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Dilution and $ZnCl_2$ Impact on Eutectic Solvents as Devulcanizing Reagent in De-linking Phenomena of Waste Ground Rubber Tire

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Abstract. As an effort to minimize the amount of solvent used in de-linking of waste ground rubber tire (WGRT) for economic benefit, impact of water dilution on devulcanization study with deep eutectic solvents (DESs) was studied. Three different ammonium-based eutectic mixtures were prepared and examination on their water content, degradation temperature and freezing point were conducted. WGRT were mixed with DESs synthesized and diluted at 0, 10, 20 and 30% at fixed sonication and heat treatment conditions. Devulcanized vulcanizates were studied in terms of their density of cross-linkages (CLD), soluble content and devulcanization efficiency (%dev). Additionally, optimized samples underwent further analysis by thermogravimetric analyser (TGA) and Horikx fitting. Analysis shows that increase in water content decreases the %dev and chances of sonoluminescence occurrence is probable due to Zn^{2+} cation, low frequency sonication as well as water, causing sudden spike in %dev. However, negligible amount of polymeric scission was experienced.

INTRODUCTION

As an initiative toward greener and sustainable development, the method of recycling has been explored in various field in order to preserve as well as minimize the utilisation of raw and natural resources [1]. However, only minimum effort has been done to recycle vulcanizates elastomers, especially waste rubber tires (WRT). This is because the formation of three-dimensional (3D) network between free polymeric chains of polymers with curing agent, sulphur [2]. This invention was found by Charles Goodyear who revolutionised automotive industries worldwide. However, recycling these vulcanizates materials has become an issue due to the 3D matrix [3].

Current practice to recycle such WRT is through open-air combustion process and landfill subjugation, which heavily pollute the atmosphere, ground - due to leeches of heavy metals, water and nests for infectious-carrying rodents [4]. Such resort is being done only after tire has expired of its usable life cycle through multiple re-treading and re-use process, which does not solve the large volume of solid and non-degradable waste [5]. Additionally, one of the efforts that has also been done was to use powdered-WRT as a filler for new tire [6]. But unfortunately, due to the incompatibility between matrix' of WRT and new vulcanizates, tire properties in overall are being compromised and could not meet the required industrial preferences [3]. As such, as of current, only 2% of overall tire is used in the production of new tire [7].

Despite that, researchers and academics have come out with various methods to selectively recycle WRT through devulcanization method. These methods include thermal, chemical, biological, mechanical, microwave,

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ultrasonic and combination of any these methods [8]. In the recent work, T. Liang *et al.* [9] investigated the impact of ultrasonic extrusion on devulcanization of styrene butadiene rubber (SBR). They found that increase in ultrasonic amplitude increases the gel fraction and reduces the degree of devulcanization due to the rubber-filler (silica) interactions induced by ultrasonic treatment. Such observation comes in agreement with their other study performed with natural rubber (NR)/SBR blend [10]. Mona Y. Elnaggar *et al.* [11] utilised the ultrasonically devulcanized rubber and blend it with virgin SBR to study the blend behaviour. The study suggests great improvement in thermal behaviour and hardness level.

In another study, S. Seghar *et al.* [12] evaluated the impact of temperature on devulcanization of WRT by means of microwave treatment. Their study concluded that as microwave energy increases, temperature increases and ultimately, soluble fraction increases. Increase in soluble fraction indicating an increase in percentage of devulcanization as vulcanizates are insoluble in organic compound. Such observation seems to corroborate with recent study performed by X. Zhang [13], regarding the use of devulcanizing solvent at a ranged of temperature. However, P. S. Garcia *et al.* indicating that devulcanization heat treatment exposure should be controlled to inhibit undesired polymeric degradation [14]. This is in agreement with previously reported study by S. Saiwari *et al.* [15] who indicate that devulcanization should occur as fast as possible at the selected or optimum parametric condition as it will promote re-linking of cleaved sulphur bridges.

Thermochemical devulcanization study was also performed by Pedro *et al.* [16] through the utilisation of zinc (II) di-thiocarbamate. Observation proofs the impact of zinc salt in devulcanization, whereby high concentration enhances regeneration while low concentration enhances re-vulcanization. In addition, amine-based solvent is the best devulcanizing agent proven by study conducted by J. K. Premachandra *et al.* [17] and oil desulphurisation study by Li *et al.* [18]. Thereby, it works as a great substitution for chemically toxic disulphides, as devulcanizing agents. S. Seghar *et al.* [12] pioneering the usage of amine-based ionic liquid (IL) in devulcanization and shows a promising results when devulcanization method is coupled with IL. Despite being a designer solvent, ILs are expensive, highly viscous, toxic, difficult to synthesise and non-biodegradable [19]. Such indicator makes it unsuitable for industrial usage, thereby alternative designer solvents, deep eutectic solvent (DES) is introduced, of which it is made from hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA) or salt.

In this study, the impact of $ZnCl_2$ salt presence and diluting the devulcanizing agent (DESs) in ultrasonic devulcanization was performed as an effort to maximize degree of devulcanization by minimizing solvent used. The DESs synthesised were characterized based on water content, melting point and degradation temperature to ensure its suitability by Karl-Fischer titration (KFT), Lyjersen-Joback Reid (LJR) relation and thermogravimetric analyser (TGA) respectively. Whereas the devulcanizates degree of devulcanization was assessed by percentage of devulcanization, soluble content and density of cross-linkages (CLD). The optimum sample(s) will undergo further analysis by TGA and Horikx analysis to validate the cleavage of sulphur bridge.

METHODOLOGY

Materials

Waste ground rubber tire (WGRT) was kindly supplied by a governmental agency, Nuclear Malaysia Sdn. Bhd. with the mesh size of 40. Chemical used in this study, at >99% purity (no additional purification was performed), which are glycerol (gly), ethylene glycol (EG), ethyl-ammonium chloride (EAC), di-ethyl-ammonium chloride (DEAC), di-ethyl-ethanol-ammonium chloride (DEEtAC) and zinc (II) chloride ($ZnCl_2$) were supplied by Merck Sdn. Bhd.

Preparation

Preparation of DES

Formulation of DESs used in this study is shown in the following Table 1. DESs were synthesized through a known method described in academic paper [20]. Synthesis was done in a moisture-controlled environment. Salts and HBD, at the formulated molar ratio, were mixed at 300 rpm in a parafilm sealed laboratory bottle at 70^{o}C, to prevent high moisture content that could crystalize and alter the solvents' inherent physicochemical properties. Synthesis is complete when homogeneous (and transparent) liquid is formed.

TABLE 1. DESs molar ratio formulation

DES	Salt / HBA Group			HBD Group		Accelerator	Water Dilution [%]	Sample Code
	EAC	**DEAC**	**DEtAC**	**Gly**	**EG**	**$ZnCl_2$**		
A1	1	0	0	5	0	0	0	1.1
							10	1.2
							20	1.3
							30	1.4
A2	1	0	0	5	0	0.25	0	1.5
							10	1.6
							20	1.7
							30	1.8
A3	1	0	0	5	0	0.5	0	1.9
							10	1.10
							20	1.11
							30	1.12
B1	0	1	0	0	3	0	0	2.1
							10	2.2
							20	2.3
							30	2.4
B2	0	1	0	0	3	0.25	0	2.5
							10	2.6
							20	2.7
							30	2.8
B3	0	1	0	0	3	0.5	0	2.9
							10	2.10
							20	2.11
							30	2.12
C1	0	0	1	0	4	0	0	3.1
							30	3.2
							20	3.3
							30	3.4
C2	0	0	1	0	4	0.25	0	3.5
							30	3.6
							20	3.7
							30	3.8
C3	0	0	1	0	4	0.5	0	3.9
							30	3.10
							20	3.11
							30	3.12

Devulcanization Process

WGRT will be mixed with the synthesized DES in 36 different portions at a fixed minimum mass ratio of 1:20 to prevent sluggish mixture formulation. The mixture was mixed at room temperature and 300 rpm overnight to ensure homogeneity of the sample. Next, samples were treated based on previously studied condition [8]. Agitated samples were first ultrasonicated for 60 minutes at 37 kHz. Upon completion, they were directly heated on a hot plate stirrer at 300 rpm and 180ºC for 55 minutes. Devulcanizates were separated from the solvent by means of vacuum filtration. Filtrates obtained were rinsed with ultrapure water for 5 times to ensure it is solvent free. Finally, filtrates were dried in oven at 70ºC overnight before characterisations.

Characterization

Characterizations of Eutectic Solvents

To ensure the usability of DES, its water content, degradation temperature and hydrogen bond formation were assessed. KFT was used to determine the percentage of water in the pure synthesized DES. As per reported, maximum allowable water content of DES is 5.0 wt% [20]. Degradation temperature was measured by TGA (TGA 8000, Perkin Elmer). Sample, at 5-10 mg, was purged with N_2 gas in a ceramic pan. Degradation was analysed in the range of 25-500ºC at 10 K/min. Finally, their melting points were approximated by LJR method shown in eq. (1) [21].

$$T_m = 122.5 + \sum n_i \Delta T_M \tag{1}$$

With respect to equation (1), Tm is the approximated melting point, n_i is the molar ratio and ΔT_M is the LJR atomic bond contributing parameters.

Characterization of Devulcanizates

For soluble content and extend of devulcanization measurements, 200 mg of sample was secured in a 2x2 inch of 20-mesh wire mesh. Samples were then immersed in toluene for 3 days (solvent refreshed each day), following ASTM D-6834 standard operating procedure. Degree of swelling (Q) and extend of devulcanization of devulcanizates (%dev) was measured by equation (2) and (3), respectively. To utilise equation (3), density of cross-linkages (ζ), mol/cm^3, was determined through Flory-Rehner equation (4), volumetric fraction (ζ_r^o) of insoluble (gel) by equation (5) and interaction between polymer-solvent (χ) by equation (6).

$$Q = \frac{m_w - m_a}{m_a} \, x \, 100\% \tag{2}$$

$$\%Dev = \frac{\zeta_i - \zeta_f}{\zeta_i} \, x \, 100\% \tag{3}$$

$$\zeta = \frac{-\ln(1-\zeta_r^o) + \zeta_r^o + \chi(\zeta_r^o)^2}{V_S\left[(\zeta_r^o)^{\frac{1}{3}} - 0.5(\zeta_r^o)\right]} \tag{4}$$

$$\zeta_r^o = \frac{m_b}{m_b + m_c\left(\frac{\rho r}{\rho s}\right)} \tag{5}$$

$$\chi = 0.429 + 0.218\,\zeta_r^o \tag{6}$$

The terms m_a, m_b, m_w and m_c are referring to recycled rubber's mass prior to imbibition, after imbibition, swelled and amount of solvent absorbed respectively. Furthermore, ρ_r, ρ_s, ζ_i, ζ_f and V_S are being identified as polymeric density, solvent's density (toluene is 867 kg/m^3), untreated rubber cross-linkage density, treated rubber cross-linkage density and molar volume of organic solvent (toluene is 306.3 mL/mol) respectively. In addition, to analyse the selective bond cleavage, especially sulphur bridges and changes between vulcanizate and devulcanizate's properties of optimum samples, Horikx and TGA analysis were performed.

RESULTS AND DISCUSSION

Eutectic Solvents' Physicochemical Properties

The analyses on water content and freezing point of the formed eutectic solvents (undiluted) are shown in Table 2 as follow. Based on the result obtained, it is confirmed that the water content of the synthesized DESs are less than 5.0 wt% [22], which indicating the DESs' properties are negligible modified. Additionally, the melting point reported also shows significant depression compared to DES' constituent components. Such is the characteristics of

DES. The melting point values also shows a quantitative value of below 333.15 K, which means it can be economically used as a liquid without the additional utilisation of heating equipment. Thermal degradation curve of these undiluted DESs is shown in Fig 1. Based on the figure, complete degradation for each DES is experienced above 473.15 K. Hence, the operating temperature selected based on our previous study is applicable [8].

TABLE 2. Moisture content and melting point of undiluted DESs

Name	Water content [%]	Melting point [K]
DES 1.1	1.95	277.38
DES 1.5	2.34	271.24
DES 1.9	2.78	265.57
DES 2.1	1.43	229.27
DES 2.5	2.17	223.08
DES 2.9	2.63	217.57
DES 3.1	1.82	240.76
DES 3.5	2.18	235.20
DES 3.9	2.64	230.14

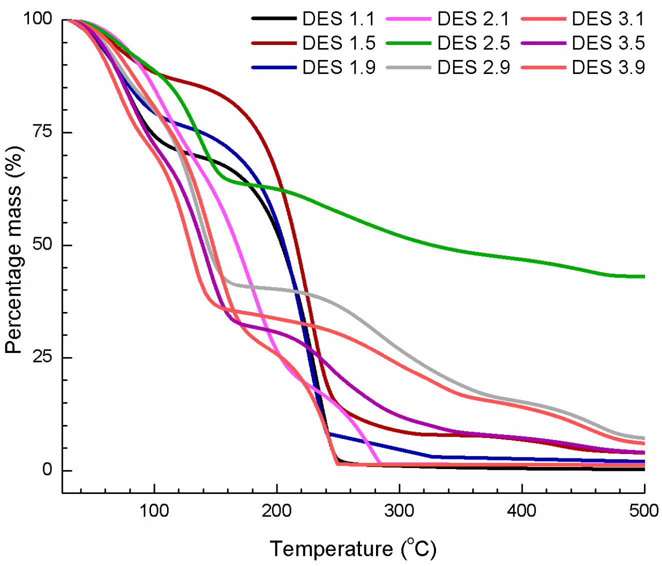

FIGURE 1. Degradation curve of DESs

Devulcanized GTR Analyses

Extend of Devulcanization and Soluble Content

Relationship study between soluble fraction, degree of de-linking and difference of density of cross-linkage (δCLD) between WGRT and devulcanizates on the effect of water dilution for different DESs was conducted. It is known that the CLD of WGRT is 8.50×10^{-5} mol/cm^3 and its soluble fraction is 2.488%. The following Fig 2 illustrate such analysis. Based on Fig 2, at first instance, it can be seen that de-linking with any solvents and at any dilution percentage, gives a not zero value for δCLD. This indicates that there is a certain degree of devulcanization which had taken place during the experiment.

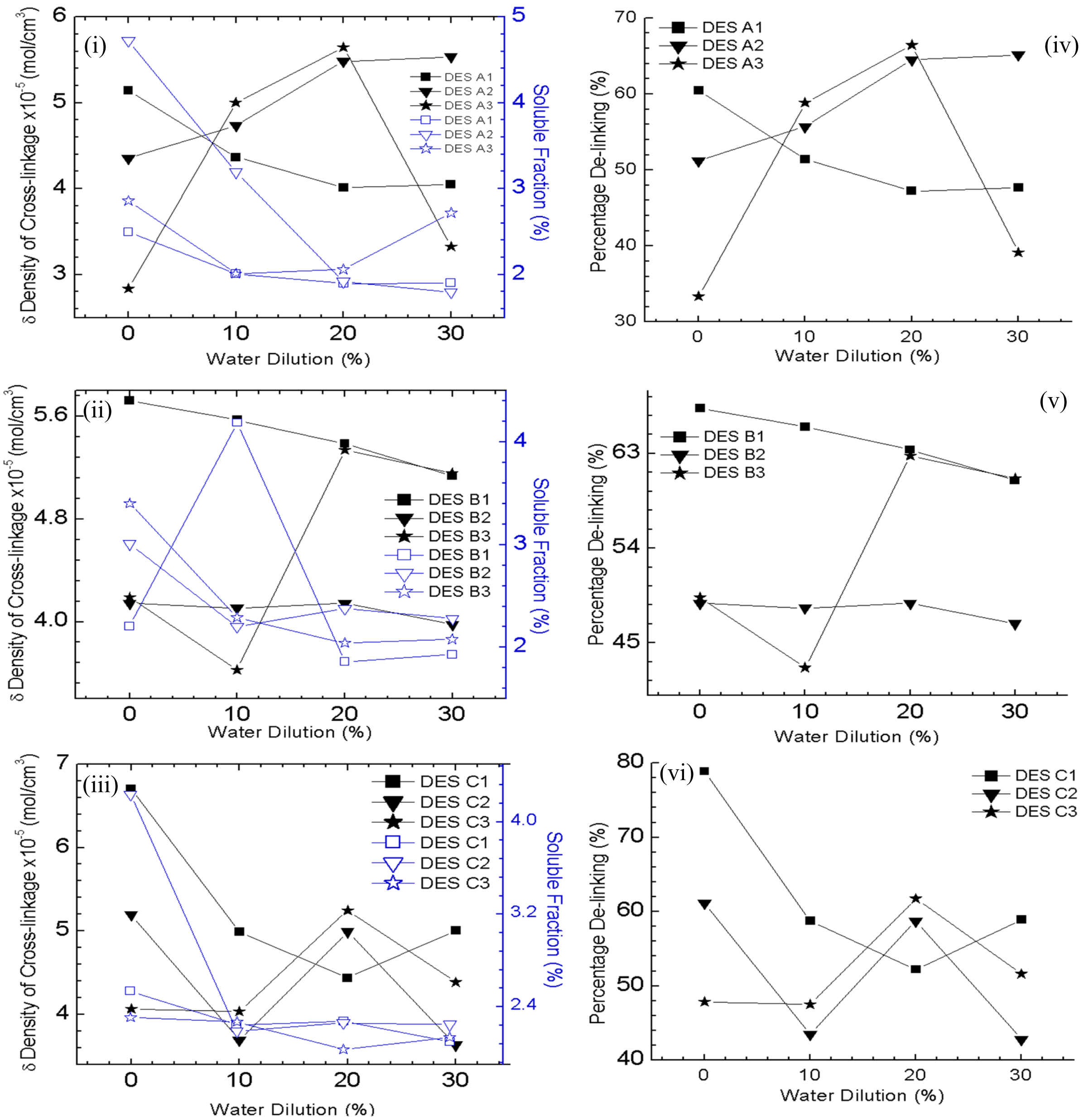

FIGURE 2. Treated vulcanizates' density of cross-linkages, parentage of soluble and devulcanization of sample, de-linked by DES (i, iv) A; (ii, v) B and (iii, vi) C

Fig 2 (i-iii) for DES type A, B and C show the same trend that at undiluted state, degree of devulcanization and δCLD of samples decreases as the molar ratio of $ZnCl_2$ increases. This is due to the nature of the DESs, whereby addition of $ZnCl_2$ salt (that has high resistance to flow) into the solvent increases the viscosity of the solvent and ultimately inhibit the mass transfer from solvent to the WGRT causing low degree of devulcanization. It is also in agreement with soluble content which decreases for A but increases for B and C.

However, due to heterogeneity of the WGRT composition, X. Column *et al.* suggest that evaluation is more recommended to be performed through δCLD and %dev [23] rather than soluble content. Such is due to the previous study performed by Ghorai *et al.* [24] and hypothesized by Song *et al.* [25] who declared that high soluble content does not proportionally related selective -S_x- scissions but rather random polymeric scissions. This is also proven in our Horikx analysis, explained in the following sub-sections.

In relation to water dilution, it is clearly seen and predicted that for all DESs in overall (disregarding heterogeneity of WGRT explained previously), δCLD and %dev decreases as a result of water dilution from 0 to 10% and 20 to 30%, which reduces the devulcanizing solvent's concentration. However, as also seen in Fig 2, maximum and irregular values were attained at 20% dilution. This observation is clearly seen for treatment with DES which includes the presence of $ZnCl_2$, but undiscoverable at the absence of $ZnCl_2$. Such phenomenon could be attributed to sonolysis reaction occurred during treatment which might be due to the presence of metal cation Zn^{2+}.

Sonolysis defines as a chemical reaction that helps the decomposition phenomenon to happens (preferably heterogeneous system), in this case devulcanization, with the presence of low frequency ultrasonic, water, metallic substance and atmospheric gasses (O_2, N_2 Ar, etc.) [26]. The process happens when radical •OH formed during ultrasonic treatment that causes cavitation of irradiated solvents, producing implosion phenomenon at very high temperature and pressure [27]. As such, •OH formed from H_2O acts as a radical scavenger as well as high temperature microbubbles of the samples, assisted the de-linking process.

This argument is corroborate with a previous study conducted by F. Cataldo *et al.* [28]. On the other hand, too high-water content causes runaway or uncontrollable ultrasonic cavitation reaction. As such, sonolysis reaction was so rapid that re-linkages of $-S_x-$ reformed. Reformation of these cross-linkages corroborates to the previous study conducted by X. Zhang *et al.* [29]. The authors mentioned that, in any case, re-linking is possible at prolong fixed temperature exposure or too high temperature and temperature gradient at fixed time.

Horikx Analysis

Based on Fig 2 previously reported, sample 1.1, 2.1 and 3.1 from DES A, B and C with 0% dilution respectively, were chosen for further studies due to their high extend of devulcanization compared to other samples. In the Horikx analysis, only evaluation on which bonds were cleaved during the devulcanization treatment was analysed with respect to control lines and as a function of %dev and soluble fraction of devulcanizates. Illustration is shown in Fig 3 as follow. Based on the Horikx curve fitting, it is clearly seen that current treatment in this study proofs that degradation occurs far from polymeric chain and more inclined towards selective sulphur bridge cleavages. Additionally, the graph also shows that sample treated with DES 2.1 experience the highest devulcanization degree compared to the other two DESs (3.1 and 1.1), which further corroborates to their previously reported Flory-Rehner analysis, at the absence of $ZnCl_2$.

To further evaluate the DESs, the number of α-H in ammonium salts plays an important role as an indicating factor for cross-linkages reactivity [30]. In this study, DES 1.1, 2.1 and 3.1 has α-H at the amount of 2, 4 and 6 respectively. Based on previously reported Fig 2, it is evident that devulcanizate treated by DES 2.1 has about twice the value of %dev compared to DES 1.1. This proves that the amount of α-H impacts the degree of devulcanization. However, DES 3.1 with 6 α-H has %dev lower (by 10%) than DES 2.1. This decrement could be because of the alcoholic functional group (-OH) in DES 3.1 that limits and inhibits extraction, especially at high temperature, but its %dev value is still higher than extraction with DES 1.1., which proves the chemical group of -OH is unsuitable for high temperature extraction. Additionally, increase in the molar ratios or treatment temperature could possibly increase the degree of devulcanization. However, in this study, those parameters were not included and further studies are required.

Degradation of controlled sample WGRT and devulcanizates treated with optimum DES is shown in Fig 4. As the testing was perform in an inert environment (e.g. N_2 gas), no thermal-oxidative degradation reaction was experienced. Based on Fig 4, four areas of degradation could be analysed accordingly.

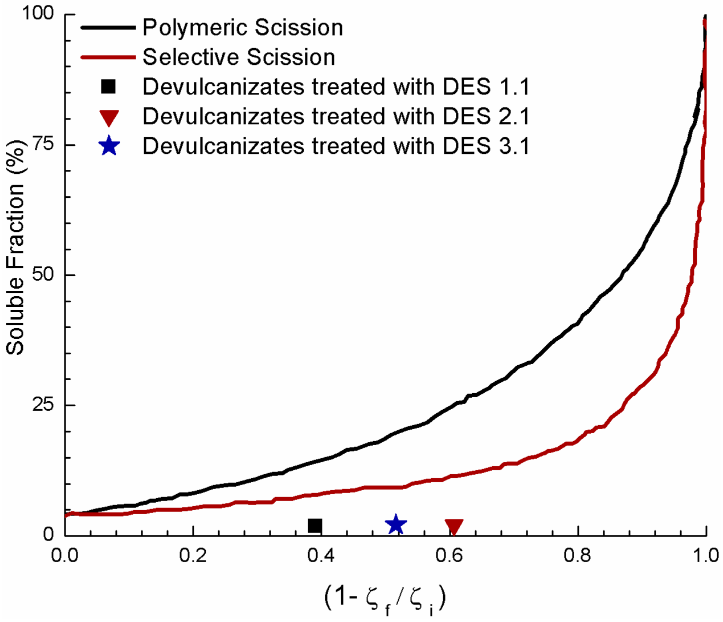

FIGURE 3. Horikx curve of devulcanizates

Thermal Analysis

Volatilization area which is an area that is associated around temperature of 100 to 300°C. In this region, waxes, oil, additives and low molecular weight compound of which present in WGRT were decomposed [29]. However, these miscellaneous components seem to be more pronounced for sample DES 1.1. second and third area is called polymeric degradation area. The two areas are associated around temperature 300 to 430°C and 430 to 500°C for degradation of NR and SBR respectively (proof that WGRT consists of NR and SBR). Whereas the last area is associated with temperature above 500°C. In this region, char residua are left. Based on Fig 6, the amount of char residua produced remained constant despite different devulcanizing solvents were used.

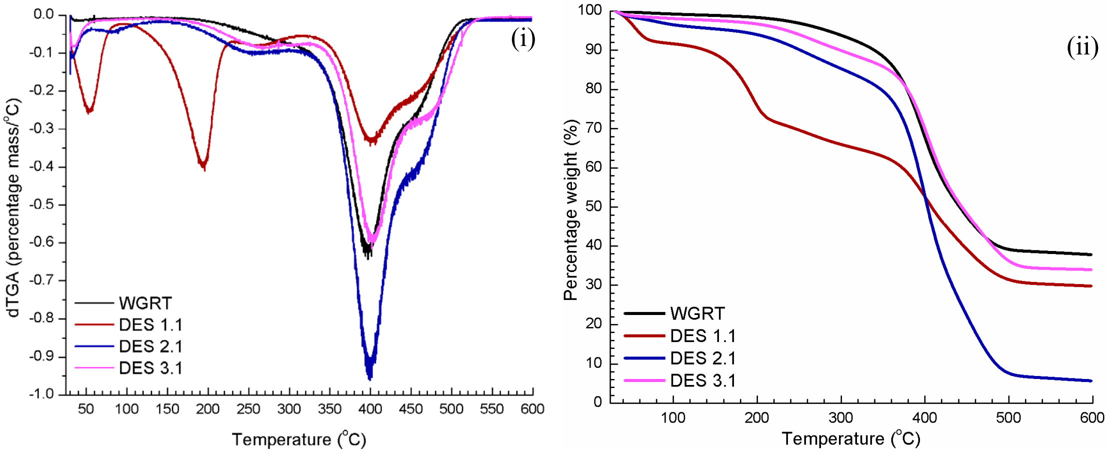

FIGURE 4. (i) dTGA and (ii) TGA curves for devulcanizates

Furthermore, the percentage weight lost from -5% to -50% comes with an increase in temperature, as miscellaneous has been degraded and only left with stable products. Nevertheless, overall thermal stability of samples tested does not have significant difference, which indicating polymeric chains are not largely altered. The existing small differences could be due to the heterogeneity of the WGRT described earlier.

CONCLUSION

This paper studies on the impact of diluting devulcanizing solvent (DES) in devulcanization study with ammonium-based DESs with water at 0, 10, 20 and 30% dilution, to minimize solvent used and enhance processing economical values. Based on Flory-Rehner analysis on CLD and percentage of devulcanization, it was seen that increase in water dilution percentage, in overall, reduces the devulcanization efficiency as density of cross-linkages decreases. Same observation was made when $ZnCl_2$ was added, as it increases the viscosity, reduces mass transport and decreases the efficiency. However, at 20% dilution, sonolysis phenomenon occurred and caused an unintentional significant increase in degree of devulcanization. This was observed for treatment with DES that has the presence of $ZnCl_2$ due to Zn^{2+} metal cation. Furthermore, Horikx analysis was also performed and confirmed that the selective cross-linkages were broken instead of polymeric. Thermal stability by TGA was also analysed and it showed no alteration between WGRT and devulcanizates, showing good retention of polymeric chains and properties.

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