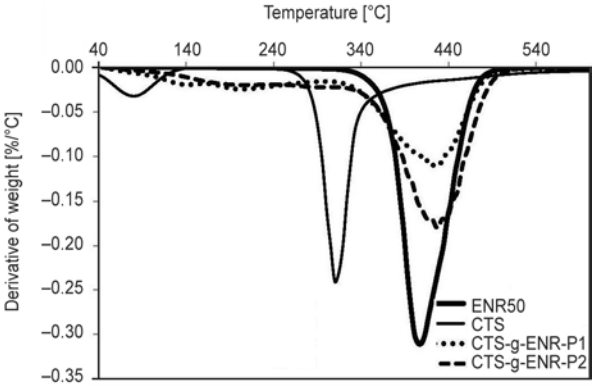

Figure 9. DTG curves for ENR50, CTS, CTS-g-ENR50-P1 and CTS-g-ENR50-P2

groups of CTS [9]. The third is the major mass loss of 56% occurred within 300 and 594°C due to a combination of chain scission of the grafted CTS and total decomposition of the rubber matrices. The amount of carbonized residue deduced from the TGA curves of CTS-g-ENR-P1 and CTS-g-ENR-P2 beyond 600°C is 24 and 9%, respectively. Therefore, it is apparent that lesser amount of CTS incorporated (grafted) onto the rubber matrices resulted in a lower amount of carbonized residue beyond 600°C. The thermal stabilities of CTS-g-ENR-P1 and CTS-g-ENR-P2 are quite similar and likely due to a combination of that of CTS and ENR50, i.e., higher than that of CTS but lower than that of ENR50.

4.7. Morphology study

SEM micrographs of CTS, ENR50 and CTS-g-ENR-P1 are shown in Figure 10. The chitosan has a flaky and uneven shape with smooth surface but the ENR50 displays a rough and groove like structure with some debris. Micrographs of the biocomposite show a one-phase morphology with a reduced gap between the chitosan and the rubber matrices suggesting not only good interfacial interactions but also very likely that CTS has been successfully grafted onto the backbone of the ENR.

4.8. Reaction pathways for the formation of CTS-g-ENR biopolymers

The plausible reaction pathways for the formation of CTS-g-ENR biopolymers are proposed in Figure 11. In a mildly acidic condition such as in solution containing $AlCl_3 \cdot 6H_2O$ (pH = 4.5), the epoxidized isoprene units of ENR50 would likely be protonated and susceptible to attack by reactive nucleophiles. How-

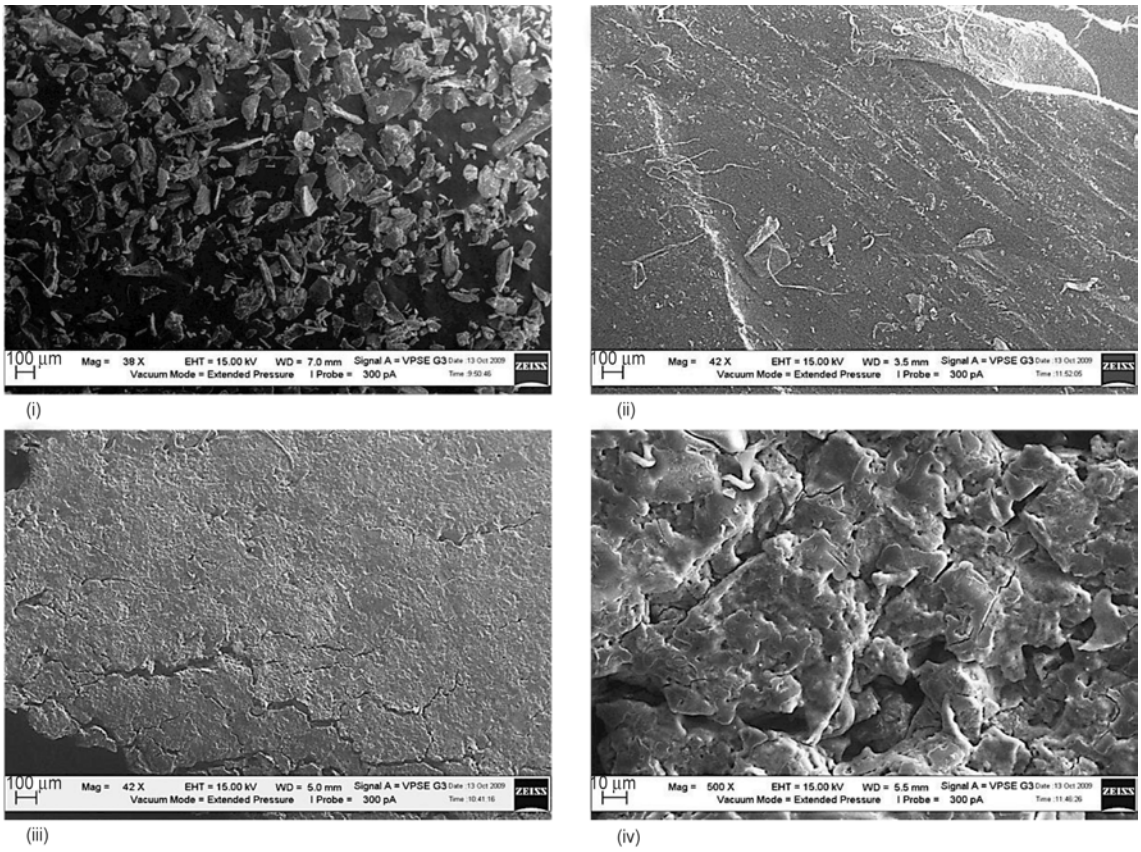

Figure 10. SEM micrographs of (i) CTS, (ii) ENR50, (iii) CTS-g-ENR-P1 at magnification of 42×, (iv) CTS-g-ENR-P1 biopolymers at magnification of 500×

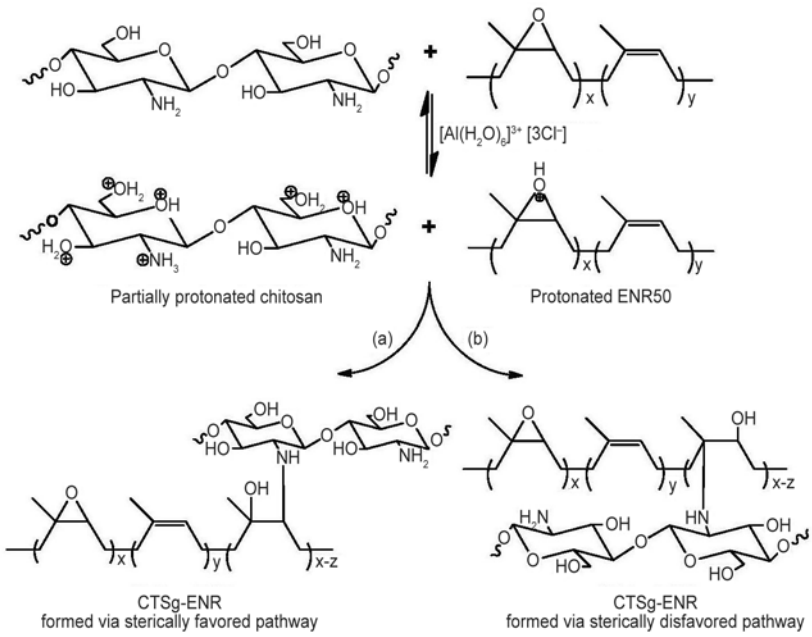

Figure 11. Reaction pathways for the formation of CTS-g-ENR biopolymers

ever under the similar mildly acidic condition, CTS being a multinucleophilic material would be partially protonated. The unhindered primary (C-6) hydroxyl group of CTS would be protonated rendering it non-reactive, whereas some of the sterically hindered primary amino (C-2) and secondary (C-3) hydroxyl groups would be free, i.e., remain as reactive nucleophiles. A primary amino group is much more reactive than a secondary hydroxyl group. As such, the grafting of CTS onto the backbone of ENR50 would involve solely the attack of the primary amino (C-2) of CTS on the protonated epoxidized isoprene units of ENR50. The attack may occur via sterically favored pathway (a) and sterically disfavored pathway (b) as illustrated in Figure 11. However, considering that CTS is a bulky polymeric entity and the fact that ENR50 remained structurally stable in the mildly acidic condition, we are of the opinion that the acid-induced reaction of ENR50 with CTS occurred preferentially or regioselectively via the sterically favored pathway. This notion is further supported by the infrared spectral analysis described above.

5. Conclusions

The effect of acidity on the stability of the molecular structure of ENR50 was investigated. It is hitherto elucidated by means of NMR spectroscopy that ENR50 remained structurally stable in 1,4-dioxane acidified by the addition of dilute HCl or $AlCl_3 \cdot 6H_2O$ solution. Based on this finding, the acid-induced reaction of ENR50 with CTS in a dual-solvent consisting of 1,4-dioxane and water (97.5:2.5% v/v) was explored. Two type of biopolymers CTS-g-ENR-P1 and CTS-g-ENR-P2 consisting of higher and lower amount CTS, respectively, grafted onto the backbone on the natural rubber derivative were prepared. The structural and physicochemical properties of the products as compared to that of the starting materials were characterized by means of FT-NMR, FT-IR, SEM, DSC and TGA techniques. The regioselectivity of the acid-induced reaction is discussed and it is concluded that the biopolymers were formed via sterically favored pathway involving the attack of the primary amino (C-2) of CTS on the protonated epoxidized isoprene units of ENR50.

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