

## **PREPARATION OF POLYMER COMPOSITES BASED ON UNSATURATED POLYESTER REINFORCED BY NATURAL FIBER AND CELLULOSE MICROFIBER FROM LUNG WASTE IN NGHE AN**

**Cao Xuan Cuong<sup>1,\*</sup>, Le Duc Giang<sup>1</sup>, Tran Viet Thuyen<sup>2</sup>, Ta Thi Phuong Hoa<sup>2</sup>**

<sup>1</sup>*Faculty of Chemistry, Vinh University, 182 Le Duan, Vinh city, Nghe An*

<sup>2</sup>*Research Center for Polymer Materials, Hanoi University of Science and Technology, 1 Dai Co Viet, Hai Ba Trung, Ha Noi*

\*Email: [caoxuancuong@gmail.com](mailto:caoxuancuong@gmail.com)

Received: 15 June 2016; Accepted for publication: 23 October 2016

### **ABSTRACT**

Unsaturated polyester composites reinforced by glass fiber and by hybrid reinforcement glass fiber - lung fiber with cellulose microfibril (MFC) were prepared and investigated. Tensile and flexural strengths of material reached the highest value at polymer composite with 48 %w glass fiber mat and 0.3 %w MFC (208.33 MPa and 243.60 MPa), while the highest impact strength reached 212.48 kJ/m<sup>2</sup> at composite containing 48 %w glass fiber but 0.5 %w MFC. Especially, with 0.3 %w MFC, the tensile fatigue cycle to failure of composite processed by vacuum bag remarkably increased, 140.28 % at composite with 48 %w glass fiber and 265.63 % at hybrid composite reinforced by glass fiber/lung fiber, compared to samples without MFC.

*Keywords:* cellulose microfibril, lung fiber, glass fiber, polymer composite, unsaturated polyester.

### **1. INTRODUCTION**

Unsaturated polyester (UPE) resins are widely used in preparation of polymer composite. In Vietnam, some studies have been carried out on improvement of the physical properties of UPE by silicafume [1], chopped aramid fibers [2], by fly ash [3]. Besides, polymer composites reinforced with natural fibers, especially, with cellulose microfibril (MFC) has been interested by many researchers due to their salient advantages compared to traditional reinforcement fibers (carbon, glass fibers...), such as, high mechanical strength, low density, biodegradability, natural renewable resources [4]. Takagaki et al. [5] used 0.1 %w and 0.3 %w MFC to improve the fatigue strength and impact properties of MFC-CF-Epoxy. In addition, MFC also improved thermal and flexural strength properties of polymer composite based on epoxy resins and polylactic acid [6, 7] and biodegradability of nanocomposite [8]. However, studies on using the natural fibrils in combination with MFC to reinforce polymer composite based on UPE virtually are at the beginning and in the first step to attract the attention of researchers.

## **2. MATERIALS AND METHODS**

### **2.1. Materials**

Unsaturated polyester resin 268 BQTN (Singapore), glass fiber mat (density: 360 g/m<sup>2</sup>), curing agent Trigonox V388 (Methyl ethyl ketone peroxide) of Akzol Nobel (China).

Lung fibers mat (density: 190 g/m<sup>2</sup>) which the average diameter was about 150 - 200 μm, was prepared by the raking method then treating alkali at Research Center for Polymer Materials, Hanoi University of Science and Technology.

The pulp with Kappa index 21 from lung foil waste that preparation by sulfate pulping method at Research Institute of Pulp and Paper industry.

### **2.2. Preparation and dispersion of MFC**

Mixture UPE/pulp was grinded by Ball Mill of Planetary Type, Model: ND2L (China). After making smooth by electric blender, the pulp mixed into UPE with 3 %w. The number of mill balls were 40 mill balls Ø10 mm and 150 mill balls Ø6 mm.

### **2.3. Preparation of polymer composite**

Polymer composites were prepared at Research Center for Polymer Materials, Hanoi University of Science and Technology. In order to investigate the influence of processing method and technological composition on physical properties of composite, 4 samples were prepared:

Group A: UPE without MFC (sample A<sub>0</sub>) and UPE with MFC in the weight ratio MFC/PEKN as 0.3 % (sample A<sub>1</sub>), 0.5 % (sample A<sub>2</sub>), 0.7 % (sample A<sub>3</sub>) and 1 % (sample A<sub>4</sub>), cured by V388 following ratio V388/PEKN as 0.6%w. Mix well and then pour the mixture into mould for curing.

Group B: Prepare composite reinforced by 48 %w glass fiber mat without MFC (sample B<sub>0</sub>) and with MFC following the weight ratios: 0.3 % (sample B<sub>1</sub>), 0.5% (sample B<sub>2</sub>), 0.7 % (sample B<sub>3</sub>) và 1 % (sample B<sub>4</sub>), based on the weight of UPE. Composite material samples with 8 layers of glass fiber mat were prepared by hand-lay up method.

Group C: Prepare copposites in same composition as group B, but use the vacuum bag with vacuum of 0.1- 0.15 at. as processing method.

Group D: Prepare the hybrid UPE/ glass fiber mat/ lung fiber mat in coat-shell structure, with 4 layers of lung fiber mat as the coat and 2 layer of glass fiber as the shell, the ratio glass fiber-lung fiber/UPE was 48 %w, V388/UPE as 0.6 %, the content of MFC in the samples were 0 % (sample D<sub>0</sub>), 0.3 % (sample D<sub>1</sub>), 0.5% (sample D<sub>2</sub>), 0.7 % (sample D<sub>3</sub>) and 1% (sample D<sub>4</sub>).

The curing process of polymer composite samples was carried out at room temperature for 12 hours, after that they were removed from mould and additionally heated at 70°C for 4 hours. Physical properties of composite samples were then tested.

### **2.4. Testing methods**

The surface morphology of destroyed samples was studied on the SEM- Scanning Electron Microscopy Jeol 6360 LV (Japan) at Advanced Institute for Science and Technology, Hanoi University of Science and Technology. Samples with the dimension 2mmx2mm were coated with an Ag layer and were then studied in vacuum room of equipment.

Tensile strength and flexural strength were tested following the standards ISO 527-1993 and ISO 178-1993 (E), on an INSTRON 2 - 100KN (USA), with the speed of 2 mm/min, temperature of 25 °C, humidity of 70 - 75 %. Impact strength IZOD test followed the ISO 180 & ASTM D256, on a Tinius Olsen (USA), at 25 °C. Fatigue properties were tested on equipment MPS 810 (Material Test System 810- USA), following standar ASTM D3479-96 (2007), the working force for fatigue cycle test was 70 % of tension-to-break force of the samples,  $f = 2\text{Hz}$  equivalent to 120 rpm, vibration amplitude of the force was 2 times of working force. These physical properties were studied at the Research Center for Polymer Materials, Hanoi University Science and Technology.

### 3. RESULTS AND DISCUSSION

#### 3.1. Influence of MFC and processing method on tensile strength

The tensile strengths of samples in Table 1 showed that with the increase of MFC content from 0.3% to 1% the, tensile strength of samples in group A decreased from 19.57 % to 78.19 %, and that of samples in group B decreased from 9.15 % to 36.14 %, compared to samples without MFC. That might be, that the MFC might cause defects in the sample, leading to decrease of the tensile strength. In groups C and D, sample  $C_1$  và  $D_1$  possessed highest tensile strength. The tensile strength of samples  $C_1$  and  $C_2$  were higher than that of  $C_0$  12.21 % and 4.56 %, and that of  $D_1$  and  $D_2$  higher 5.35% and 3.83% compared with  $D_0$ . Samples  $C_3$  and  $C_4$ ,  $D_3$  and  $D_4$  also possessed decreasing tensile strength with increasing MFC content.

Table 1. Tensile strength (MPa) of polymer composite.

MFC content	Group A		Group B		Group C		Group D	
0%	$A_0$	43.33	$B_0$	165.82	$C_0$	185.66	$D_0$	82.30
0.3%	$A_1$	34.85	$B_1$	150.65	$C_1$	<b>208.33</b>	$D_1$	<b>86.70</b>
0.5%	$A_2$	25.89	$B_2$	137.41	$C_2$	194.12	$D_2$	85.45
0.7%	$A_3$	13.87	$B_3$	126.28	$C_3$	168.51	$D_3$	64.89
1%	$A_4$	9.45	$B_4$	105.89	$C_4$	159.33	$D_4$	57.65

In comparison of samples of group C with group B it can be seen that with the same MFC content, the tensile strength in group C were much higher than that in group B. Polymer composite reinforced by glass fiber mat containing 0.3 % MFC, processed by vacuum bag, reached the highest tensile strength (208.33 MPa). The presence of small MFC content and utilisation of vacuum bag in processing lead to better quality of composite and show higher effect in processing of material, compared to hand-lay up method, due to higher pressure on the vacuum bag containing sample.

#### 3.2. Influence of MFC and processing method on flexural strength

The result of flexural strength test listed in Table 2 showed that with increasing MFC content, the flexural strength of samples in group A decreased from 26.52 to 78.48. However flexural strength in groups B, C and D slightly increased with MFC content of 0.3 %, and then decreased with higher MFC content. It can be seen that with the MFC content of 0.3 %, samples

B<sub>1</sub>, C<sub>1</sub> and D<sub>1</sub> showed the highest flexural strength in group B,C,D, respectively. With the same MFC content, group C possessed better flexural strength: strength of C<sub>0</sub> was 18.33 % higher than B<sub>0</sub>; of C<sub>1</sub> 16.76 % higher than B<sub>1</sub>, of C<sub>2</sub> 23.89 % higher than B<sub>2</sub>, of C<sub>3</sub> 15.23% higher than B<sub>3</sub>, and that of C<sub>4</sub> was 18.46 % higher than that of D<sub>4</sub>.

Table 2. Flexural strength (MPa) of polymer composite.

MFC content	Group A		Group B		Group C		Group D	
	0%	A <sub>0</sub>	70.90	B <sub>0</sub>	192.40	C <sub>0</sub>	227.67	D <sub>0</sub>
0.3%	A <sub>1</sub>	52.10	<b>B<sub>1</sub></b>	<b>208.63</b>	<b>C<sub>1</sub></b>	<b>243.60</b>	<b>D<sub>1</sub></b>	<b>132.70</b>
0.5%	A <sub>2</sub>	49.54	B <sub>2</sub>	186.74	C <sub>2</sub>	231.36	D <sub>2</sub>	128.52
0.7%	A <sub>3</sub>	21.30	B <sub>3</sub>	162.78	C <sub>3</sub>	187.57	D <sub>3</sub>	124.71
1%	A <sub>4</sub>	15.26	B <sub>4</sub>	149.34	C <sub>4</sub>	176.91	D <sub>4</sub>	101.32

The result showed that the processing method vacuum bag can cause material with higher flexural strength than hand-lay up method. The composite material reinforced by glass fiber containing 0.3 % MFC and processed by vacuum bag reached highest flexural strength (243.60 MPa).

### 3.3. Influence of MFC and processing method on impact strength

The result of impact test listed in Table 3 showed, the presence of a small MFC content from 0.3 to 0.5 % led to improvement of impact strength of all sample groups. It can be seen that impact strength of sample A<sub>1</sub> was 66.84 % higher and of A<sub>2</sub> was 70.82 % higher than that of A<sub>0</sub>. Impact strength of B<sub>1</sub> and B<sub>2</sub> were 18.04 % and 27.34% higher than that of B<sub>0</sub> 18.04 %. Similarly, C<sub>1</sub> and C<sub>2</sub> possessed better impact strength compared to C<sub>0</sub> (21.34 % and 24.39 %), at D<sub>1</sub> and D<sub>2</sub> also 14.4 % and 11.36 % higher compared to D<sub>0</sub>. It might be, with small dimension, MFC can adsorb better impact force, change the direction of micro fracture, reducing development speed of fracture inside sample, leading to a delay of material destroy. However, at the MFC content of 0.7 % or more, the impact strength slightly decreased at all samples.

Table 3. Impact strength (kJ/m<sup>2</sup>) of polymer composite.

MFC content	Group A		Group B		Group C		Group D	
	0%	A <sub>0</sub>	9.80	B <sub>0</sub>	158.28	C <sub>0</sub>	170.82	D <sub>0</sub>
0.3%	A <sub>1</sub>	16.35	B <sub>1</sub>	186.84	C <sub>1</sub>	207.28	<b>D<sub>1</sub></b>	<b>35.75</b>
0.5%	A <sub>2</sub>	16.74	<b>B<sub>2</sub></b>	<b>201.55</b>	<b>C<sub>2</sub></b>	<b>212.48</b>	D <sub>2</sub>	34.80
0.7%	A <sub>3</sub>	15.40	B <sub>3</sub>	177.23	C <sub>3</sub>	197.56	D <sub>3</sub>	33.10
1%	A <sub>4</sub>	13.20	B <sub>4</sub>	155.38	C <sub>4</sub>	187.20	D <sub>4</sub>	32.40

From Table 3 it can also be seen that at the same MFC content, all the samples of group C possessed higher impact strength than that of group B. So, polymer composite reinforced by

glass fiber mat, processed by vacuum bag have had better impact strength than processed by hand-lay up method.

### 3.4. Influence of MFC and processing methods on fatigue property

The results of tensile, flexural and impact tests showed that the MFC content of 0.3 % was the optimal content for preparation of polymer composite and it would be used to investigate fatigue property. The presence of MFC strongly improved the fatigue property of material. At 0.3 % MFC, sample  $D_1$  was destroyed after 23826 cycles compared to 10166 cycles of  $D_0$  (increased 265.63 %),  $C_1$  at 34312 cycles compared to 14248 of  $C_0$  (increased 140.82 %); and sample  $B_1$  at 23826 cycles compared to 10166 cycles of  $B_0$  (increased 134.37 %). For polymer composite with glass fiber mat, processing by vacuum bag also gave much better fatigue property than by hand-lay up method. For example, without MFC fatigue property of  $C_0$  increased 40.15% compared to  $B_0$  (14248 cycles compared with 10166 cycles); with 0.3 % MFC sample  $C_1$  was destroyed at 34312 cycles compared to 23826 cycles of  $B_1$  (increased 44.01 %).

### 3.5. Study on surface morphology

SEM images of polymer composite have been given in Figure 1. It can be seen that without MFC polymer composite surface showed a brittle fracture with big flat surface and a lot of cracking lines (Fig. 1a and Fig. 1c).

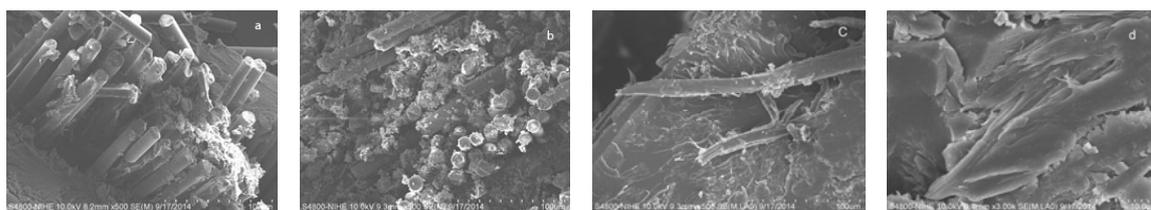


Figure 1. SEM images of polymer composite without MFC (1a) and with 0.3% MFC (1b); polymer composite reinforced by glass fiber mat- lung fiber mat without MFC (1c) and with 0.3% MFC (1d).

In polymer composite containing MFC (Fig.1b and Fig.1d), the matrix resin showed the fracture with small pieces, forming a rough surface. That means that MFC played an important role in protection of polymer composite, slowing down the development of the crack and rupture in composite, and therefore can improve physical properties of material. Processing by vacuum bag with low pressure in the bag may cause a better wettability of the resin on the reinforcement and MFC surface, leading to better quality of material

## 4. CONCLUSIONS

The study on preparation of polymer composite based on UPE, reinforced by glass fiber-lung fiber and MFC, and on its physical properties showed, that the vacuum bag is an effective processing method giving material with higher physical properties compared to hand-lay up method. By addition of 0.3 %w and 0.5 %w MFC, polymer composite UPE/glass fiber mat and hybrid composite UPE/glass fiber mat-lung fiber mat processed by vacuum bag possessed higher tensile, flexural and impact strength. Especially, the presence of MFC can remarkably improve

fatigue property of material, 140.82 % for composite UPE/glass fiber and 265% for hybrid composite, in comparison with material without MFC.

## REFERENCES

1. Trịnh M. Đ., Bùi C., Bạch T. P., Nguyễn T. P. N. - Nghiên cứu chế tạo vật liệu polyme compozit trên cơ sở nhựa nền polyeste không no và silicafum, Tạp chí Hóa học **49** (1) (2011) 91-94.
2. Nguyễn M. T., Trần V. D., Nguyễn Đ. L. - Tính chất mài mòn của compozit trên cơ sở nhựa polyeste không no gia cường bằng sợi aramit ngắn, Tạp chí Hóa học **49** (3) (2011) 375-379.
3. Bạch T. P., Nguyễn T. D. - Nghiên cứu ảnh hưởng của tro bay đến tính chất cơ học vật liệu polyme compozit nền nhựa polyeste không no, Tạp chí Hóa học **50** (2) (2012) 178-181.
4. Phan T. M. N., Trần V. D., Đoàn T. Y. O., Nguyễn H. T. - Nghiên cứu chế tạo compzit sinh học trên cơ sở nhựa polyeste không no gia cường bằng mat nửa lai tạo với mat thủy tinh, Tạp chí Hóa học **47** (1) (2009) 75-80.
5. Norifumi T., Kazuya O., Toru F. - Improvement of fatigue strength and impact properties of plain-woven CFRP modified with micro fibrillated cellulose, In: Proceedings of the 6th Asia-Australasian conference on composite materials (ACCM/6), Kumamoto, 23-26 September, (2008) 499-501.
6. Mohamed J. G., Mostafa A. E., Kazuya O., Toru F. - Effect of microfibrillated cellulose on mechanical properties of plain-woven CFRP reinforced epoxy, Composite Structures **92** (2010) 1999-2006.
7. Jue L., Per A., Lawrence T. D. - Surface modification of microfibrillated cellulose for epoxy composite applications, Polymer **49** (5) (2008) 1285-1296.
8. Marielle H., Berglund L. A. - Structure and properties of cellulose nanocomposite films containing melamine formaldehyde, Journal of Applied Polymer Science **106** (4) (2007) 2817-2824.

## TÓM TẮT

CHẾ TẠO VẬT LIỆU POLYME COMPOZIT TRÊN CƠ SỞ NHỰA POLYESTE KHÔNG NO GIA CƯỜNG BẰNG SỢI THỰC VẬT VÀ VI SỢI XENLULOZƠ TỪ PHẾ THẢI CỦA CÂY LỪNG Ở NGHỆ AN

Cao Xuân Cường<sup>1,\*</sup>, Lê Đức Giang<sup>1</sup>, Trần Việt Thuyền<sup>2</sup>, Tạ Thị Phương Hòa<sup>2</sup>

<sup>1</sup>Khoa Hóa học, Trường Đại học Vinh, số 18 Lê Duẩn, Tp Vinh, Nghệ An

<sup>2</sup>Trung tâm nghiên cứu vật liệu polyme, Trường Đại học Bách Khoa Hà Nội, số 1 Đại Cồ Việt, Hai Bà Trưng, Hà Nội

\*Email: caoxuancuong@gmail.com

Vật liệu polyme compozit trên cơ sở nhựa polyeste không no (PEKN) gia cường bằng mat thủy tinh và compozit lai tạo mat thủy tinh/mat sợi lừng có bổ sung vi sợi xenlulozơ (MFC) đã

được chế tạo và khảo sát một số tính chất cơ lý. Polyme composít có độ bền kéo đứt và độ bền uốn đạt giá trị lớn nhất lần lượt là 208,33 MPa và 243,60 MPa ở mẫu vật liệu gia cường bằng 48 % mat thủy tinh và 0,3 % MFC (về khối lượng), còn mẫu vật liệu gia cường bằng 48 % mat thủy tinh và 0,5 % MFC (về khối lượng) có độ bền va đập lớn nhất là 212,48 kJ/m<sup>2</sup>. Đặc biệt, độ bền mỏi của polyme composít gia cường 48 % mat thủy tinh và 0,3 % MFC được gia công bằng phương pháp túi hút chân không tăng 140,28 %, còn polyme composít lai tạo mat thủy tinh-mat sợi lùg và MFC tăng 265,63 % so với mẫu vật liệu không có MFC.

*Từ khóa:* vi sợi xenlulozơ (MFC), sợi lùg, sợi thủy tinh, polyme composít, polyeste không no.