Walailak J Sci & Tech 2007; 4(2): 237-248.

New Raw Materials with Defined Amounts of Bark Slivers from Field Coagula

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ABSTRACT

This research illustrates the opportunity of using field coagula directly as raw materials for rubber manufacturing without transforming to block or crepe rubber. Field coagula with different amounts of wood, mostly bark slivers, varying from 0 to 50 wt %, reveal a linear relationship between the viscosity and wood contents. The measurement of the viscosity is performed using an oscillating disk rheometer and a Mooney Viscometer. This linear relationship is independent of changes in the molecular weight of these samples and therefore confirms that the increasing of the viscosity observed here is due only to changes in wood content. The result of further investigation on more than twenty samples of field coagula also supported this linear relationship. This implies that the linear relationship found here may be general to all field coagula treated by the procedures stated herein and that it may be used as a tool in the production of rubber goods from field coagula. Additionally, this relationship is successfully used to prepare rubber/wood composites with the precise amounts of slivers from field coagula.

Keywords: Natural rubber, field coagula, viscosity, wood content

INTRODUCTION

Field coagula are natural rubber formed at the rubber plantation by the process of latex coagulation from either acid or natural manner and the slivers of bark collected during tapping are also included. Since field coagula consist of unknown ratios of rubber and wood, the rubber industry has never used them directly as raw materials. Before use, coagula typically have to be transformed to block and crepe rubber by applying multiple millings and water-washings in order to remove as much of this non-rubber content as possible [1-3]. Sometimes, industry refuses to use field coagula for the production of block and crepe rubber, especially ones with high amounts of wood because of the difficulty in removing this component. Therefore, the manufacturing of block and crepe rubber from field coagula takes time and adds cost while these rubber products are used as raw materials for the production of the low-end goods; e.g., rubber caps and floor mats [1-3]. Consequently, field coagula have become unwanted and very cheap raw rubber materials. The attempt to use them directly for some low-end rubber products without removing the wood content is a significant challenge because this may lower the cost of the low-end products and add more value to this raw natural rubber. However, this raises concern about the fluctuation of wood contents in this material as well.

In this work, a two-roll mill was used for the systematic mastication of field coagula and for the systematic variation of rubber/wood ratios [4]. Oscillating disc rheometers and Mooney Viscometers are also used to measure the flow properties of samples, e.g., viscosity, by monitoring the torque required to oscillate and rotate a rotor placed within the sample, respectively [5,6]. Thus, the higher the viscosity the samples have, the greater the required torque.

After systematic procedures were performed on samples of field coagula, a linear relationship between the viscosity and the wood contents in five samples with different amounts of wood were found. The results also showed the same linear tendency when the viscosity and wood contents of more than twenty separated samples were plotted together. Then, this relationship might be used as a tool to approximate the levels of wood contamination in the rubbery portion of field coagula. Additionally, samples with particular levels of bark slivers could systematically be prepared from field coagula using this linear relationship. Therefore, the results reported here illustrate that the fluctuation of wood contents is not an obstacle to success in using field coagula directly as a raw material for low-end rubber products.

MATERIALS AND METHODS

General Methods. Fresh field coagula (1 - 3 days old), consisted of unknown ratios of coagulated filed latex and bark slivers collected during tapping, were gathered from rubber plantations with RRIM 600 rubber trees aged 10 - 25 years old. Air dry sheet rubber (ADS) was purchased from the Rubber Estate Organization, Naborn, Nakhon Si Thammarat. Linear fitting was carried out by using Microcal Origin 6.0. The

pictures of extracted bark slivers were taken using a digital camera with ~ 24× zoom, ~ 6.0 million effective pixels and 1/2.5 inch CCD.

Preparation of Coagula. Chunks of field coagula were chopped into small pieces with dimensions of ~ 1.5 × 1.5 × 1.5 cm^3. They were then soaked by immersion into 20 liters of water to provide a uniform level of water content for all field coagula. The increase in weight of soaked coagula was followed and after 52 h of immersion, no more weight change was observed. Thus, the soaking time of 52 h was used to saturate all chopped coagula before use. They were then moved to a 50 ºC hot air oven and heated until completely dry. The weight of the samples decreased and reached a stable state after 48 h. Thus, all soaked field coagula was dried for 48 h in order to provide the same heat history for all samples.

Milling of Coagula. Dry pieces of coagula were, then, milled in an 8" × 16" two roll mill with a speed of 30 rpm and a fiction ratio between front and rear rolls of 1:1.2. The batch size and milling time used for all experiments was 800 g and 12 min, respectively. During milling, parts of wood contents, mostly bark slivers, separated from a rubbery part and were collected for further use. Meanwhile, other solid materials beside the wood bark (i.e., clay, big chunks of leaves or twigs) were also screened out. However, they were rarely found. The masticated samples in the form of sheets with a thickness of ~ 0.5 mm were kept in the dark at room temperature overnight before use.

Measurement of Viscosity. An oscillating disk rheometer (ODR) and a Mooney Viscometer were used to monitor the viscosity of milled samples. A Gortech oscillating disc rheometer was used at a frequency of 100 Hz, an isothermal temperature of 100 ºC, and an arc of ± 1 º. The appearance dynamic viscosity of samples (S") was recorded for 4 min and the average value was reported [5,7-9]. A Visctech Mooney Viscometer was used with a large rotor at 2 rpm and 100 ºC. The sample's viscosity (ML 1+4@100 ºC) was determined according to ASTM D1646-00 [6]. The values shown in this report are the average from at least 3 samples.

Molecular Weight Determination. Molecular weights of milled samples were determined by using gel permeation chromatography (GPC) with a Breeze Waters GPC system. A standard polystyrene mixed column served as a stationary phase. Tetrahydrofuran was used as a solvent and the mobile phase with an injection rate of 1 ml/min. The value of weight average molecular weight (M_w) reported here is an average from at least 2 samples [10].

Dissolving and Filtering of Milled Samples. To find out the exact amount of bark slivers in masticated samples, pieces measuring 2 × 2 × 0.5 cm^3 were dissolved in 100 ml of toluene and stirred gently. Within 3 days, the rubbery part completely dissolved and the bark slivers separated. To ensure that no rubber remains in the previously separate slivers, this portion was immerged into 100 ml of toluene and stirred gently for a further 24 h. The slivers were then filtered under pressure in order to separate undissolved components.

RESULTS AND DISCUSSION

The Relationship between Viscosity and Wood Contents in Field Coagula

After oven drying, these coagula were milled and then remixed with the slivers, previously collected from two-roll mills, in order to form a composite material with different rubber/wood ratios. This milling and remixing must be finished within 12 min in order to minimize the difference in conditioning of the samples [11,12]. The exact amounts of wood in these samples were determined by dissolving pieces ~ 2 × 2 × 0.5 cm^3 in size in 100 ml toluene and followed by filtration. Drying of the filtered portion showed that it is composed of particles and fibers of wood of various shapes and sizes (**Figure 1**). Bark slivers in all samples were expected to be about in these forms since they had passed through the same treatments. Using of the aforementioned procedures five batches of milled coagula consisted of ~ 10, 20, 30, 40, and 50 wt % of wood. In fact, samples with >50 wt % of slivers were found at the rubber plantation; however, during milling and remixing, the entire amount of slivers rarely incorporated into the milled materials within 12 min. Thus, they are not included into this study.

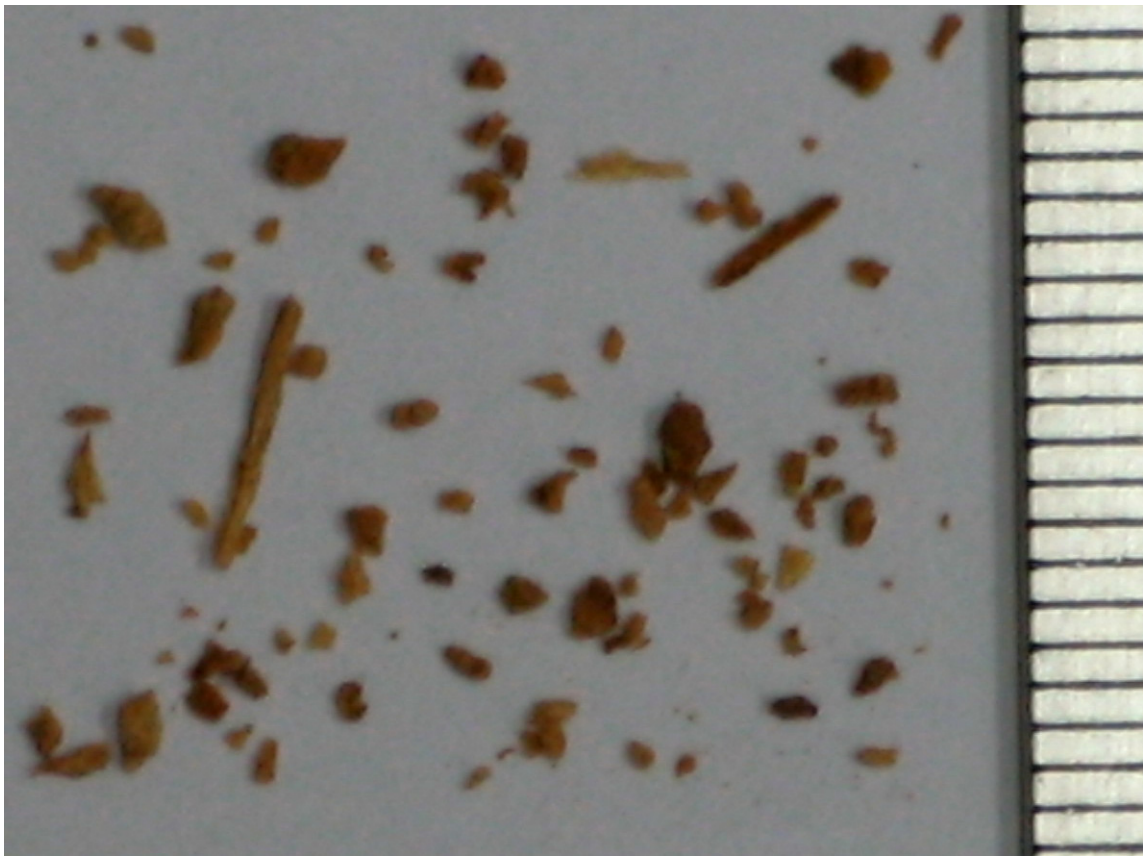

Figure 1 Bark slivers extracted from 12-min milled samples. The distance between each thick mark on the right is one millimeter.

The different levels of bark slivers in these five samples may be expected to play different roles in their viscosity [13-15]. To test this hypothesis, an ODR and a Mooney Viscometer were used to investigate the viscosity of these milled samples. The viscosity was plotted against the wood content (**Figure 2**) and it was found that the viscosity increased as the amounts of wood increased from 0 - 50 wt % and this tendency was linear with the values of R-squared of 0.97 and 0.93 from the ODR and Mooney Viscometer respectively. However, the relationship between viscosity and wood contents for samples with wood contents of 0 - 20 wt % is a little bit out off this tendency. This may be due to the poor dispersity of wood when it is present in small amounts. In this plot, 12 min masticated ADS was used as the sample to represent 0 wt % of wood. As reported elsewhere, the difference in the molecular weight might affect the viscosity of samples [15]. To rule out this possibility, the values of M_w for these five samples were examined using gel permeation chromatography (GPC). From **Table 1**, the molecular weight decreases as the wood content increases. This may be due to the greater shear force enhanced by slivers to rubber molecules during milling in two-roll mills. The decrease in molecular weight as the percentage of wood content increases rules out the possibility that the increase in viscosity in **Figure 2** is due to the changes in the molecular weight of the samples. This supports the hypothesis that the increasing of viscosity found herein is due to the increasing of wood content, a low deformable portion, in the samples.

Table 1 Average molecular weight (M_w) by GPC of samples containing different amounts of wood.

Wood content (wt %)	M_w (g/mol)
0	630,000
10	610,000
20	620,000
30	570,000
40	570,000
50	550,000

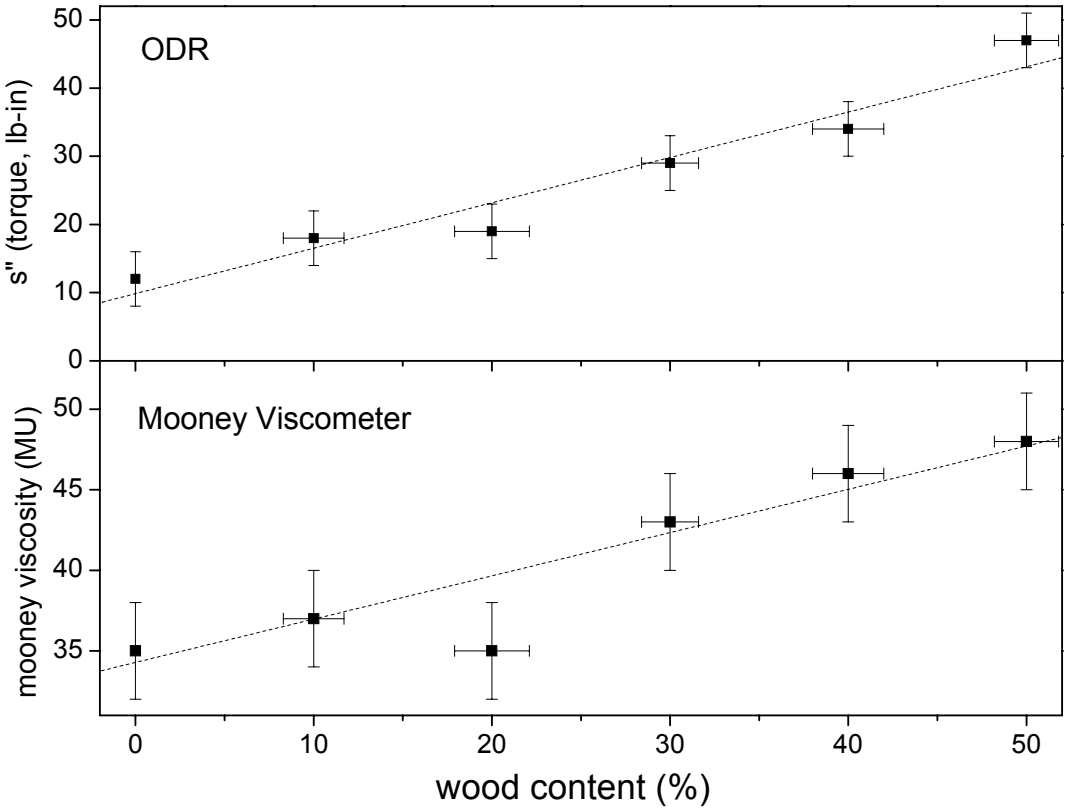

Figure 2 The relationship between the viscosity, obtained from ODR and Mooney Viscometer measurements, and exact amounts of wood. Each data point is the average of at least three samples and the error bars indicate twice the standard deviation.

To ensure that the relationship between the viscosity and wood contents reported in **Figure 2** is linear and general to the field coagula containing wide ranges of rubber/wood ratios, the viscosity and the exact amounts of wood content of 21 milled samples prepared from separate field coagula were examined. Milling time for every sample was 12 min and wood contents were examined by the dissolution and filtering methods mentioned previously. As expected, the results (**Figure 3**) show a linear relationship between viscosity and wood contents with the values of R-squared of 0.95 and 0.91 from the ODR and Mooney Viscometer respectively. The linear relationship from **Figure 2** is also shown in this plot for comparison (dashed lines) and it is found that ones from both experiments fit well. However, it did not show very good fitting when the samples contained less than 20 wt % of wood as previously found in **Figure 2**. The results found here support the linear relationship between viscosity and the levels of bark slivers. Thus, it should be possible to use this relationship for the approximation of wood contents in milled coagula from a simple viscosity measurement. Moreover, using these two instruments takes only minutes while the dissolving and filtering methods take days to perform. However, this method might not be effective for the samples containing low amounts of wood, such as below 20 wt %.

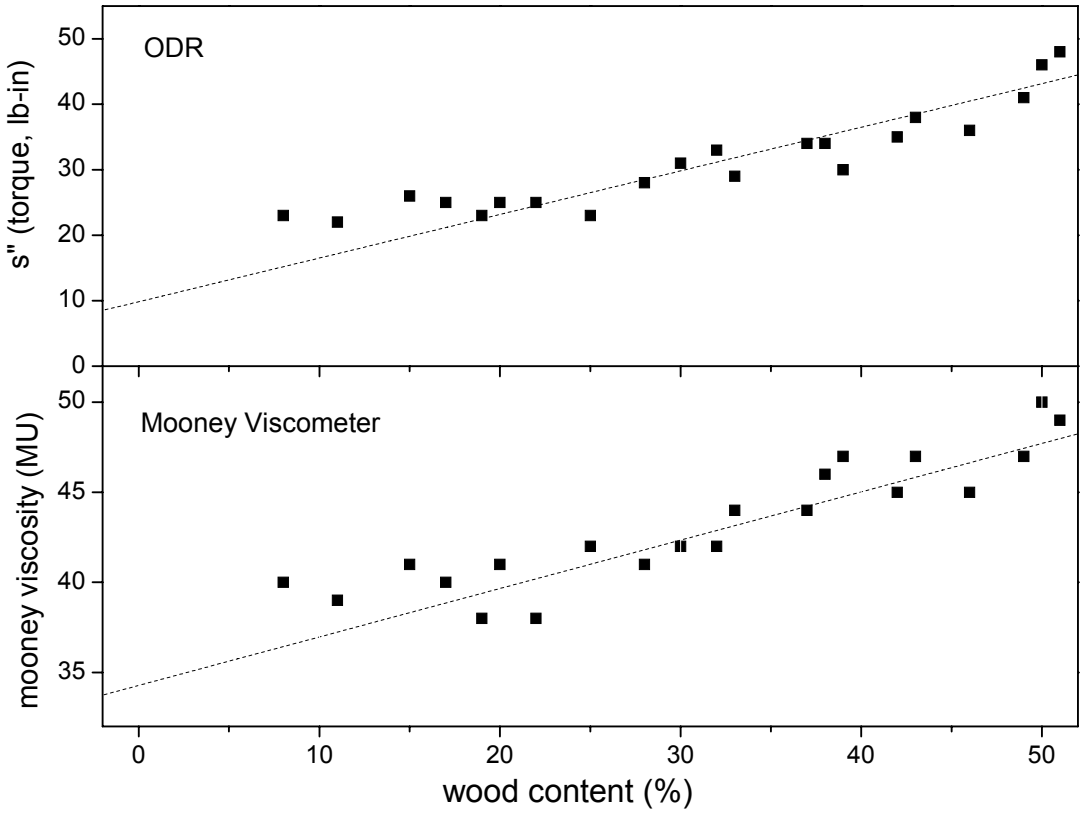

Figure 3 The relationship between the viscosity, obtained from ODR and Mooney Viscometer measurements, and exact amounts of wood of 21 samples.

The Preparation of Raw Material with Defined Amounts of Slivers from Field Coagula

In rubber manufacturing, the consistence of compounding is an important factor in establishing production uniformity. Thus, uniform raw material from field coagula is needed while they are being composted of various rubber/wood ratios. To test that this condition can be achieved, milled samples with a wood content of ~ 30 wt % were prepared. In this experiment, twenty separate samples of dry coagula were masticated using the procedures mentioned previously, and the viscosity of all samples was measured by using an ODR and a Mooney Viscometer. The values of viscosity were then used to determine the percentage of wood from the linear relationship mentioned before. If the measurement indicated that the wood content in any milled sample was below 30 wt %, additional amounts of slivers, collected during masticating, were then added into the milled sample. Similarly, if the measurement indicated that the wood content in any sample was above 30 wt %, extra ADS was added. After performing these procedures to twenty samples, all of them would expectedly that consist of 30 wt % of slivers. They were then dissolved in toluene and filtered and the amounts of wood determined precisely. The wood contents of these treated samples were, then,

plotted together in **Figure 4** revealing a narrow distribution of wt % of wood with an average of 32±3 wt % using the linear relationship from the ODR and 31±2 wt % when using that from the Mooney Viscometer.

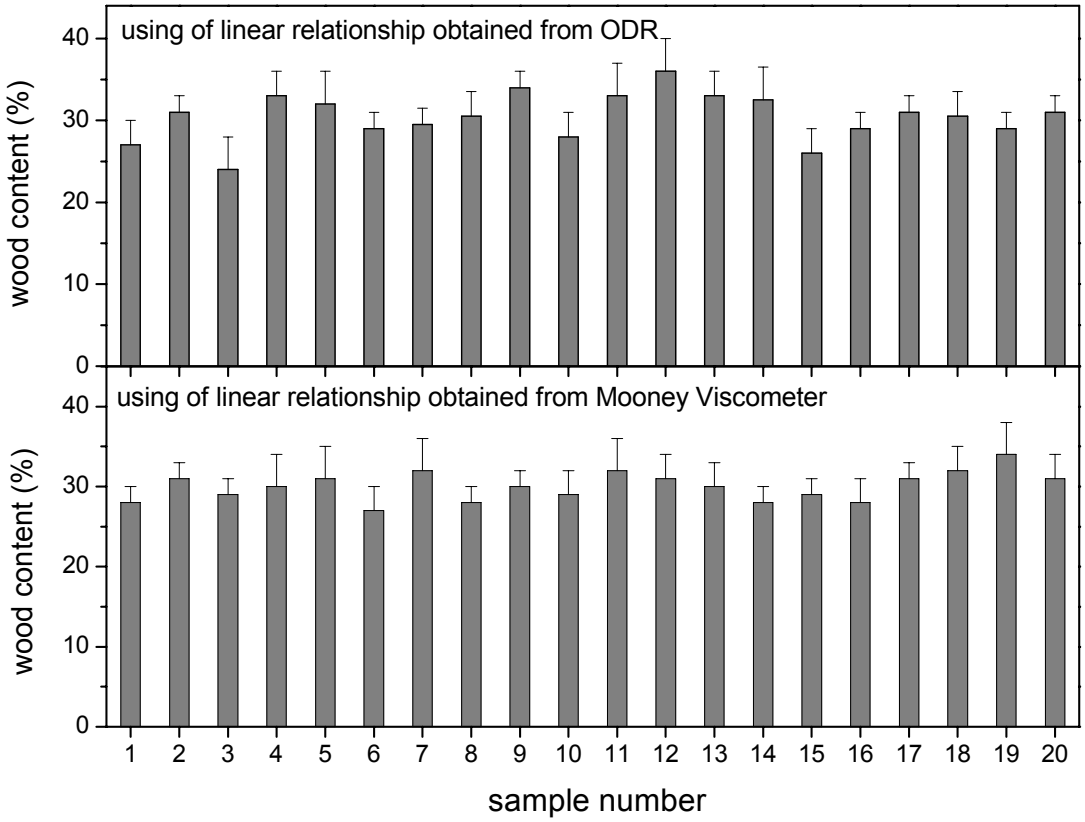

Figure 4 The exact amounts of wood in samples prepared by using the linear relationship created from both ODR and Mooney Viscometer. All samples aim to about 30 wt % of wood. The error bars on each column indicate the standard deviation for that sample.

To confirm the results found in **Figure 4**, another experiment was performed in which milled samples with a wood content of ~ 50 wt % from twenty other batches of field coagula. After following the same procedures, the results (**Figure 5**) also revealed a narrow distribution of wood portions with an average of 49±3 wt % from the ODR and 51±3 wt % from the Mooney Viscometer. Therefore, the results displayed in **Figures 4** and **5** strongly support the hypothesis that the relationship between viscosity and wood contents can be used as "a tool" for the preparation of uniform materials with particular amounts of wood from field coagula. Thus, this research provides an opportunity for field coagula to be an alternative raw material for the manufacturing of some (low quality) rubber products.

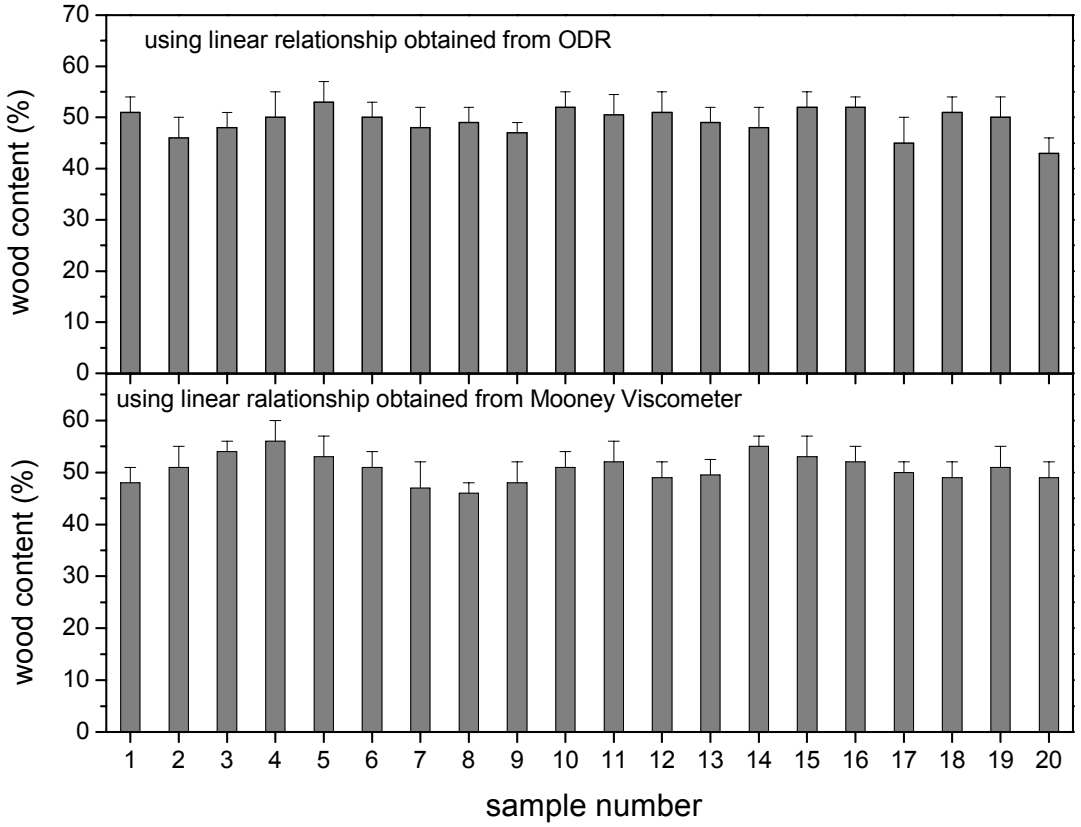

Figure 5 The exact amounts of wood in samples prepared by using the linear relationship created from both ODR and Mooney Viscometer. All samples aim to about 50 wt % of wood. The error bars on each column indicate the standard deviation for that sample.

CONCLUSIONS

The raw rubber/wood composite material with defined amounts of bark slivers from field coagula has been successfully prepared. A linear relationship between the viscosity, measured by an ODR and a Mooney Viscometer, and wood contents of samples is first observed. This linear relationship was expected to approximate the amounts of wood in field coagula. Further studies indicate that this linear relationship fits well to that of the viscosity and wood contents of a further 21 separate samples. This linear relationship was also used to prepare two sets of samples with ~ 30 and 50 wt % of wood respectively from field coagula. It was found that they display narrow distributions of wood contents of 32±3 and 49±3 wt % when using the linear relationship obtained from an ODR and of 31±2 and 51±3 wt % when using one obtained from a Mooney Viscometer.

ACKNOWLEDGEMENTS

I gratefully acknowledge the National Research Council of Thailand for the support of this study through the Institute of Research and Development, Walailak University. I also thank Dr. Sarinya Chawaphun from The King Mongkut's Institute of Technology, North Bangkok, for providing me with Mooney testing.

REFERENCES

[1] AD Roberts. *Natural Rubber Science and Technology*, Oxford University Press, Oxford, 1988, p. 59-117.
[2] AFS Budiman. The future development of natural rubber production and quality in Indonesia. Information Center of Natural Rubber, Available at: http://www.rubber-stichting.info/art2nr5.html, accessed April 2007.
[3] RCMA, Available at: http://www.rcma-rubber.com/tech/process.asp?image=tech, accessed April 2007.
[4] JL White. *Rubber Processing: Technology, Materials, Principles*, Hanser/Gardner Publications, Ohio, 1995, p. 222-40.
[5] RP Brown. *Physical Testing of Rubber*, Applied Science Publishers, England, 1979, p. 79-95.
[6] ASTM Designation: ASTM D1646-00, Standard Test Methods for Rubber Properties- Viscosity, Stress Relaxation, and Pre-Vulcanization Characteristics. American Society for Testing and Materials, PA, 2000, p. 318-29.
[7] MD Eisner, SAK Jeelani, L Bernhard and EJ Windhab. Stability of foams containing proteins, fat particles and nonionic surfactants. *Chem. Eng. Sci.* 2007; **62**, 1974-87.
[8] JL White and VM Lobe. Comparison of the predictions of viscoelastic and plastic-viscoelastic fluid model to the rheological behaviour of polystyrene and polystyrene-carbon black compounds. *Rheologica Acta* 1982; **21**, 167-75.
[9] DJ Dick, Available at: https://www.ptonline.com/sample/1-56990-278-X.pdf, accessed July 2007.
[10] ASTM Designation: ASTM D5296-97, Standard Test Method for Molecular Weight Averages and Molecular Weight Distribution of Polystyrene by High Performance Size-Exclusion Chromatography. American Society for Testing and Materials, PA, 2000, p. 467-80.
[11] W Brostow and RD Corneliussen. Kinetics of milling of polymers. *Mater. Chem. Phys.* 1986; **14**, 1-8.
[12] D De, A Das, D De, B Dey, SC Debnath and BC Roy. Reclaiming of ground rubber tire (GRT) by a novel reclaiming agent. *Eur. Polym. J.* 2006; **42**, 917-27.
[13] TQ Li and MP Wolcott. Rheology of HDPE–wood composites. I. Steady state shear and extensional flow. *Composites: Part A* 2004; **35**, 303-11.

[14] JV Gruber and PN Konish. Aqueous viscosity enhancement through helical inclusion complex cross-linking of a hydrophobically-modified, water-soluble, cationic cellulose ether by amylase. *Macromolecules* 1997; **30**, 5361-66.
[15] Y Tong, T Liu, S Veeramani and T-S Chung. Bulk viscosity and its unstable behavior upon storage in polyimide precursor solutions. *Ind. Eng. Chem. Res.* 2002; **41**, 4266-72.

บทคัดย่อ

สุฤกษ์ คงทอง

วัตถุดิบชนิดใหม่ที่สามารถเตรียมให้มีปริมาณของสะเก็ดไม้ที่แน่นอนได้ จากเศษยางจากสวน

งานวิจัยนี้ได้แสดงให้เห็นถึงโอกาสที่จะนำเศษยางจากสวนเข้าสู่กระบวนการผลิตผลิตภัณฑ์จากยางพาราได้โดยตรง โดยไม่จำเป็นต้องนำเศษยางไปผ่านกระบวนการแปรรูปเป็นยางแท่งและยางเครพก่อน โดยพบว่าเศษยางจากสวนซึ่งมีส่วนของสะเก็ดไม้จากเปลือกของต้นยางปะปนอยู่ในปริมาณ 0 - 50 % โดยน้ำหนักนั้น ให้ความสัมพันธ์เชิงเส้นตรงระหว่างค่าความหนืดที่วัดได้จากเศษยางตัวอย่างกับปริมาณของสะเก็ดไม้ที่ปะปนอยู่ในตัวอย่างดังกล่าว ซึ่งการวัดค่าความหนืดที่ใช้ในงานวิจัยนี้ใช้เครื่องทดสอบสองชนิดคือ oscillating disk rheometer และ Mooney Viscometer โดยความสัมพันธ์เชิงเส้นตรงที่พบดังกล่าว ไม่ขึ้นอยู่กับแนวโน้มการเปลี่ยนแปลงของน้ำหนักโมเลกุลของเศษยางตัวอย่าง ดังนั้นผลการทดลองนี้จึงยืนยันได้ว่าการเพิ่มขึ้นของความหนืดที่พบในความสัมพันธ์ข้างต้น เนื่องมาจากตัวแปรคือปริมาณของสะเก็ดไม้ที่เพิ่มขึ้นเท่านั้น ผลการศึกษาเพิ่มเติมจากตัวอย่างของเศษยางมากกว่า 20 ตัวอย่างก็ยืนยันความสัมพันธ์เชิงเส้นตรงดังกล่าวเช่นเดียวกัน จากผลการทดลองที่พบนี้สามารถตีความได้ว่า เศษยางใดๆก็ตามที่ได้ผ่านกระบวนการที่ระบุไว้ในงานวิจัยนี้ น่าจะแสดงความสัมพันธ์เชิงเส้นตรงระหว่างค่าความหนืดและปริมาณสะเก็ดไม้ได้ ดังนั้นจึงน่าจะสามารถใช้ความสัมพันธ์นี้เพื่อเป็นเครื่องมือสำหรับกระบวนการผลิตผลิตภัณฑ์ยางจากเศษยางได้ นอกจากนั้นผู้วิจัยยังประสบความสำเร็จในการใช้ความสัมพันธ์ดังกล่าวเพื่อเตรียม rubber/wood composites ที่มีปริมาณของสะเก็ดไม้ที่แน่นอนได้จากเศษยางจากสวน

สำนักวิชาวิศวกรรมศาสตร์และทรัพยากร มหาวิทยาลัยวลัยลักษณ์ อำเภอท่าศาลา จังหวัดนครศรีธรรมราช 80161