

# Synthesis and Characterization of Styrene-Ethylene-Propylene-Styrene (SEPS) Grafted with Maleic Anhydride (MAH) for Use as Coupling Agent in Wood Polymer Composite

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## Abstract

Styrene-Ethylene-Propylene-Styrene (SEPS) block copolymer was grafted with maleic anhydride (MAH) by reactive extrusion (SEPS-g-MAH) using an organic peroxide as initiator in the grafting. SEPS-g-MAH was synthesized for use as coupling agent in wood polymer composite (WPC). Identification of this compatibilizer was made using Fourier transform infrared spectroscopy (FTIR) and the grafting degree was determined with titration. The characteristic peaks in FTIR analysis indicated the presence of MAH in the copolymer.

**Keyword-** Reactive extrusion, grafting, coupling agent, WPC, grafting degree.

## I. INTRODUCTION

Polymers contribute significantly in unsuitable disposal of solid waste which in turn contributes to increase pollution. Regardless of the excellent properties of polymers, these materials are used and thrown away without being recycled or reused [1]. This situation has prompted the search of solutions that involve post-consumer polymeric materials.

Composite of polymeric matrix and wood flour have been recently proposed as an alternative due to their low cost, low density, low manufacturing energy and as environmentally friendly products [2, 3]. Indeed, the wood polymer composite (WPC) industry is interested in using these recycled polymers since these materials are less expensive and have great performance [4, 5].

Although, WPC have better characteristics than their constituent elements individually, the main disadvantage of WPC is the incompatibility between the polar character of wood flour and non-polar polymeric matrix. This poor adhesion leads to weak thermal and mechanical properties of the composites; therefore, methods of compatibilization of immiscible polymer blends must be applied to improve the adhesion between phases, such as wood treatment, a matrix treatment and/or a coupling agent [3, 6, 7].

Coupling agent is used to increase the interfacial adhesion between immiscible polymer blend. The addition of coupling agents, that is formed as block or graft copolymer during melt mixing, generates a chemical bridge between cellulosic reinforcement and polymeric matrix [8], the graft polymers with hydrophilic functional group like maleic anhydride (MAH) are recommended, due to their very reactive OH groups of wood flour [3, 6]; although excessive functionalization and too many branches of functional groups in the main chain will limit the free engagement surface [9]. Thermoplastics elastomers (TPE), as SEPS based copolymers, have received much interest since they can be used as coupling agents due to their unique properties of the block copolymer structure [10]. These grafted copolymers are also reusable and easily to be processed.

Figure 1 shows the structures of SEPS-g-MAH and the interactions between the coupling agent and the hydroxyl groups on the surface of the wood flour. Since MAH graft have preference for aliphatic carbons of block polymers [11], the double bond of MAH can react with the tertiary carbon on the principal chain of the polymer, eliminating a hydrogen atom [11]. The anhydride groups react with the surface hydroxyl groups of wood, forming ester bonds, while the blocks of copolymer show affinity with polymer matrix due to similar polarities [12].

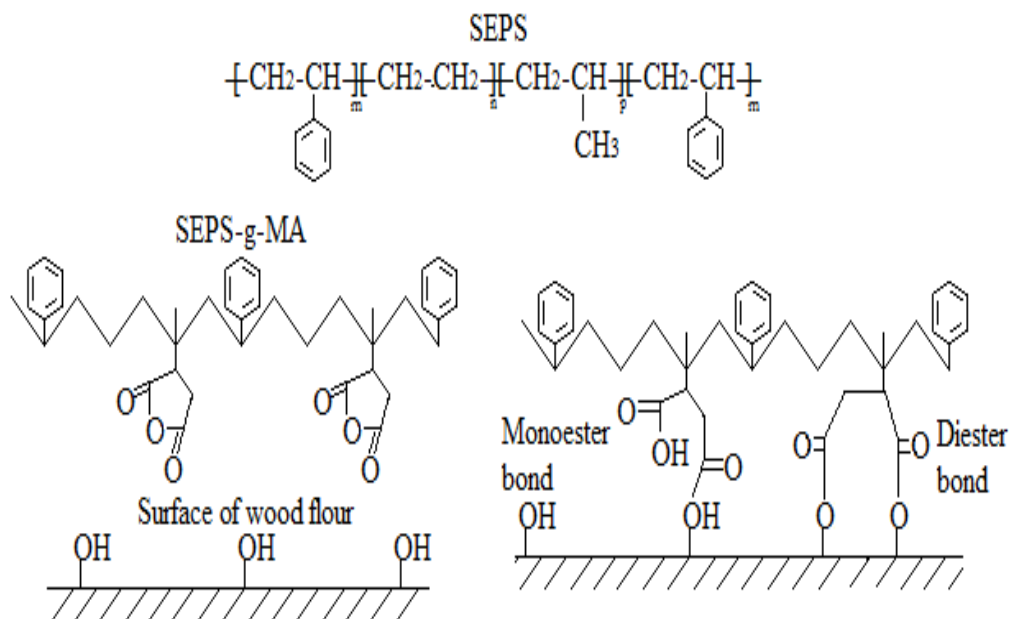


Fig. 1. SEP-g-MAH structure and his monoester and diester bond with OH groups of wood flour.

This paper presents the synthesis with reactive extrusion of thermoplastic Elastomer on styrene basis (SEPS) grafted with MAH (SEPS-g-MAH) to be used like coupling agent in a WPC. The grafted copolymer was analyzed using FTIR and the grafting degree was determined by titration.

## II. MATERIALS AND METHODS

### A. Materials

MAH was used to grafted the SEPS copolymer of Kraton Performance Polymers Inc. and the organic peroxide (2,5 Dimethyl 2,5 Di(tert-butylperoxy) hexane) 101PP20 LUPEROX® of Arkema Inc. was used as initiator. The xylene was used as solvent in the determination of grafting degree; a solution 0.05N of potassium hydroxide in methanol, 0.03 N solution of trichloroacetic acid in xylene and cresol red indicator were used in the titration.

### B. Synthesis of coupling agent SEPS-g-MAH by reactive extrusion

The SEPS-g-MAH coupling agent was prepared by functionalizing radicals, SEPS copolymer with MAH was extruded in a laboratory mixing extruder, LME Atlas Electric Device. A mixture of SEPS was prepared with 6% MAH and 0.5% LUPEROX® 101PP20 and the temperature of extruder was in the range of 180 to 220 ° C and 40 rpm.

### C. FTIR Measurements

FTIR spectra were obtained using a Perkin-Elmer Spectrum One FTIR Spectrometer in the 400-1000  $\text{cm}^{-1}$  wave number range, to identify that the reaction occurred in SEPS copolymer with MAH, by reactive extrusion.

### D. Determination of the grafting degree of MAH in SEPS.

The grafting degree onto SEPS was determined by a titration method. The procedure adopted was as follows: 0.5 g of SEPS-g-MAH was dissolved in 50 ml xylene at boiling temperature; using a stirring hotplate, previously a few drops of distilled water were added to hydrolyze the maleic anhydride groups. 10 mL of a solution of 0.05 N potassium hydroxide in methanol, was added to above solution. The formed solution was titrated with 0.03 N trichloroacetic acid using cresol red in xylene as indicator. A blank solution with only SEPS was then treated in the same way as described above. The degree of grafting was calculated using the following equation:

$$G(\% \text{ wt}) = \frac{(V_0 - V_i) \times N}{2 \times W \times 1000} \times 98 \times 100\% \quad (1)$$

Where, G (% wt) is the grafting degree of MAH onto SEPS,  $V_0$  and  $V_i$  are the acid volume, in mL, consumed in the titration of blank solution and sample of SEPS-g-MAH, respectively;  $N$  is the acid concentration in mol/L, the value of 98 is related with molecular weight of MAH and  $W$  is the weight of the sample of SEPS-g-MAH in g [13, 14].

### III. RESULTS AND DISCUSSIONS

#### A. Characterization of SEPS-g-MAH by FTIR

The FTIR spectra for SEPS and SEPS-g-MAH are shown in Fig. 2. There are similarities between both spectra, corresponding to the functional groups. Several bands around 3000 and 2850  $\text{cm}^{-1}$  are due mainly to the asymmetric and symmetric stretching of alkyl  $\text{CH}_2$  and  $\text{CH}_3$  groups. The symmetric and asymmetric bending of these same groups are observed at 1470-1370  $\text{cm}^{-1}$  in the FTIR spectrum.

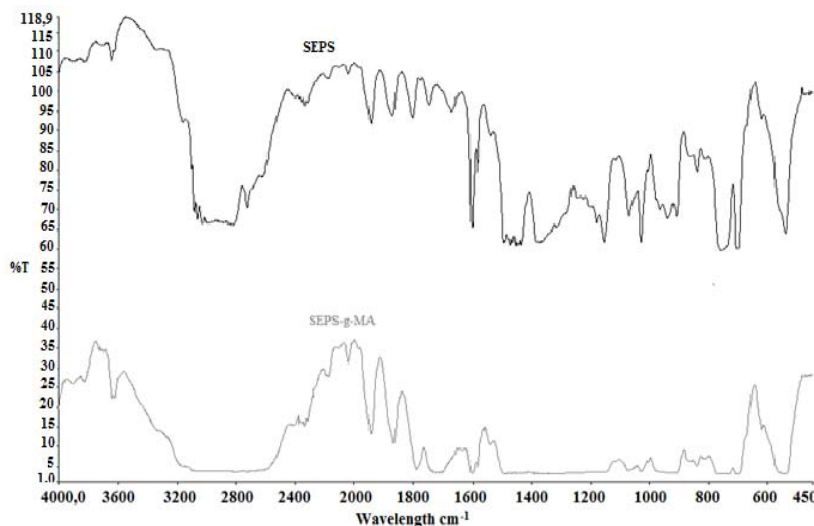


Fig. 2. Infrared spectra for SEPS and SEPS-g-MAH

The C-H stretch bands of hetero aromatic structure are presented in the region 3100 and 3000  $\text{cm}^{-1}$ . Combination of bands and overtone of C-H out of plane occur around 2000 and 1700  $\text{cm}^{-1}$ . Two particular peaks out-of-plane bending of C-H bonds are observed at 770 and 690  $\text{cm}^{-1}$ , that could be due to monosubstituted aromatic compound of the SEPS copolymer, see Fig. 2 and 3. Stretching bands of C=C bonds present in the benzene ring are observed at 3100-3000  $\text{cm}^{-1}$ .

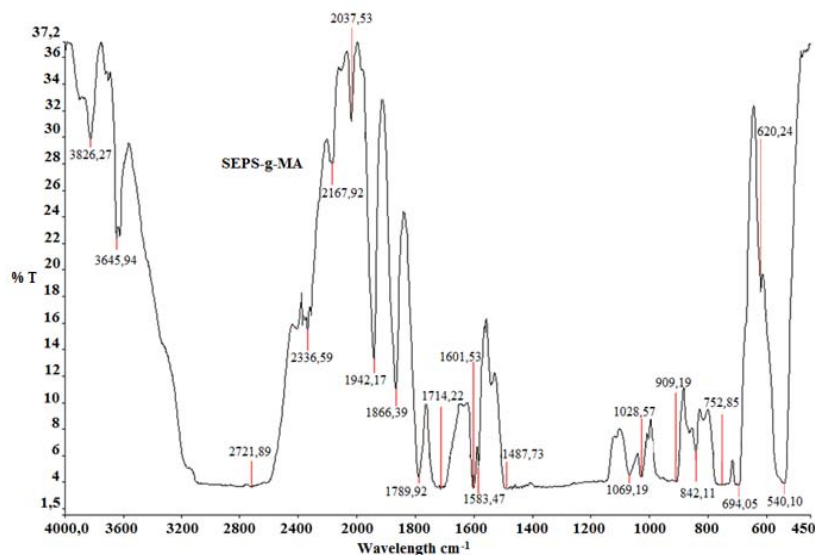


Fig. 3. Infrared spectra for SEPS-g-MAH

Although there are common groups in both spectra; in the infrared spectra corresponding to the SEPS-g-MAH, stretching absorption bands of carbonyl groups ( $\text{-C=O}$ ) were observed at 1866  $\text{cm}^{-1}$  (low intensity) and 1789  $\text{cm}^{-1}$  (medium intensity), which can be assigned to the cyclic anhydride [15, 16]. The peak at 1714  $\text{cm}^{-1}$  was related to  $\text{C=O}$  stretching group of hydrolyzed MAH in SEPS-g-MAH [15-17].

#### B. Determination of the grafting degree of MAH on SEPS.

A 2.75 mL and 1.6 mL volume of solution 0.03 N trichloroacetic acid in xylene was required in the titration of SEPS-g-MAH sample and blank solution with only SEPS, respectively. The grafting degree was calculated using the Equation (1), considering that the sample weight of grafted copolymer was 0.5 g.

$$G(\text{wt}\%) = \frac{(2.75\text{mL}-1.6\text{mL}) \times 0.03 \text{ mol/L}}{2 \times 0.5 \text{ g} \times 1000} \times 98 \times 100\% = 0.3381\%$$

The proportions of maleic anhydride and initiator were based on results of previous research. These studies reported amounts of peroxide between 0.3 and 1.5 w% with content of MAH between 2 and 6.1 w% to the grafting of anhydride maleic onto polypropylene (PP) [18, 19]. No references were found about graft copolymer (SEPS-g-MAH). The MAH grafted on SEPS is accompanied with undesirable side reactions  $\beta$ -scission, generating low molecular weight chains and short chains with a terminal radical, this occurs in excess of initiator or absence of MAH to react with the macroradical of SEPS [20, 21]. The results of grafting degree are related directly with reaction times and the amounts of peroxide and anhydride used in the process, as was corroborated with other results in which the grafting of MAH on PP was between 0.12 % and 1.33 % [13, 22].

#### IV. CONCLUSION

The grafting of maleic anhydride onto SEPS was confirmed by the presence of characteristic peaks in 1866 and 1789  $\text{cm}^{-1}$  in FTIR analysis. Similar results of grafting degree were found by other authors [20-22], than corroborated the reactive extrusion as process for the free radical grafting of MAH onto SEPS copolymer.

The grafting of MAH onto aliphatic carbons backbone of SEPS copolymer was confirmed using infrared spectroscopy due to the absence of other linkages that indicated other bond sites onto chemical structure of block copolymer.

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