

# DYNAMIC MECHANICAL THERMAL AND THERMOMECHANICAL CHARACTERIZATIONS OF POLYOLEFIN COMPOSITES FILLED RICE HUSK AND SAW DUST

## ĐÁNH GIÁ CÁC ĐẶC TRƯNG CƠ NHIỆT ĐỘNG VÀ CƠ NHIỆT CỦA COMPOSITE NỀN POLYOLEFIN ĐỘN TRÁU VÀ MÙN CƯA

Hanna Brodowsky<sup>1</sup>, Doan Thi Thu Loan<sup>2</sup>

<sup>1</sup>Leibniz-Institut für Polymerforschung Dresden e. V., Germany; Email: brodowsky@gmx.de

<sup>2</sup>The University of Danang, University of Science and Technology, Vietnam; Email: dtloan2001@yahoo.com

**Abstract** - The composites based on bio-fillers and polymers have attracted great interest due to increasing environmental concern, their low cost and renewable resource. In this study, the dynamic mechanical thermal and thermomechanical characterizations of polyolefin (Polypropylene – PP and polyethylene - PE) as well as three composite systems including rice husk (RH) filled polypropylene composite, rice husk filled polyethylene composite and saw dust (SD) filled polyethylene composite were investigated. The effect of two type of compatibilizers, maleic anhydride grafted polypropylene (2 wt% MAPP) for polypropylene matrix composite and maleic anhydride grafted polyethylene (4 wt% MAPE) for polyethylene matrix composites, on dynamic mechanical thermal properties (Storage modulus -  $E'$ , loss modulus -  $E''$ , damping factor -  $\tan \delta$ ) of three composite systems were studied. Moreover, the coefficient of thermal expansion and dimension change of neat matrices (PP, PE) and three composite systems (PP/RH, PE/RH and PE/SD) with compatibilizers were also investigated by thermomechanical analysis.

**Key words** - Sawdust; Rice husk; Polyethylene; Polypropylene; Composite; Compatibilizer; DMTA, TMA

**Tóm tắt** - Composite trên cơ sở độ bền sinh khối và polymer đã thu hút nhiều sự quan tâm do những vấn đề về môi trường ngày càng tăng, giá thành thấp và nguồn nguyên liệu tái tạo. Trong nghiên cứu này, các đặc trưng cơ nhiệt động và cơ nhiệt của polyolefin (Polypropylene và polyethylene) và ba hệ composite bao gồm composite nền polypropylene độ bền trấu, composite nền polyethylene độ bền trấu và composite nền polyethylene độ bền mùn cưa được khảo sát. Ảnh hưởng của hai loại chất tương hợp, polypropylene ghép maleic anhydride (2% trọng lượng) dùng đối với composite nền polypropylene và polyethylene ghép maleic anhydride (4% trọng lượng) dùng đối với composite nền polyethylene, đến tính chất cơ nhiệt động (gồm modul dự trữ -  $E'$ , modul tổn thất -  $E''$  và hệ số suy giảm -  $\tan \delta$ ) của ba hệ composite được nghiên cứu. Hơn nữa, hệ số giãn nở nhiệt và sự thay đổi kích thước của polyolefin và ba hệ composite (PP/trấu, PE/trấu và PE/mùn cưa) có chứa chất tương hợp cũng được khảo sát bằng phép phân tích cơ nhiệt.

**Từ khóa** - mùn cưa; trấu; polyethylene; polypropylene; composite; chất tương hợp; DMTA, TMA

## 1. Introduction

In recent years, bio-flour filled thermoplastics have received considerable attention because they have several advantages, such as renewable resource, light weight, low cost, reasonable strength and stiffness, recyclability, biodegradability. The most common thermoplastics used in bio-flour filled thermoplastics are polyethylene, poly(vinyl chloride), and polypropylene. Various types of bio-fillers have been exploited including wood, hemp, sisal, flax, rice husk, jute and others.

Rice husk (RH) and saw dust (SD) are the major agricultural and forestal residues produced with huge amount in Vietnam as a byproduct during the rice milling and wood processing. However, they have been used ineffectively. Only some are used for daily cooking in the rural areas, the others have been dumped in rivers or burnt in open piles, that cause the environmental problems.

In this study, polypropylene (PP) and polyethylene (PE) were chosen as the polymer matrices for the composites. The bio-fillers used were rice husk and saw dust.

However, when non-polar PP, PE were used as matrices for the composites the incompatibility between the hydrophobic polymers and hydrophilic bio-fillers has a big problem. According to the previous studies, the best solution to the problem was using the compatibilizers [1], [2], [3]. Therefore, MAPP and MAPE were used as compatibilizers for polypropylene matrix composite and polyethylene composites, respectively.

The objective of this study is to evaluate the dynamic mechanical thermal and thermomechanical characterizations of polyolefin (PP, PE) and bio-filler (RH, SD)/ polyolefin composites using the dynamic mechanical thermal and thermomechanical analysis methods.

## 2. Experimental

### 2.1. Materials

Polypropylene Advanced PP-1100N and high density polyethylene EL-Lene H5818J were supplied by Advanced Petrochemical Co. and SCG Plastics Co., Ltd-Thailand, respectively. Two compatibilizers, maleic anhydride grafted polypropylene (MAPP) Polybond 3200 and maleic anhydride grafted polyethylene (MAPE) Polybond 3029, were provided by Chemtura, USA.

Rice husk was obtained from a rice mill factory in Danang, Vietnam and ground. Sawdust from Acacia auriculiformis tree was collected from a Wood processing factory in Danang, Vietnam. Rice husk and saw dust were sieved and dried in oven at 80°C for 24h before preparing the composites.

### 2.2. Methods

#### 2.2.1. Preparation of the composites

Composites were produced in a two-stage process, as optimized in the previous studies with the formulas as seen in Table 1. In the first stage, bio-fillers and polyolefin were compounded without and with compatibilizers (MA) using the twin-screw extruder Rheomex CEW100 QC, Haake,

Germany. The mixing zone temperature of the extruder was 160°C for PE and 190°C for PP matrix composites. The rotation speed of the screws was 50 rpm. In the second stage, the extrudate in the form of strands was cooled to room temperature and then granulated. The compound granules were dried at 80°C for 24 h before injection molding. The specimens were prepared using an injection molding machine MiniJet II, Haake, Germany at cylinder temperatures of 180°C for PE and 190°C for PP matrix composites under an injection pressure of 800 bar [1], [2], [3].

### 2.2.2. Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical thermal analysis was carried out (TA Instruments DMTA Q800 V20.24 Build 43) in nitrogen ( $N_2$ ) atmosphere. The dimensions of the test specimens were 17.5 x 10 x 4 mm. The tests were performed using a three point bending-rectangular measuring system at 1 Hz test frequency. The heating rate was 1 °C/min in the temperature range of -50 – 150°C.  $E'$  (storage modulus),  $E''$  (loss modulus), and  $\tan \delta$  (damping peak) of the samples were measured as a function of temperature.

### 2.2.3. Thermomechanical analysis (TMA)

The thermal expansion tests of the composites and pure polyolefin samples were conducted using a thermomechanical analyzer (TMA Q400 V7.4 Build 93, TA Instruments) from -10°C to 100°C at a heating rate of 2°C/min in a nitrogen atmosphere. Expansion mode with a constant compression load of 0.02 N was applied to the specimen in the testing process. The tested specimens were cut to the shape of a rectangular prism of size 5mm×5mm×4 mm.

**Table 1.** Formulas for producing the composites

Material	Composition (wt%)					
	PP/RH	PP/RH (MA)	PE/RH	PE/RH (MA)	PE/SD	PE/SD (MA)
RH	50	50	50	50	-	-
SD	-	-	-	-	50	50
PP	50	48	-	-	-	-
PE	-	-	50	46	50	46
MAPP	0	2	-	-	-	-
MAPE	-	-	0	4	0	4

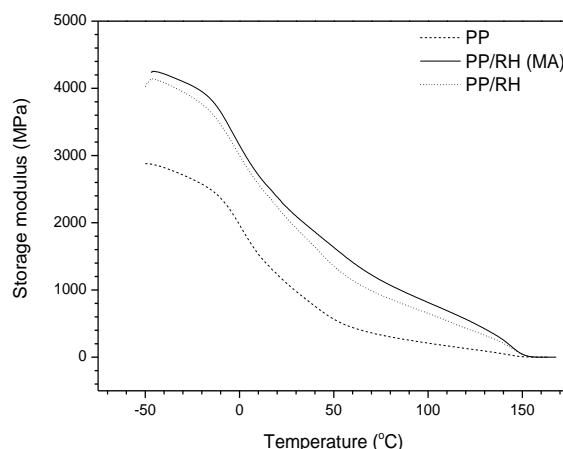
## 3. Results and discussion

### 3.1. Dynamic mechanical analysis (DMA)

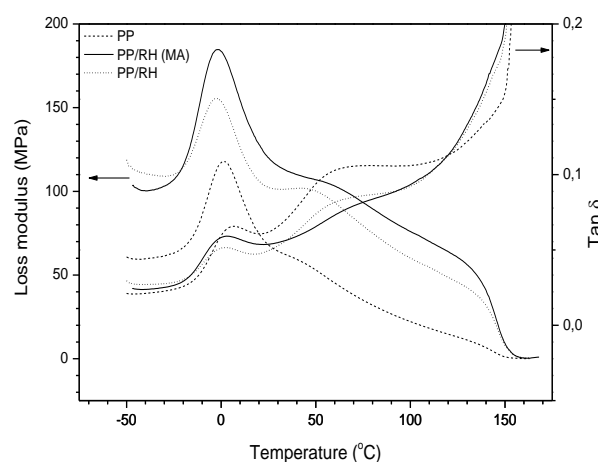
Fig. 1÷6 shows the  $E'$ ,  $E''$  and  $\tan \delta$  values of PP, PE, wood and three composite systems without and with compatibilizers.

Storage modulus ( $E'$ ) of polypropylene and polypropylene matrix composites were higher than those of pure polyethylene and polyethylene matrix composites (Figure 1, 3, 5). The fillers improved the storage modulus of both PP and PE polyolefin. This is the expected effect caused by the addition of more rigid fillers into semi-rigid polyolefin matrices. In all systems, the storage modulus

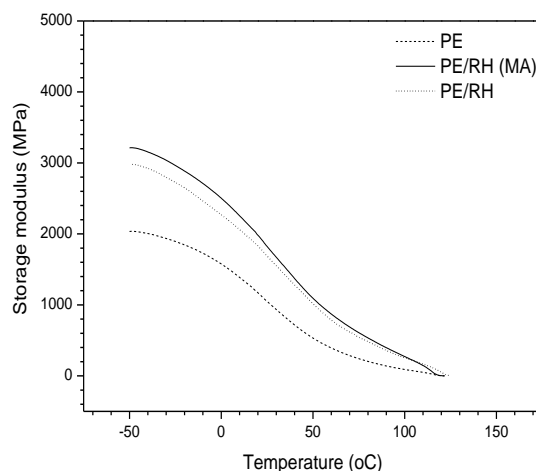
drops with increasing temperature due to the increased segmental mobility of the polymer chains. The  $E'$  value of polypropylene systems decreased rapidly when the temperature was at above 0°C. Whereas, the  $E'$  value of wood and polyethylene systems decreased linearly with increasing temperature at first, then decreased rapidly at temperatures above 30°C.



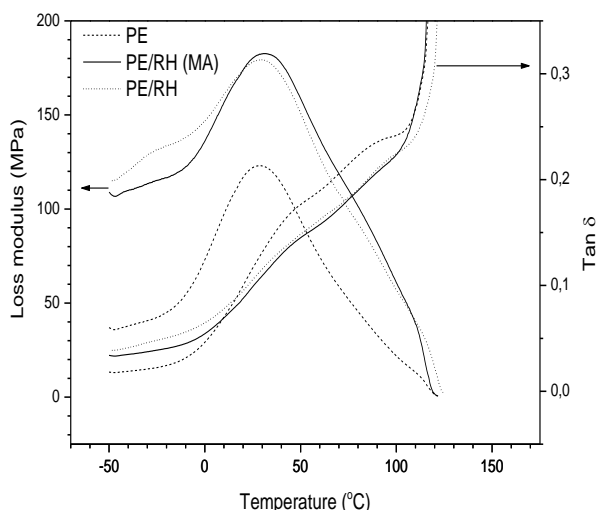
**Figure 1.** Storage modulus of PP and PP/RH composites without and with 2% compatibilizer (MA)



**Figure 2.** Loss modulus and  $\tan \delta$  of PP and PP/RH composites without and with 2% compatibilizer



**Figure 3.** Storage modulus of PE and PE/RH composites without and with 4% compatibilizer



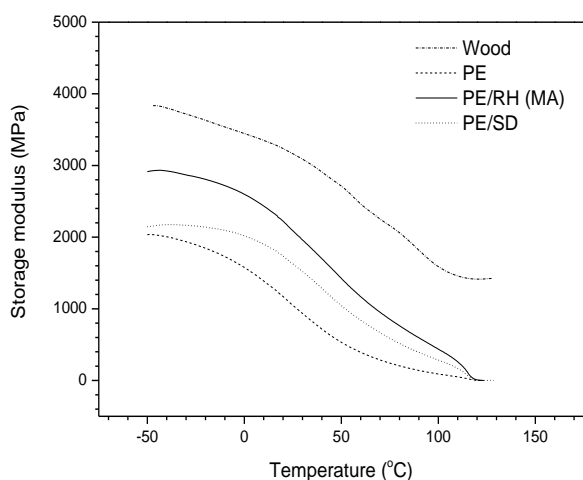
**Figure 4.** Loss modulus and  $\tan \delta$  of PE and PE/RH composites without and with 4% compatibilizer

without and with compatibilizers are presented in Figure 2, 4, 6. Loss modulus ( $E''$ ) – is a measure of the absorbed energy due to the relaxation and is associated with viscous response of the viscoelastic materials.  $E''$  of polyolefin and composites increased with temperature and had a peak in the transition region about 0°C and 30°C for PP and PE systems, respectively.  $\tan \delta$  – the damping factor, a ratio of the loss modulus to the storage modulus ( $E''/E'$ ), is used to investigate viscoelastic properties of the materials.

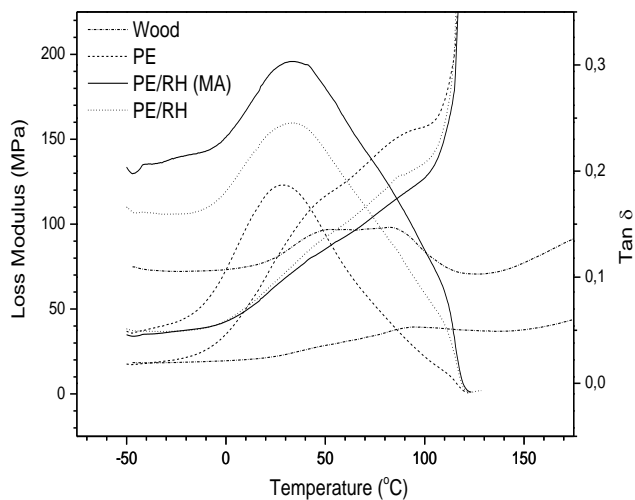
The  $\tan \delta$  peak can also provide information on the  $T_g$  and energy dissipation of composite materials. With increasing temperature, the  $\tan \delta$  values of PP and PP matrix composites (Fig. 1 ÷ 2) increased due to the increased polymer chain mobility of the matrix and exhibited two relaxation peaks in the vicinity of 5°C and 70°C. The low-temperature peak is related to the glass transition of the amorphous polymer fractions and can be considered as the glass transition temperature ( $T_g$ ) [4],[5]. A slight decrease in glass transition temperature, which determined from the  $\tan \delta$  curves, was observed in samples with added rice husk filler in polypropylene matrix. The amorphous phase of the polypropylene is responsible for the glass-rubber transition and it is the place where the filler particles must be located [5]. Therefore, the amorphous polymer chains are supposed to show high segmental mobility when they contain the dispersed particles. Although the composition of the systems is the key parameter in determining the damping properties, other factors such as the interaction among the dispersed phase and the polymer matrix will also affect damping. A slight increase in  $\tan \delta$  values has been observed in the PP composites with MAPP comparing to the unmodified one in the region of the  $T_g$  transition. Although this is only a marginal effect, it can be related to the interfacial action of MAPP that improves the damping properties of the materials [6].

The high-temperature peak corresponds to the  $\alpha$  transition related to the PP crystalline fractions. Two different mechanisms are proposed to explain  $\alpha$  relaxation: a) mobility of rigid amorphous molecules entrapped as defects in the crystals and/or b) lamellar slip and rotation of the crystals [4]. The  $\alpha$  transition peak of the modified PP composite (81°C) was higher than that of the unmodified one (72°C). That can be a result of the existence of enhanced transcrystallinity around the fibers in the modified composites [7].

For the polyethylene system,  $\tan \delta$  curves of neat PE and the composites (Fig. 3÷6) had less distinctive  $\alpha$  transition process compared to the loss modulus curves and there was not the peak corresponding to the  $T_g$  of polyethylene (approximately -130°C) because it was not sufficiently cooled down to this temperature while carrying out the test. The  $\alpha$  relaxation is generally attributed to segmental motions in the non-crystalline phase [8]. The  $\alpha$  transition of the composites shifted to higher temperature compared to neat polyolefin. An addition of compatibilizer also led to shift slightly the  $\alpha$  transition curve to the higher temperature. That is an indication of the presence of some processes, which have restricted the mobility of the chains



**Figure 5.** Storage modulus of wood, PE and PE/SD composites without and with 4% compatibilizer



**Figure 6.** Loss modulus and  $\tan \delta$  of wood, PE and PE/SD composites without and with 4% compatibilizer

The temperature dependence of loss modulus and  $\tan \delta$  for the polyolefin, wood and three composite systems

in the crystalline phase so that more energy is required for the transition happens. Therefore the bio-fillers somehow restricted the matrix polymer chains and increased the  $\alpha$  transition temperature [9].

### 3.2. Thermomechanical analysis (TMA)

TMA expansion curves in x direction and the CTE values of the modified matrix composites (PE/RH (MA), PE/SD (MA) and PP/RH (MA)) are shown in Fig. 7÷8. The TMA method for measurement of the coefficient of thermal expansion (CTE) is useful for understanding the dimensional changes of bio-filler composite materials as well as the thermal stresses caused by increasing temperature [10], [11]. A lower CTE value of the composites indicates that the bio-filler composites undergo lower dimensional change when exposed to cold or warm atmospheric change [12].

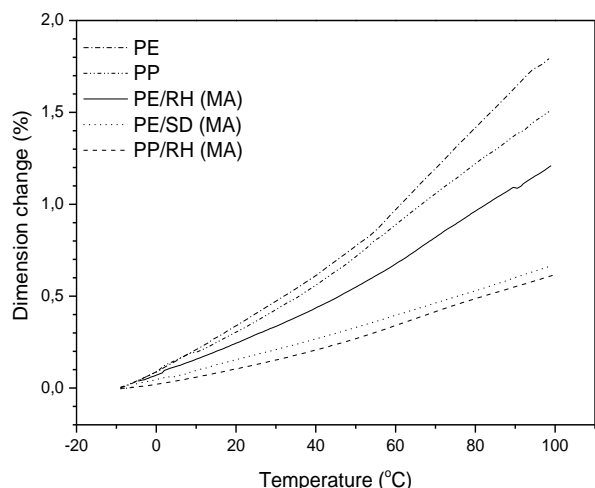


Figure 7. Dimension change of polyolefin and filler/polyolefin composites in x-direction

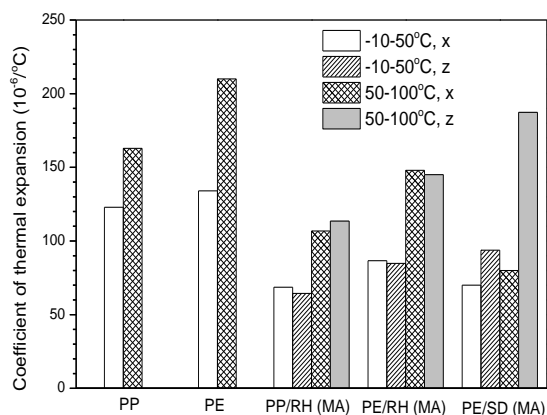


Figure 8. Coefficient of thermal expansion of polyolefin and filler/polyolefin composites

The CTE values of pure PE and PP were  $134.10^{-6}/^{\circ}\text{C}$  and  $123.10^{-6}/^{\circ}\text{C}$  for the temperature range of  $-10\div 50^{\circ}\text{C}$ , respectively. These values were higher for the range  $50\div 100^{\circ}\text{C}$  ( $210.10^{-6}/^{\circ}\text{C}$  for PE and  $163.10^{-6}/^{\circ}\text{C}$  for PP). CTE values of pure PE and PP decreased 30÷62% by adding 50 wt% filler. While the CTE values of rice husk

composites are isotropic, the difference of CTE values in longitudinal and transverse directions of the saw dust composite is quite high, especially in the high temperature range  $50\div 100^{\circ}\text{C}$  ( $94.10^{-6}/^{\circ}\text{C}$  in x - direction and  $187.10^{-6}/^{\circ}\text{C}$  in z-directions). This reflects on the one hand the anisotropic behavior of the saw dust [13] and on the other hand the aspect ratio of the SD particles which in injection moulding leads to orientation of the filler particles.

### 4. Conclusions

Storage modulus of polyolefin matrix composites were higher than those of pure polyolefin and were improved after the addition of compatibilizers.

The results showed that better interactions among the matrix and the dispersed phase were accomplished.

Moreover, the coefficient of thermal expansion of polyolefin decreased upon adding rice husk and saw dust fillers. While the CTE values of rice husk composites are isotropic, the difference of CTE values in longitudinal and transverse directions of the saw dust composite is quite high.

**Acknowledgements:** Author is thankful to the technicians at Leibniz institute of polymer research Dresden, Germany and the students at Danang University of Science and Technology (Tran Thi Nghia, Nguyen Thanh Huan, Ngo Ngoc Hien Chuong, Pham Thai Mai Linh, Pham Thi Men, Le Van Truong) for carrying out part of the experiments.

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