Compatibility and Thermal Properties of Maleic Anhydride-grafted-Polystyrene Containing Microcrystal cellulose (Avicel) as Raw Material for Soil Binder

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Abstract. Polymeric resins have been utilized widely as soil or dust binders in building and road construction industries. In this work maleic anhydride (MA) was grafted into polystyrene (PS) resins in a bench-scale xylene reflux reactor in the presence of benzoyl peroxide (BPO) to improve their adhesion properties, whereas the grafting efficiency was characterized using FTIR spectroscopy. Further processings were then carried out with addition of varied loading of microcrystal cellulose (Avicel), 1-5%, to improve their mechanical and thermal properties. It was found that addition of Avicel into the MA-g-PS resins up to 4% improved tensile strength and Young’s modulus. The presence of BPO may initiate chain scission of the MA-g-PS resins, which decreased the melting temperature as well as heat of combustion. Morphological analysis of surface of the resin specimens using electron microscopy (SEM) indicated rougher surface when BPO and Avicel were added in the resins. It was expected that binding of MA-g-PS/Avicel resins onto surface of sand and soil aggregates will be higher.

1. Introduction

Utilisations of polymeric resin in building and road constructions is not limited as structural and engineering materials, but also as resin emulsion (water and oil-based latexes) for polymer concretes, aggregate binders (soil stabilizers), and paint binders (water-borne binders), [1]. Especially as water-based resin emulsion (WRE), it has been utilized in strengthening foundation in road constructions in the USA, [2]. And generally, the WRE used as soil stabilisers are polycrylates and polyacrylamides with solid polymer contents up to 55%, [3]. When compared to oil-based resin emulsion (ORE), the WRE is not only more economical, but also more environment friendly and healthy since it reduces the use of (sometimes a toxic and carcinogenic) organic solvents, [4].

On the other hand, polystyrene as commodity (cheap and abundantly produced) polymer resins (fresh as well as recycled), recently has only been used as packagings and general purposes consumer’s goods, instead of more valued-added engineering materials [5]. Whereas when used in aggressive and higher temperature outdoor environments (under UV-radiation in sunlight), the resin easily undergoes degradations and deteriorations, which decreases its physical and mechanical properties [6],[7]. After modification, stabilization, and emulsification processes (using additives comonomers, antioxidants, and surfactants), the polymer resin can be produced as water-borne resin latex emulsion (WRE) for paint binders, and soil stabilisers [8], [9], [10]. In this work, the commodity polystyrene resins (fresh and recycled) have been processed to produce raw material for water-based resin emulsion, with higher mechanical and thermal properties for application as raw materials for soil
and dust stabilizers in building and road constructions. The technique involves processing of polystyrene resin in a bench scale modification xylene reflux reactor, with addition of maleic anhydride (MA) as modifier, microcrystal cellulose (Avicel) as reinforcement, and in the presence of benzoil peroxide (BPO) as initiator.

2. Experimental
The work start with selections of comonomers (maleic anhydride, styrene, and divinylbenzene) used as compatibilizers, and reactive processing radical generator (benzoyl peroxide, dicumyl peroxide) as initiators. The modification processes were carried out in a bench-scale reflux reactor intensive stirring for (1-6 hours), using (toluene, xylene) solvent under nitrogen atmosphere, [11]. Further processings were then carried out with addition of varied loading of microcrystal cellulose (Avicel), 1-5%, to improve their mechanical and thermal properties [12]. The reaction mixtures were then evaporated in vacuum evaporator, dried in vacuum oven at 80 °C to constant weight. The dried resins were then compression moulded at 170 °C and cut to produce film specimens (thickness: 0.1-0.2 mm) for mechanical testing according to ASTM D638. Efficiency of the modification reactions were investigated using infrared spectroscopy (FTIR) analysis of the specimens before and after exhaustive Soxhlet extraction in dichloromethane. Compatibility, morphology and thermal properties of the modified-polystyrene resins were studied using Scanning Electron Microscopy (SEM), and Differential Scanning Calorimeter (DSC) analysis.

3. Results and Discussion
3.1 Grafting efficiency of maleic anhydride (MA) in polystyrene (PS) matrix
Grafting efficiency of maleic anhydride (MA) after reactive modification in reflux of polystyrene (PS) solution in xylene was investigated using FTIR spectroscopy of film specimens before and after exhaustive Soxhlet extraction in dichloromethane for 4 hours. FTIR spectra of the film (PS-g-MA) before and after extraction were shown in Figure 1 (a and b).

It was shown that FTIR spectra of both specimens (before and after extraction) indicated the existence of absorption peaks at wave number 1604 cm\(^{-1}\) (stretching), and at 1373 cm\(^{-1}\) (bending) of carbonyl group of maleic anhydride (>C=O). And when intensities of the absorption peaks were compared to that of respective corresponding absorption peaks of hydrocarbon (C-H) group at 3464 cm\(^{-1}\), the ratio did not change significantly. This revealed that the maleic anhydride compatibilizer has been unextractable and efficiently grafted (physico-chemically) into polystyrene resin. In addition both FTIR spectra did not show any absorption peak in the wave number area of 1700-1800 cm\(^{-1}\), which is particularly representing the existence of carbonyl group of carboxylic acid [-(C=O)-OH]. And this is indicating that during the modification reactions the maleic anhydride directly bounded onto the polystyrene backbone without side reaction to produce maleic acid. However, there is no absorption peak data shown which indicating how the MA grafted chemically onto PS macromolecular backbone. And it is inevitable that BPO radical formed at the beginning of the reaction may initiate various possible side reactions, such as: homopolymerisation to produce poly/oligomaleic anhydride [-\((MA)\_n\]-, and this may further grafted and even crosslinked onto PS backbone.
Figure 1a. FTIR spectrum of PS-g-MA film specimen
3.2 Mechanical properties and compatibility of MA-grafted-polystyrene containing Avicel (PS-g-MA/BPO/Avicel) resins

Mechanical properties of maleic anhydride-grafted-polystyrene resins containing Avicel (PS-g-MA/Avicel) with various loading (1-5%), as shown in Table 1, were tested according to ASTM D638 using Universal Tensile Testing RTF, Load Cell 5000 N, rate 5 mm/minute.

Table 1. Mechanical properties testing of (PS-g-MA/BPO/Avicel) samples using Universal Tensile Testing RTF, Load Cell 5000 N, testing rate 5 mm/minute.

| No | Samples              | Avicel (%) | Tensile Strength (MPa) | Elongation (%) | Modulus (MPa) |
|----|----------------------|------------|------------------------|----------------|---------------|
| 1  | PS/MA/BPO            | 0          | 7.72                   | 2.59           | 170.70        |
| 2  | PS/MA/BPO/Avicel1    | 1          | 13.71                  | 10.76          | 189.77        |
| 3  | PS/MA/BPO/Avicel2    | 2          | 14.03                  | 9.16           | 190.43        |
| 4  | PS/MA/BPO/Avicel3    | 3          | 13.58                  | 7.77           | 210.77        |
| 5  | PS/MA/BPO/Avicel4    | 4          | 16.34                  | 6.15           | 211.64        |
| 6  | PS/MA/BPO/Avicel5    | 5          | 10.14                  | 5.59           | 194.05        |

It was shown from Table 1 and Figure 2a-2f, that in general addition of Avicel (1-5%) into the PS-g-MA resins increased their mechanical properties. Especially using addition of 4% Avicel the tensile
strength and modulus increased from 7.72 to 16.334 MPa, and from 170.70 to 211.64 MPa, respectively. This is indicating that the PS-g-MA resin has interacted well on the surface of the Avicel particles, although when the Avicel loading up to 5% the mechanical properties decreased slightly, which due to agglomeration of the Avicel particles.

Figure 2. Graphs of stress-strain in mechanical properties testing using Universal Tensile Testing RTF, Load Cell 5000 N, speed 5 mm/minute, according to ASTM D638 of film specimen of PS-g-MA without Avicel (a) and with varied loadings of Avicel: 1% (b), 2% (c), 3% (d), 4% (e), and 5% (f)
3.3 Thermal properties of PS-g-MA/BPO/Avicel using Differential Scanning Calorimeter (DSC)

Figures 3a to 3c and Table 2 showed thermographs and the data of endothermic and exothermic processes of PS/MA, PS-g-MA/BPO, and PS-g-MA/BPO/Avicel samples, measured using: DSC-60; C30935300214SA, temperature range 30°-500 °C, temperature rate 15°/minute, in Nitrogen gas atmosphere, flow rate 30 mL/minute, Cell Alumina, and sample weight 5 mg. They showed endothermic as well as exothermic peaks, which represented melting and decomposition processes of the heated resins. It was shown that addition of BPO and Avicel decrease endothermic peak temperature slightly (from 164.45° to 159.00 °C), followed by slight decrease on the heat capacity (-63.38 to -72.25 J/g), which is related to chain scission of the resins macromolecules. The exothermic process also showed decrease on temperature peaks when the BPO and Avicel were added (from 424.78° to 407.81 °C), and followed by substantial increase on heat capacity (from 280.38 J/g to 903.10 J/g). It seemed that, especially with addition of BPO efficiency of the decomposition process is higher.

![Thermograph of PS/MA sample](image)

**Figure 3a.** Thermograph of PS/MA sample, measured using: DSC-60; C30935300214SA, temperature range 30°-500 °C, temperature rate 15°/minute, in Nitrogen gas atmosphere, flow rate 30 mL/minute, Cell Alumina, and sample weight 5 mg.
Figure 3b. Thermograph of PS-g-MA/BPO sample, measured using: DSC-60; C30935300214SA, temperature range 30°C-500 °C, temperature rate 15 °/minute, in Nitrogen gas atmosphere, flow rate 30 mL/minute, Cell Alumina, and sample weight 5 mg.

Figure 3c. Thermograph of PS-g-MA/BPO/Avicel (4%) sample, measured using: DSC-60; C30935300214SA, temperature range 30°C-500 °C, temperature rate 15 °/minute, in Nitrogen gas atmosphere, flow rate 30 mL/minute, Cell Alumina, and sample weight 5 mg.
Table 2. Thermograph data of (a) PS/MA, (b) PS-g-MA/BPO, and (c) PS-g-MA/BPO/Avicel (4%) samples, measured using: DSC-60; C30935300214SA, temperature range 30°-500 °C, temperature rate 15°/minute, in Nitrogen gas atmosphere, flow rate 30 mL/minute, Cell Alumina, and sample weight 5 mg.

| No | Samples | Endothermic Process (Melting) | Exothermic Process (Decomposition) |
|----|---------|-------------------------------|-----------------------------------|
|    |         | Peak | Start | End | Calory | Peak | Start | End | Calory |
| 1  | PS/MA   | 164.45 | 154.10 | 169.63 | -63.38 | 424.78 | 415.96 | 462.38 | 280.38 |
| 2  | PS-g-MA/BPO | 159.00 | 145.94 | 164.07 | -72.25 | 407.81 | 360.06 | 467.41 | 903.10 |
| 3  | PS-g-MA/BPO/Avicel(4%) | 159.30 | 148.73 | 164.17 | -70.06 | 408.09 | 372.75 | 460.64 | 420.17 |

3.4 Morphology characteristic of PS-g-MA/BPO/Avicel samples
Microscopic surface images of film specimens were shown in Figure 4(a-c), i.e. that of: (a) (PS/MA) without BPO, and with addition of BPO, (b) (PS-g-MA/BPO), and with Avicel 4% (c) (PS-g-MA/BPO/Avicel). It was clear that without BPO the blending process of PS/MA did not resulted in homogenous and physic-chemical interaction blends, which showed porous surface with diameter 10-30 µm (Figure 4a). When BPO was added in the reactive blending process the PS-g-MA/BPO experienced physic-chemical interaction, in which the MA comonomer grafted onto the PS backbone initiated by BPO and formed more homogenous blend (pore diameter < 10 µm, Figure 4b). The grafted MA has also shown to function as compatibilizer to finely distribute the Avicel particle as shown in Figure 4c.
4. Conclusion

It was found that addition of Avicel into the MA-g-PS resins up to 4% improved tensile strength and Young’s modulus. The presence of BPO may initiate chain scission of the MA-g-PS resins, which decreased the melting temperature as well as heat of combustion. Morphological analysis of surface of the resin specimens using electron microscopy (SEM) indicated rougher surface when BPO and Avicel were added in the resins. It was expected that binding of MA-g-PS/Avicel resins onto surface of sand and soil aggregates will be higher.

**Figures 4.** Micrographs using electron microscope (SEM) JEOL *series* JSM-6510LA (magnification 500 times) on film specimen surface of: (a) PS/MA without BPO, (b) PS-g-MA/BPO, and (c) PS-g-MA/BPO/Avicel (4%).
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