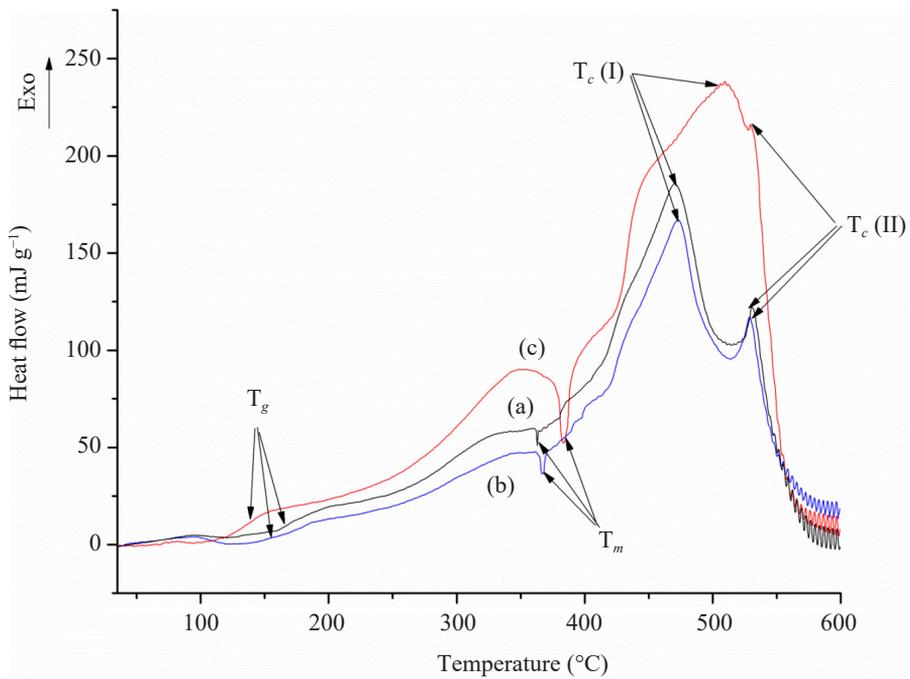

Figure 7: Thermograph of DSC (a) PEMBA 2%, (b) PEMBA 4%, and (c) PEMBA 6%.

Table 4: Result of DSC analysis study PEMBA.

Copolymer	T_g (ºC)	T_m (ºC)	T_c (I) (ºC)	T_c (II) (ºC)
PEMBA 2%	181.5	363.1	470.4	531.0
PEMBA 4%	159.7	367.0	472.9	529.0
PEMBA 6%	128.7	383.4	508.9	529.4

The T_g is the range of temperature where the amorphous phase of polymer transforms from glassy materials into rubbery-like materials.[29] In Table 4, the data showed that T_g was shifted by changing the composition of MBA. Increasing MBA composition in PEMBA shifted the T_g to a lower temperature.

The thermograph DSC (Figure 7) showed that endotermic melting of PEMBA 2%, 4% and 6% occurred at a temperature of 360ºC–385ºC. The melting point of PEMBA shifted to a higher temperature when the composition of MBA was increased. It was caused by rigidity of PEMBA increased by rising the composition of MBA. Thus, a higher temperature was needed to melt PEMBA.

Crystallisation of PEMBA occurred in two steps, called fractionated crystallisation. This phenomenon takes place once the amount of active heterogeneities is at the magnitude identical arrangement than the number of domains, thus a significant population of domains still have several types of heterogeneity.[30] In the first crystallisation temperature, i.e., T_c (I), it was possible that PEMBA that had a lower molecular mass would crystallise, and in the second crystallisation temperature, i.e., T_c (II), possibly PEMBA that had a higher molecular mass would crystallise.

4.   CONCLUSION

In summary, we present a convenient way to synthesise PEMBA through cationic copolymerisation of eugenol and MBA using H_2SO_4 as an initiator in a nitrogen atmosphere without the use of solvent. Composition of MBA reacted with eugenol influenced the product of PEMBA. Increasing the MBA composition caused a decrease in the average of the relative molecular mass of PEMBA, a smaller shape of PEMBA, shifted the glass transition to a lower temperature, and increased the melting transition of PEMBA.

5.   ACKNOWLEDGEMENTS

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