

ภาคผนวก ก

วัสดุ อุปกรณ์และเครื่องมือที่ใช้ในงานวิจัย

1. เตาอบไมโครเวฟที่ใช้ในครัวเรือน (microwave oven) รุ่น Sanyo™ EM-X 412



รูปที่ ก.1 เตาอบไมโครเวฟรุ่น Sanyo™ EM-X 412

2. เตาอบความร้อน (thermol oven) MEMMERT รุ่น D 06061, UM 500



รูปที่ ก.2 เตาอบความร้อนรุ่น D 06061, UM 500

3. เครื่องทดสอบแรงดึงและตัดโค้ง (universal testing machine, UTM) รุ่น AG –100kN



รูปที่ ก.3 เครื่องทดสอบแรงดึงและตัดโค้งรุ่น AG –100kN

4. เครื่องทดสอบแรงกระแทก รุ่น ZWICK 5102.202



รูปที่ ก.4 เครื่องทดสอบแรงกระแทก รุ่น ZWICK 5102.202

5. เครื่อง DMTA รุ่น DMTA V 9002-50010



รูปที่ ก.5 เครื่อง DMTA รุ่น DMTA V 9002-50010



รูปที่ ก.6 ช่องใส่ตัวอย่างของเครื่อง DMTA รุ่น DMTA V 9002-50010

6. เครื่อง DSC รุ่น PERKIN ELMER DSC7



รูปที่ ก.7 เครื่อง DSC รุ่น PERKIN ELMER DSC7

7. เครื่อง TGA รุ่น PERKIN ELMER TGA7



รูปที่ ก.8 เครื่อง TGA รุ่น PERKIN ELMER TGA7

8. กล้อง SEM รุ่น JSM-5800 LV



รูปที่ ก.9 กล้อง SEM รุ่น JSM-5800 LV

9. เครื่องเลื่อยจิกซอร์ (scroll saw) รุ่น CH-S16



รูปที่ ก.10 เครื่องเลื่อยจิกซอร์ (scroll saw) รุ่น CH-S16

10. เบ้าพิมพ์ที่ทำจากเทฟลอนเป็นรูปวงกลม



รูปที่ ก.11 เบ้าพิมพ์ที่ทำจากเทฟลอน

11. เส้นใยแก้วชนิดเส้นใยสานแบบสุ่ม



รูปที่ ก.12 เส้นใยแก้วชนิดเส้นใยสานแบบสุ่ม

ภาคผนวก ข

สมบัติการต้านแรงดึงของอีพ็อกซีสูตร I และ II อบแบบหลายระดับความร้อน

จากที่ได้กล่าวมาแล้วว่าในเบื้องต้นได้ออกแบบสภาวะอบในเตาอบไมโครเวฟของอีพ็อกซีเรซินสูตร I ทั้งหมด 21 สภาวะอบ โดยแบ่งเป็นการอบแบบ 2 ชั้นตอน 16 สภาวะอบ และการอบ 3 ชั้นตอน 5 สภาวะอบ สภาวะอบของอีพ็อกซีสูตร I ได้แสดงไว้ในตารางที่ ข.1

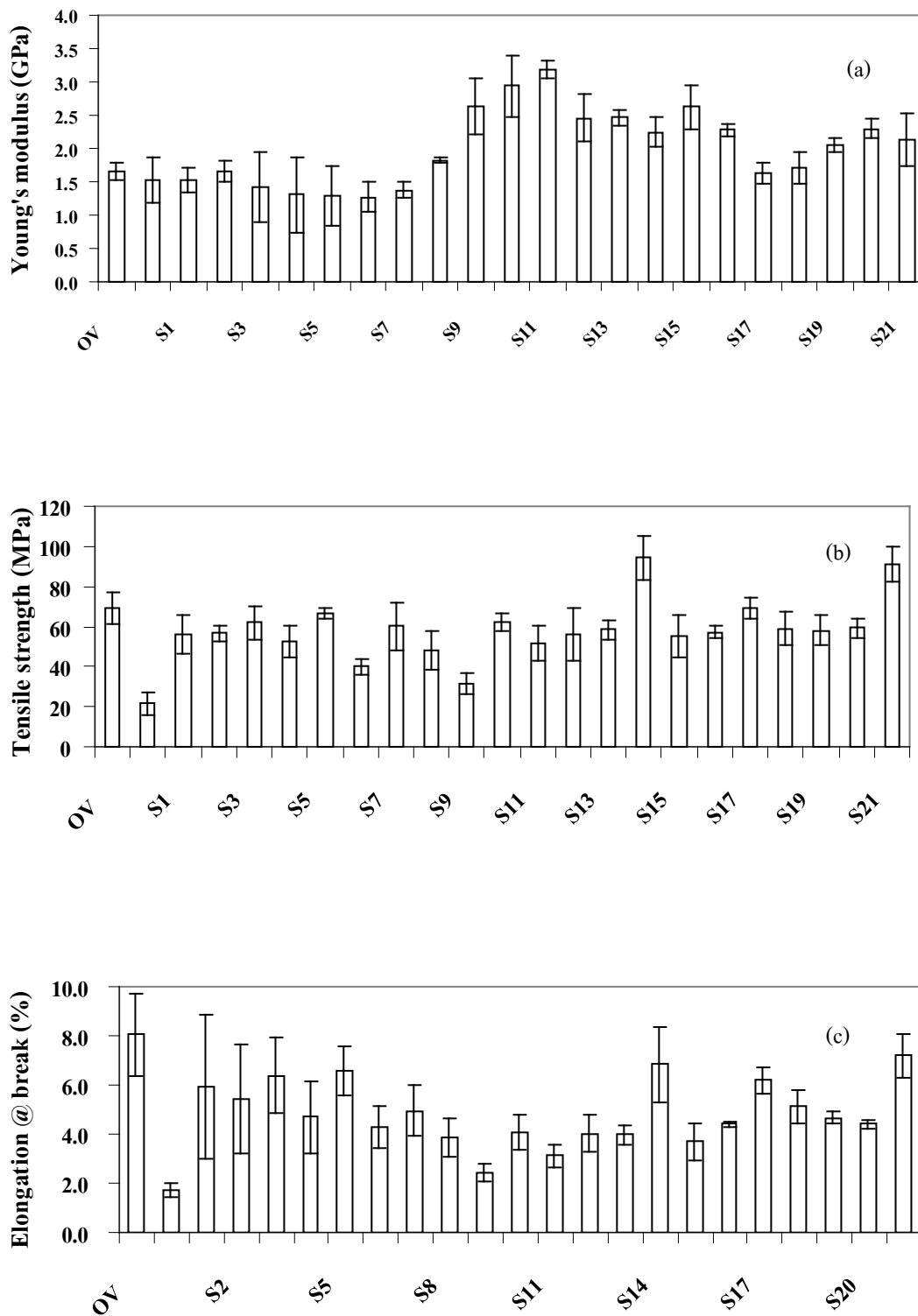
ตารางที่ ข.1 สภาวะอบของอีพ็อกซีสูตร I อบแบบแบบหลายระดับความร้อนในเตาอบไมโครเวฟ

สภาวะอบ			
S1	L2-10 + L3-8	S11	L2-25 + L3-5
S2	L2-10 + L3-10	S12	L2-25 + L4-5
S3	L2-10 + L4-5	S13	L2-25 + L5-5
S4	L2-5 + L3-10	S14	L2-25 + L6-5
S5	L2-5 + L4-5	S15	L2-30 + L5-5
S6	L2-15 + L3-5	S16	L2-20+L3-10
S7	L2-15 + L3-10	S17	L2-15 + L3-10 + L4-5
S8	L2-15 + L4-5	S18	L2-15 + L3-10 + L5-5
S9	L2-20 + L3-5	S19	L2-20 + L3-5 + L4-5
S10	L2-20 + L4-5	S20	L2-20 + L3-10 + L4-5
		S21	L2-20+L3-10+L5-5

สภาวะอบในตารางที่ ข.1 แสดงให้เห็นว่า S10 คือ 2S/1, S11 คือ 2S/2, S14 คือ 2S/3, S17 คือ 3S/1, S20 คือ 3S/2 และ S21 คือ 3S/3 ผลการทดสอบสมบัติการต้านแรงดึงที่ทดสอบได้แสดงไว้ในตารางที่ ข.2 และรูปที่ ข.1

ตารางที่ ข.2 สมบัติการต้านแรงดึงของอีพ็อกซีสูตร I อบแบบหลายระดับความร้อนในไมโครเวฟ

สภาวะอบ	มอดุลัสของยัง (GPa)		ความคงทนต่อแรงดึง (MPa)		ความเครียด ณ จุดขาด (%)	
	เฉลี่ย	S.D.	เฉลี่ย	S.D.	เฉลี่ย	S.D.
S1	1.53	0.18	55.80	9.50	5.94	2.93
S2	1.65	0.16	56.80	3.83	5.44	2.23
S3	1.43	0.53	61.90	8.20	6.37	1.53
S4	1.31	0.57	52.90	7.97	4.68	1.45
S5	1.29	0.44	66.70	2.48	6.58	1.01
S6	1.27	0.22	40.04	3.87	4.27	0.84
S7	1.38	0.12	60.04	11.66	4.95	1.05
S8	1.82	0.04	48.28	9.54	3.83	0.78
S9	2.63	0.42	31.96	5.26	2.40	0.36
S10	2.94	0.46	62.58	4.36	4.07	0.71
S11	3.18	0.13	51.41	8.80	3.12	0.45
S12	2.46	0.35	56.14	13.27	4.02	0.75
S13	2.47	0.12	58.43	4.97	3.99	0.39
S14	2.25	0.22	94.17	10.95	6.84	1.53
S15	2.62	0.34	55.24	10.27	3.68	0.76
S16	2.28	0.10	57.32	2.80	4.40	0.08
S17	1.63	0.15	69.02	5.05	6.19	0.55
S18	1.71	0.23	58.80	8.41	5.11	0.70
S19	2.05	0.10	58.08	7.57	4.67	0.27
S20	2.30	0.15	59.19	5.10	4.40	0.18
S21	2.13	0.39	91.11	8.34	7.19	0.91



รูปที่ ข.1 สมบัติการต้านแรงดึงของอีพ็อกซีเรซินสูตร I: (a) มอดุลัสของยัง; (b) ความคงทนต่อแรงดึง; (c) ค่าความเครียด ณ จุดขาด

ในเบื้องต้นออกแบบสภาวะอบในเตาอบไมโครเวฟของอีพ็อกซีเรซินสูตร II ทั้งหมด 9 สภาวะอบ โดยแบ่งเป็นการอบแบบ 2 ชั้นตอน 8 สภาวะอบ และการอบ 3 ชั้นตอน 1 สภาวะอบ สภาวะอบของอีพ็อกซีสูตร I ได้แสดงไว้ในตารางที่ ข.3

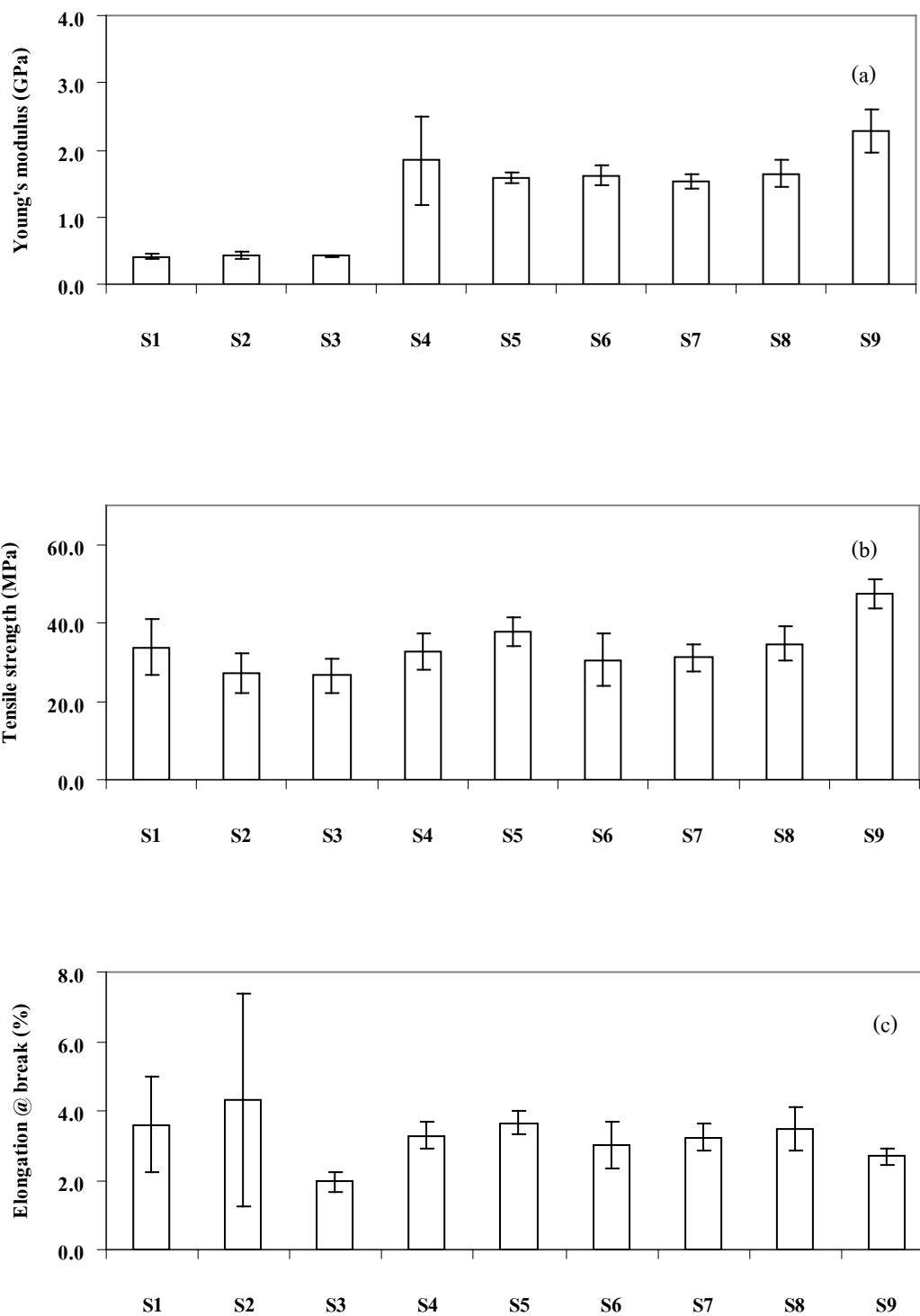
ตารางที่ ข.3 สมบัติการต้านแรงดึงของอีพ็อกซีสูตร II อบแบบหลายระดับความร้อนในไมโครเวฟ

สภาวะอบ			
S1	L2-5 + L4-3	S6	L2-10 + L4-3
S2	L2-5 + L3-5	S7	L2-10 + L4-5
S3	L2-3 + L4-3	S8	L3-5 + L4-3
S4	L2-10 + L3-5	S9	L2-10 + L3-7 + L4-3
S5	L2-10 + L3-7		

สภาวะอบในตารางที่ ข.3 แสดงให้เห็นว่า S7 คือ 2S/1, S8 คือ 2S/2 และ S9 คือ 3S/3 ผลการทดสอบสมบัติการต้านแรงดึงที่ทดสอบได้แสดงไว้ในตารางที่ ข.4 และรูปที่ ข.2

ตารางที่ ข.4 สมบัติการต้านแรงดึงของอีพ็อกซีสูตร I อบแบบหลายระดับความร้อนในไมโครเวฟ

สภาวะอบ	มอดูลัสของยัง (GPa)		ความคงทนต่อแรงดึง (MPa)		ความเครียด ณ จุดขาด (%)	
	เฉลี่ย	S.D.	เฉลี่ย	S.D.	เฉลี่ย	S.D.
S1	0.41	0.04	33.67	7.17	3.60	1.37
S2	0.42	0.05	27.19	5.19	4.30	3.07
S3	0.42	0.02	26.54	4.46	1.95	0.30
S4	1.84	0.66	32.81	4.60	3.29	0.39
S5	1.59	0.08	37.77	3.69	3.66	0.32
S6	1.62	0.16	30.59	6.79	3.03	0.68
S7	1.53	0.10	31.22	3.42	3.24	0.38
S8	1.65	0.20	34.66	4.29	3.47	0.63
S9	2.29	0.32	47.48	3.52	2.69	0.23



รูปที่ 4 สมบัติการต้านแรงดึงของอีพ็อกซีเรซินสูตร II: (a) โมดูลัสของยัง; (b) ความคงทนต่อแรงดึง; (c) ค่าความเครียด ณ จุดขาด

ภาคผนวก ค

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Comparison between Microwave and Thermal Cure of Glass Fiber - Epoxy Composites: Effect of Microwave - Heating Cycle on Mechanical Properties

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Comparison between Microwave and Thermal Curing of Glass Fiber - Epoxy Composites: Effect of Microwave - Heating Cycle on Mechanical properties

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ABSTRACT:

The objective of this study was to compare the mechanical properties between epoxy composites cured by thermal heating and microwave heating. Epoxy-anhydride (100:80) resins reinforced with glass fiber were cured in a domestic microwave oven and in a thermal oven. Hardening agents included methyl tetrahydrophthalic anhydride (MTHPA) and methyl hexahydrophthalic anhydride (MHHPA). For composites containing MTHPA and MHHPA, thermal curing was performed at 150°C for 25 and 15 min respectively. Microwave curing was carried out at various conditions, including 1-step, 2-step, and 3-step heating cycle, whereby each cycle employed different power level and time. Tensile properties, notched Izod impact resistance and flexural properties (three-point bending) were tested according to ASTM standards. It is found that the microwave-cured composites produced mechanical properties as good as the thermally cured composites. The 2-step and 3-step heating cycle using in the microwave curing process produced better mechanical properties higher than those obtained from the microwaved 1-step and thermally curing process. This is attributed to the slow increase in temperature during the beginning of the microwave curing process whereby the very low power level was applied in the first cycle of the multi-step heating process. This affected the slower rate of viscosity increment, resulting in better wettability of the glass fiber with enhanced interfacial adhesion between the fibers and the resins. The viscosity of resins affected the homogeneity of the crosslinked structure. Therefore, rapid increment in viscosity may cause defects in the structure because of the entrapment of uncrosslinked resins.

Key words: composites, crosslinking, curing of polymers, resins, glass fiber, epoxy

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INTRODUCTION

Since the mid-1980s, there has been a great deal of interest in microwave-cured processing of polymers. There have been a lot of researchers in the area of microwave-cured processing for epoxy resins as reviewed by Tanrattanakul and SaeTiaw¹. Microwave processing for polymer applications include crosslinking of polymer networks, polymerization of thermoplastics, curing of laminates, and joining and repairing of composites. The use of microwave-cured processing is expected to greatly reduce curing time and therefore the operating cost would be lower. A reduction in residual stress in the processed materials and an improvement in the final properties of the material are to be expected. Although most published articles of microwave-cured processing in polymer have been reported on crosslinking and polymerization of resins, however some researchers studied the microwave-cured composites, for examples, glass fiber/epoxy composites²⁻⁸, glass fiber/epoxy laminates⁹, carbon fiber/epoxy composites^{10,11}, glass-graphite/polyimide composites¹², carbon fiber/polyimide composites¹³, glass fiber/PMMA composites^{14,15}, graphite/epoxy laminates¹⁶, and thermoplastic composites¹⁷. Boey et al.²⁻⁴ showed that the microwave-cured epoxy-amine system reinforced with glass fiber had strength and stiffness as high as or better than that cured in a thermal curing process. They suggested that the two main process parameters affecting the final mechanical properties of the thermoset composites are the cure cycle and the reduction in void content. To effect the former, a conventional thermal process is used normally, with the cycle duration lasting a matter of hours. It is commonly known that in the case of polymer matrix composites, the load is taken mainly by the fiber and the fiber-matrix interfacial strength is very important due to load transfer. Interfacial properties of the microwave-cured composites have been reported^{6,7}. In general, the fiber-matrix interface is considered to be an intensive chemico-physical linking which depends on the local curing process, or more precisely, local thermal transfer across the interface⁶. For the E-glass fiber/epoxy system, the E-glass fiber cannot be heated by microwaves due to the transparency, the epoxy is heated and it then heats the E-glass fibers by thermal conduction. So heat passes through the interface from the epoxy to the glass fiber. In the case of thermal curing, the E-glass fibers are heated first and then the epoxy. The thermal gradient across the interface decreases from the fiber to the epoxy. Bai and Djafari⁶ reported that although the microwave-cured samples provided more voids but their mechanical properties were similar to those of the thermally cured samples, and the fiber-matrix interface of the microwave-cured samples was

stronger than that of the thermally cured samples. They proposed that if the curing is too fast and the pressure is too low, the voids are susceptible to being trapped in the materials after curing, which results in a degradation of properties. Yue and Looi⁷ also found that the interfacial shear strength of the microwave-cured composites was higher, but the strength from the pull-out test became lower. Liu et al¹² employed a domestic microwave oven for fabricating polyimide composites by using multi-step heating cycle because of the reaction path of resin used. They mentioned that the electrically conducting fibers, such as graphite and carbon fibers, absorb the microwave energy more efficiently than the nonconducting materials, and microwave process may enhance the bonding between resin and fiber matrix. Fang and Scola¹³ reported that microwave-cured carbon fiber/polyimide composites showed better interfacial adhesion than that of thermally cured composites.

The aim of this study was to study the processability of microwave curing process for epoxy-anhydride system reinforced with glass fiber by using a domestic microwave oven. Mechanical properties of the microwave-cured composites have been compared to those of the conventional thermal cured composite. The improvement of mechanical properties of the microwave-cured composites and the origin of this improvement will be discussed. The direct comparisons between the kinetics of curing activated by thermal and microwave heating are beyond the scope of this study, and the kinetic mechanisms during the polymerization of the reactive system are not the aim of this article.

EXPERIMENTAL

Materials

The epoxy resin was a general-purpose-grade of diglycidylether of bisphenol A (DGEBA) with $n = 0.15$ and epoxy equivalent weight (EEW) = 184 – 189 grams/equivalent. Two hardeners were employed: methyl tetrahydrophthalic anhydride (MTHPA) and methyl hexahydrophthalic anhydride (MHHPA). The accelerator included tris-2,4,6-dimethyl aminomethyl phenol (DMP-30). MTHPA contained an unknown accelerator, whereas MHHPA contained no accelerator. The glass fiber was chopped strand mat with specific weight = 300 g/m². All chemicals were commercial-grade and were used as received.

Sample preparation

The main suppliers of the anhydride hardeners suggested using approximately 80 – 90 wt % of the anhydride/epoxy stoichiometric ratio to obtain better properties. For that reason, we employed a ratio of 80:100 anhydride/epoxy. The concentration of the accelerator (DMP-30) was 4 parts per hundred parts of epoxy resin. The sample designation and compositions are listed in Table I. After good mixing, air bubbles were released from the resin before it was poured into a mold. A Teflon mold (20 cm in diameter and 5 cm deep) was used for both thermal and microwave curing. The resin and the glass fiber were weighed to maintain a constant resin-to-fiber ratio (15 wt% fiber). After pouring the resin for 1/4 of mold volume, a glass fiber mat soaked with the resin was placed into the mold, and the rest of the resin was filled. A conventional oven was employed for thermal curing. Microwave curing was performed in a domestic, commercial microwave oven at a frequency of 2.45 GHz. The microwave oven was equipped with a turntable to prevent formation of hot spots due to non-uniform heating. This microwave oven was fitted with a voltage controller to facilitate the processing power (to be specified). The maximum output is 800 W, and the power output can be manually adjusted between 10 to 100%, represented by power levels (L1 –L10). Each power level consisted of a time period when the power was on followed by a period when the power was off, and the timings are given in Table II. The microwave oven calibration was reported earlier¹. In this work, the applied power was based on physical performance and mechanical properties of cured samples. No air bubbles and no burning were criteria for good performance specimens. The heating conditions for microwave and thermal curing are described in Table III. Microwave curing processes were classified into 3 types: 1-step heating (1S), 2-step heating (2S) and 3-step heating (3S). The single step heating (1S) was done by using only one power level. The multi-step heating was done by using two or three power levels successively. Based on our product design, thermal curing was operated at 150°C and cure time should be between 15 – 30 min. The composite I needed 25 min to get a solid specimen, whereas the composite II could be solidified within 15 min. Initially curing condition in the microwave oven was produced by trial and error, and the aim was to use the lowest power level and the shortest time. Curing conditions for both composites were not necessary to be similar.

Mechanical property testing

The tensile properties, flexural properties (three-point bending) and notched Izod impact resistance were tested according to ASTM D638, ASTM D790 and ASTM D256 respectively. The tensile testing was conducted at a tension speed of 5 mm/min and at a gauge length of 50 mm. The three-point-bending test was executed at a speed of 5.3 mm/min with a span width of 100 mm; the specimen dimensions were 25 mm by 120 mm. The impact resistance was tested with a 2J-pendulum. The specimen thickness was approximately 3.5 mm. Five specimens or more were tested for every sample for all the testings.

Sample characterization

The extent of conversion of the cured samples was determined by using differential scanning calorimetry (DSC) at a heating rate of 10°C/min from 30 to 300°C. The dynamic mechanical thermal analysis (DMTA) was employed to investigate α transitions. The testing was performed in a three-point-bending mode at a heating rate of 5°C/min with a strain control of 0.02%. The applied frequency was 1.8 Hz within the temperature range of -120 to 250°C. The thermal gravimetric analysis (TGA) was performed at a heating rate of 10°C/min from 30 to 800°C under nitrogen environment. Fractured surfaces of impact-tested specimens were coated with gold prior to observation with a scanning electron microscope (SEM). An increase in temperature of curing resin was investigated. After curing at a certain time, the resin was taken away from the heating source and the resin temperature at the center of the mold was measured immediately by using an infrared thermometer. This process took time approximately 5 s. The temperature profile was plotted as a function of cure time. Viscosity of resin cured in a certain time was determined by using Brookfield™ viscometer. Those cured resins were kept in the freezer (-10°C) prior to measurement.

RESULTS AND DISCUSSION

Mechanical properties of composites

Figures 1 – 3 represent tensile properties, flexural properties and impact strength of the composite I respectively. The “OV” (thermal curing) and “1S” (1-step microwave curing) samples are similar in terms of single step process. The thermally cured samples showed higher tensile and flexural properties than the microwaved samples, except strain at break. In contrast,

impact strength of the microwaved samples was higher. Mechanical properties of the composite II are shown in Figures 4 – 6. Comparing the “OV” to “IS” samples, the microwaved sample exhibited higher flexural modulus and strength, whereas the rest of their mechanical properties was lower than those of thermally cured samples. Considering the curing time of both composites, the microwaved samples were cured under shorter time period. The composite I took 25 and 10 min in the thermal oven and microwave oven respectively. The composite II took 15 and 7 min in the thermal oven and microwave oven respectively. As mentioned earlier, the requirement for microwave curing condition was using the minimum power level and time. For single step curing of the composite I, the power level 3 (L3) was the minimum applicable level, however the cure time cannot be longer than 10 min because if more than 10 min used, the specimens will be burnt. Likewise, curing at L3 for 7 min was the mildest condition for 1-step heating of the composite II. The higher power level or the longer time caused the samples to be burnt or very brittle. For a domestic microwave oven, the setting time is not equal to the actual heating time¹. The actual heating time for L3 at 10 and 7 min was 180 and 125 s respectively. This means the microwave oven spent only 30% of the setting time for irradiation. Although we could obtain good mechanical properties from the single step process with shorter time in microwave oven, we realized that better mechanical properties of the microwaved samples could be derived if we used the proper heating condition.

It is well known that microwave heating is different from thermal heating. The microwave energy is absorbed by the molecules through the polarization or dipole reorientation of functional groups, which is consequently converted into thermal energy¹². As a result, heat is generated within the molecule, and, thereby, a homogeneous heating pattern is created in the materials. This process is attributed to inside-out solidification of curing resin. On the other hands, in conventional thermal heating, heat energy is transferred from the surfaces (outside) to inside of the material by the conduction of the heating medium, resulting in outside-in solidification. Different states of heating between microwave and thermal heat may cause differences in viscosity and temperature profile of curing resin, which should affect crosslinking, fiber-matrix interfacial adhesion, and homogeneity of resin-microstructure. We believed that if we increased cure time in the microwave oven, we would receive better mechanical properties. To do so, we needed to preheat the resin. Therefore, our strategy was using cycled heating by preheating in the beginning and followed by regular heating, as called “multi-step heating”.

As expected, the multi-step process (2S and 3S) increased the mechanical properties as shown in Figures 1 - 6. Remarkably, modulus and strength of both composites cured by multi-step heating were higher than those of thermally cured samples and single-step microwaved samples. Because the proper condition for multi-step heating was difficult to predict, therefore the initial experiment was by trial and error. However, we have tried several conditions for both composites, and conditions which offered good mechanical properties are shown in Table III. The composite I needed longer cure time than the composite II, this may be due to different accelerator type and content and different hardener type. Based on the preliminary study, the 3-step heating of the composite I took too much cure time, hence, we chose only one condition (3S-1). The 2S-3 heating condition seemed to be the best condition of the composite I. It showed extremely high flexural properties and higher tensile strength than the 3S-1 and OV sample. Conclusively, the 2-step heating is appropriate for the composite I in this study. There was no effort to obtain the very good mechanical properties from the 3-step heating of the composite. In contrast, the 3S-3 sample, 3-step heating, provided the best mechanical properties among the composite II. All its properties were higher than those of OV-, 1S-, and 2S-samples. In our studies it is necessary to employ the multi-step heating in the microwave oven to obtain higher mechanical properties and this procedure also yielded higher mechanical properties than the thermal curing. We believe that the interfacial adhesion will increase when the right multi-step process is used, further proved by the increase in flexural strength.

Curing characteristics

It was successful to obtain the high modulus and strength from the multi-step heating process in the microwave oven, 2S-3 and 3S-3 for the composite I and II, respectively. It was interesting to study why the multi-step heating was better than the single step heating and why the composite I preferred the 2-step heating whereas the composite II preferred the 3-step heating. Based on DSC results, no exothermic peak was observed. Normally, we expected that higher glass transition temperature of the composite showed higher modulus and strength. The α transition temperature of the 1S and 3S-3 samples of the composite II were 138 and 143°C respectively (Figure 7). Unfortunately, the β transition temperature could not be observed. The storage modulus at the plateau region (at 200°C) of the 3S-3 sample was higher than that of the 1S sample, reflecting the higher crosslink density. Although the difference in this transition

temperature was not to a great extent, DSC results showed significant differences. T_g of the 1S, 2S-1, and 3S-3 samples became 78, 106, and 115°C respectively. As a result, the relationship between mechanical properties and molecular architecture (or morphology) of the composites in this study is corresponded to the above assumption. However, we would like to state that the differences in T_g may not always relate to mechanical properties. For example, the thermally cured carbon fiber/polyimide composite¹³ showed lower T_g but higher flexural strength than the microwave-cured composite. This is because the interfacial adhesion between fiber and matrix also plays an important role on the mechanical properties.

TGA technique exhibited very useful information. The TGA thermograms of 1S, 2S-1, and 3S-3 samples of the composite II are displayed in Figure 8. The 1S and 2S-1 samples showed 2-step degradation process and started degradation around 200°C, whereas the 3S-3 sample showed 1-step degradation process and started degradation after 240°C. An extent of the first degradation decreased from 6.6 % in the 1S sample to 4.2 % in the 2S-1 sample. It seemed that the crosslink density ranked in the following order: 3S-3 > 2S-1 > 1S. We verified these phenomena by investigating the resin II, containing no glass fiber. The experimental results were similar, the 1S and 3S-3 samples showed 2-step and 1-step degradation processes respectively (Figure 9). There are differences in the 1-step and 2-step degradation process due to the differences in microstructure or structure homogeneity of the resins. For some reasons, there were some defects in the crosslinked structure, some prepolymer or some uncrosslinked epoxy in the 1S and 2S-1 samples and this imperfection was attributed to the first degradation and relatively low mechanical properties. Therefore, the 3S-3 sample of the composite II was the best sample. This assumption was supported by TGA thermograms of the composite I as illustrated in Figure 10. The 3S-1 sample showed the small degradation before 200°C, whereas this degradation was not observed in the 2S-3 sample. As stated earlier, the 2-step heating process was the preferential process for the composite I. This is because the 3S-1 sample may contain imperfection as stated earlier, represented by the first degradation before 200°C. It appeared that TGA data coincided with its mechanical properties such as the higher mechanical properties and the higher degradation temperature. It is established that the lower degree of cure was observed in microwave samples and explained by the entrapment of reactive function within the network¹⁸. This is not in our study because DSC results showed no further crosslinking reaction,

therefore, we believed that the imperfection of the samples derived from the entrapment of uncrosslinked resin in the network.

Viscosity and temperature profile effect

We assumed that factors affecting structure homogeneity of epoxy resin and fiber-matrix interfacial adhesion were resin viscosity and temperature profile during curing process. Rapid increase in viscosity may cause imperfection such as defects in crosslinking because of the entrapment of uncrosslinked resin¹⁹. When the resin became too viscous in the early state of crosslinking process, flowability or diffusion of epoxy and hardener were lowered, which caused locally inhomogeneous structure. The viscosity effect, associated with the progress of the reaction, hindered more and more the Brownian motion and lowered the kinetics of curing²⁰. We have measured viscosity of resins cured in the thermal oven and microwave oven at a certain period. The setting temperature of the thermal oven was 150°C. Changes in viscosity during curing are shown in Figure 11. Viscosity increased with curing time. Some parts of the composite I were slightly solidified or became jelly-liked at the following conditions: L3 - 7.5 min and L5 - 2.5 min, whereas the following conditions provided solid fraction: L4 – L6 for 5 min. These specimens were unable to measure viscosity. In the same way, the composite II containing jelly-liked or solid-liked fraction was disregarded, including L2 - 15 min, L3 - 5 min, and L4 – 3 min. It appeared that the increase in viscosity of the resins obtained from the thermal oven and the microwave oven at L2 was similar, and the higher power level, the higher rate of changes in viscosity. Remarkably, viscosity at L2 for 25 min and 10 min of the composite I and II respectively were very high compared to viscosity at L3 for 5 min and 3 min of the composite I and II respectively. Concerning to heating condition of the composite I, the 1S sample was converted into a partial solid around 7.5 min and became a complete solid at 10 min at L3. Although, the 1S sample solidified prior to the 2S-3 sample (curing condition: L2/25min + L6/25min), its viscosity before gelation (3,420 cP at L3 - 5 min) was lower than that of the resin cured at L2 – 25 min (21,300 cP). This indicated that the rate of change in viscosity seemed to be more important than the viscosity before gelation and the slower rate was more favorable. We also observed the viscosity changes of the multi-step composite II, the 2S-1 and 3S-3 samples. Their curing conditions were L2/10min + L4/5min and L2/10min + L3/5min + L4/3min. Both samples became a partial solid at the second heating of cure cycle, L4 – 3 min and L3 – 5 min for

the 2S-1 and 3S-3 samples respectively. The viscosity before gelation of the 1S sample (98,900 cP at L3-3min) lowered than that of the 2S-1 and 3S-3 samples (134,000 cP at L2-10min). The system preferred relatively slow rate of increase in viscosity.

The temperature profile of the curing resins elucidated the effect of curing cycle. Figure 12 illustrates the temperature profile of both composites. Fresh resin was employed for each cure time, and sample size was the same as that prepared for mechanical properties testing. The thermal oven was set at 150°C, the microwave oven was set at L2 – L6 and also set for the multi-step condition. Temperature was measured immediately after turning off the microwave power or taking away from the thermal oven. Therefore, these temperatures reflect the true sample temperature. Temperature increased with increasing cure time, and some conditions showed a peak of the maximum temperature. These peaks represented the solidification temperature. For the 1-step heating process, the higher power level provided the higher rate of temperature increment, similarly to the viscosity behavior. The lowest rate of temperature increment was obtained from L2, and the maximum temperature at L2 was lower than 100°C for both composites. Undoubtedly, the resins could not be cured at L2, no matter how long the curing duration. The slow increase in temperature of L2 lowered the viscosity increment compared to using other power levels. The faster rate of temperature increment at L3 – L6 brought about the higher viscosity, which may accelerate the local crosslinking process or entrap the uncrosslinked epoxy in the network resulting in an inhomogeneous microstructure. For the multi-step heating of the composite I, the 3-step heating condition may be inappropriate, compared to the 2-step heating process. Obviously, the 3-step sample solidified faster than the 2-step one, as represented by the maximum temperature. Similar behavior was observed in the composite II, the 2-step cured sample became a solid prior to the 3-step cured sample (the better sample). This study showed that the slower solidification produced better mechanical properties. Similarly to the viscosity results, the slow rate of increase in temperature is preferable. It should be noted that the 2-step heating process could be better or worse than the 3-step, depending on the cure cycle. In order to obtain the optimum results, the best condition allowing the slow rates of temperature and viscosity increment must be available.

Fiber-matrix interfacial adhesion

The higher power level caused the higher temperature in the resin because the higher power level provided longer time for irradiation, thus more heat generation occurred inside the resins. This was attributed to higher viscosity. By using the very low power level (L2) to act as preheating and to gradually increase viscosity, this enhanced the wettability of glass fiber and promoted interfacial adhesion between glass fiber and epoxy resin. The effect of microwave resin preheating on RTM laminates was reported²¹. It was proposed that preheating altered the viscosity and thermal “age” of the thermosetting resins. It was anticipated that a lower resin viscosity would improve fiber wet-out, increasing the mechanical properties of the laminate. SEM micrographs of the composite I and II are demonstrated in Figures 13 and 14 respectively. No void in the matrix was observed in every sample. The interfacial adhesion could be observed from the fractured surface. The cleaner, smoother surface of the glass fiber indicated the lower interfacial adhesion because lesser matrix adhered on the fiber. We observed the entire fractured surface and randomly took photographs of each sample. More resin adhered to the fiber surface of the microwave-cured (multi-step) composite than to the fiber surface of the thermally cured composites. This suggests that adhesion of the resin to the fiber surface for the microwave-cured (multi-step) composite was better than in the thermally cured composite. The 2S-3 and 3S-3 sample of the composite I and II respectively, showed a considerable amount of resin adhering to the fiber surface, whereas the failure surface of the OV and 1S samples were essentially free of resin. This was a strong indication that better wetting of the fiber by the resin occurred in the multi-step microwave-cured system than in the thermally cured system. The interfacial adhesion of the present composites may be ranked in the following order: 2S-3 > 3S-1 > OV, 1S (for the composite I); 3S-3 > 2S-1 > 1S > OV (for the composite II). This result is similar to that reported by Bai and Djafari⁶ and Fang and Scola¹³, the fiber-matrix interface of the microwave-cured composites was stronger than that of the thermally cured composites. However, in the case of microwave curing, the cure cycle is one of the most important parameter that should be of concerned.

CONCLUSIONS

This work has shown that the microwave oven was able to cure the glass reinforced epoxy composites as good as or better than the thermal oven and the multi-step heating in the

microwave oven was necessary. Appropriate heating cycle in the microwave oven was critical to provide good mechanical properties. By means of preheating, the increase in temperature was not too high, this gave rise to the slow rate of increase in viscosity which improved fiber wet-out and reduced entrapment of uncrosslinked resin in the network. The rate of change in viscosity seemed to be more important than the viscosity before gelation, and the slow rate was preferable. The improvement in mechanical properties of the appropriate multi-step heating in the microwave oven was derived from better interfacial adhesion.

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TABLE I
Sample Designation and Composition

Composite	Hardener	Accelerator
I	MTHPA	Unknown
II	MHHPA	4% DMP-30

TABLE II
Duration of Microwave Heating at Each Power Level

Power setting (Level)	Duration power on (s)	Duration power off (s)
2	3	14
3	5	12
4	7	10
5	9	8
6	11	6

TABLE III
Heating Condition

Code	Composites I			Composites II		
	Source of heat	Condition	T* (sec)	Source of heat	Condition	T* (sec)
OV	Thermal oven	150°C, 25 min	1500	Thermal oven	150°C, 15 min	900
1S	Microwave oven	L3/10	180	Microwave oven	L3/7	125
2S-1		L2/20 + L4/5	339		L2/10 + L4/5	234
2S-2		L2/25 + L3/5	357		L3/5 + L4/3	167
2S-3		L2/25 + L6/5	465		L2/15 + L4/5	285
2S-4		L2/20 + L3/10	393		L2/10 + L4/7	285
2S-5		-			L3/5 + L4/5	216
3S-1		L2/20+L3/10+L5/5	555		L2/10+L3/5+L4/3	275
3S-2		-			L2/10+L3/5+L4/5	324
3S-3		-			L2/10+L3/7+L4/3	310
3S-4		-			L2/10+L3/3+L4/7	338
3S-5		-			L2/15+L3/5+L4/5	375

Note: Lx/y = curing at microwave power level “x” for “y” min. T* = actual heating time.

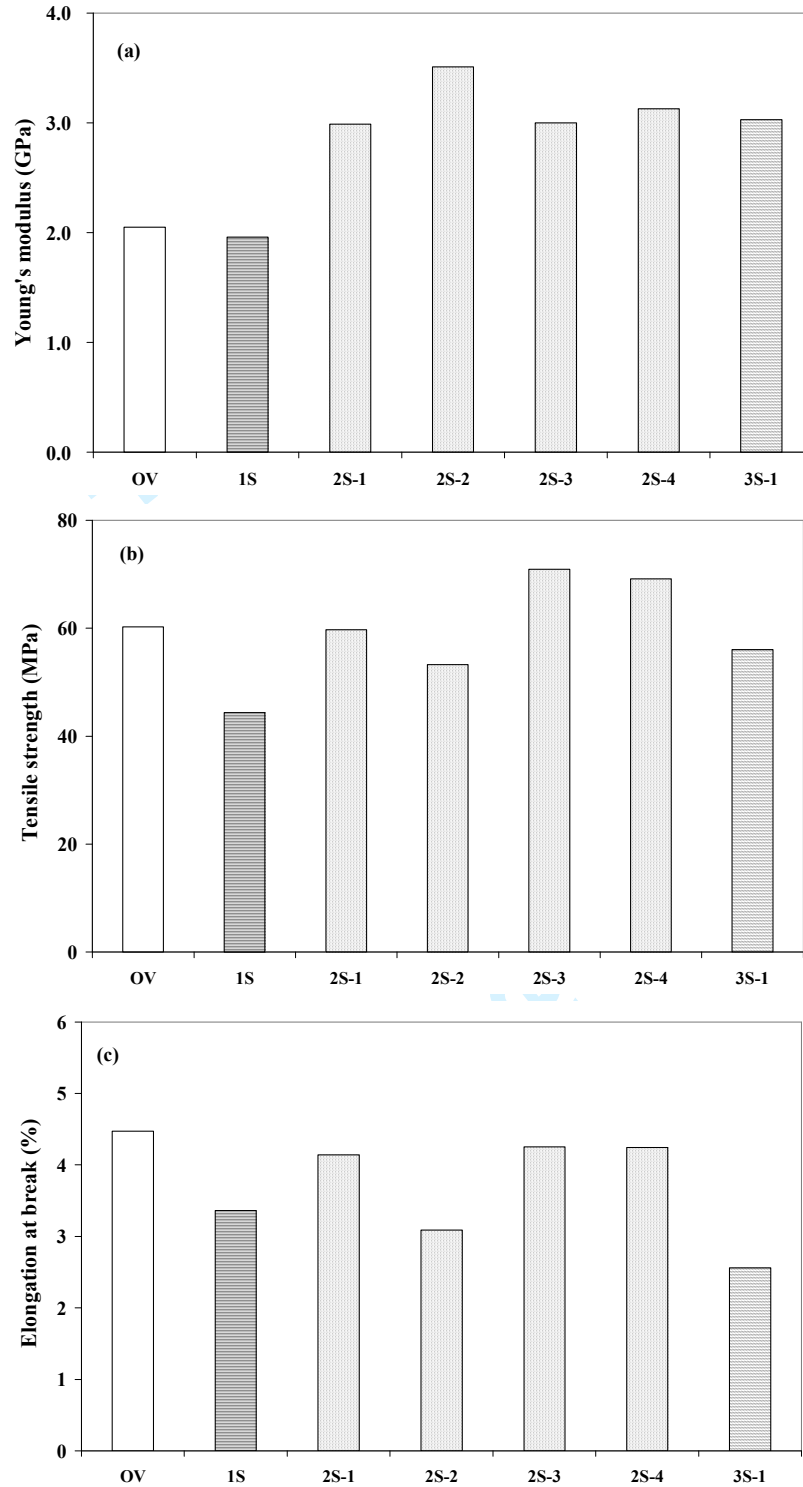


Figure 1 Tensile properties of composites I. (a) Young's modulus; (b) tensile strength; (c) elongation at break. OV= oven curing, 1S = 1-step curing, 2S = 2-step curing, and 3-S = 3-step curing.

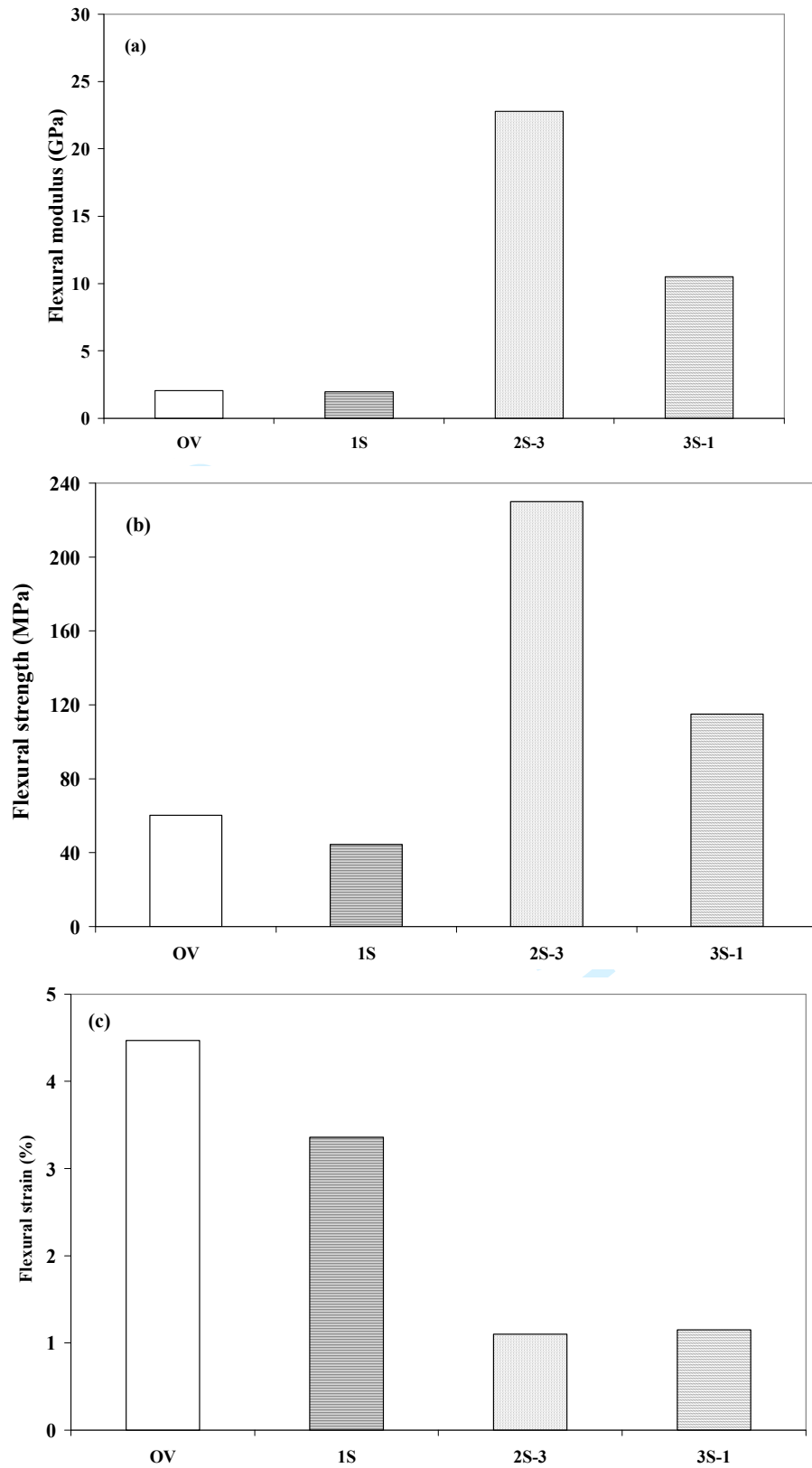


Figure 2 Flexural properties of composites I. (a) Flexural modulus; (b) flexural strength; (c) flexural strain.

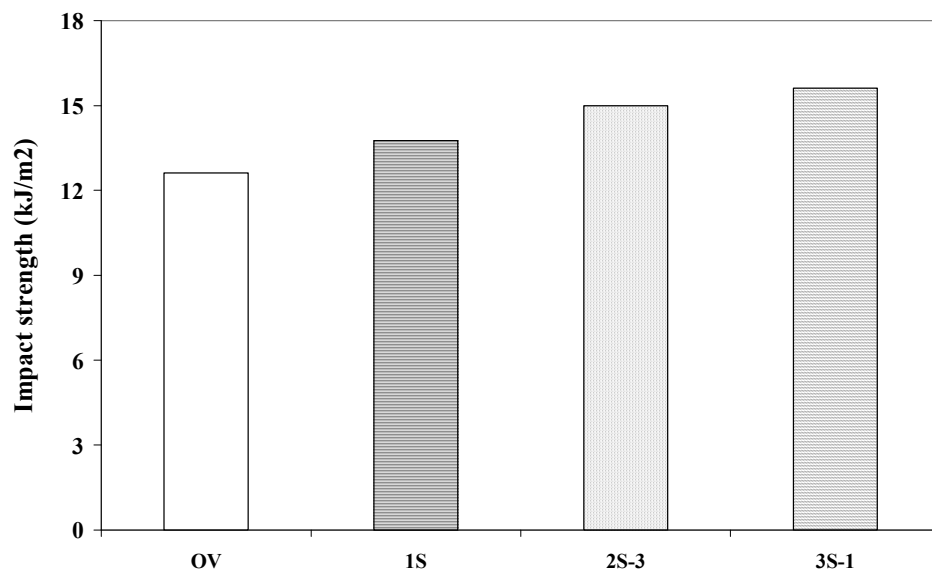


Figure 3 Impact strength of composites I.

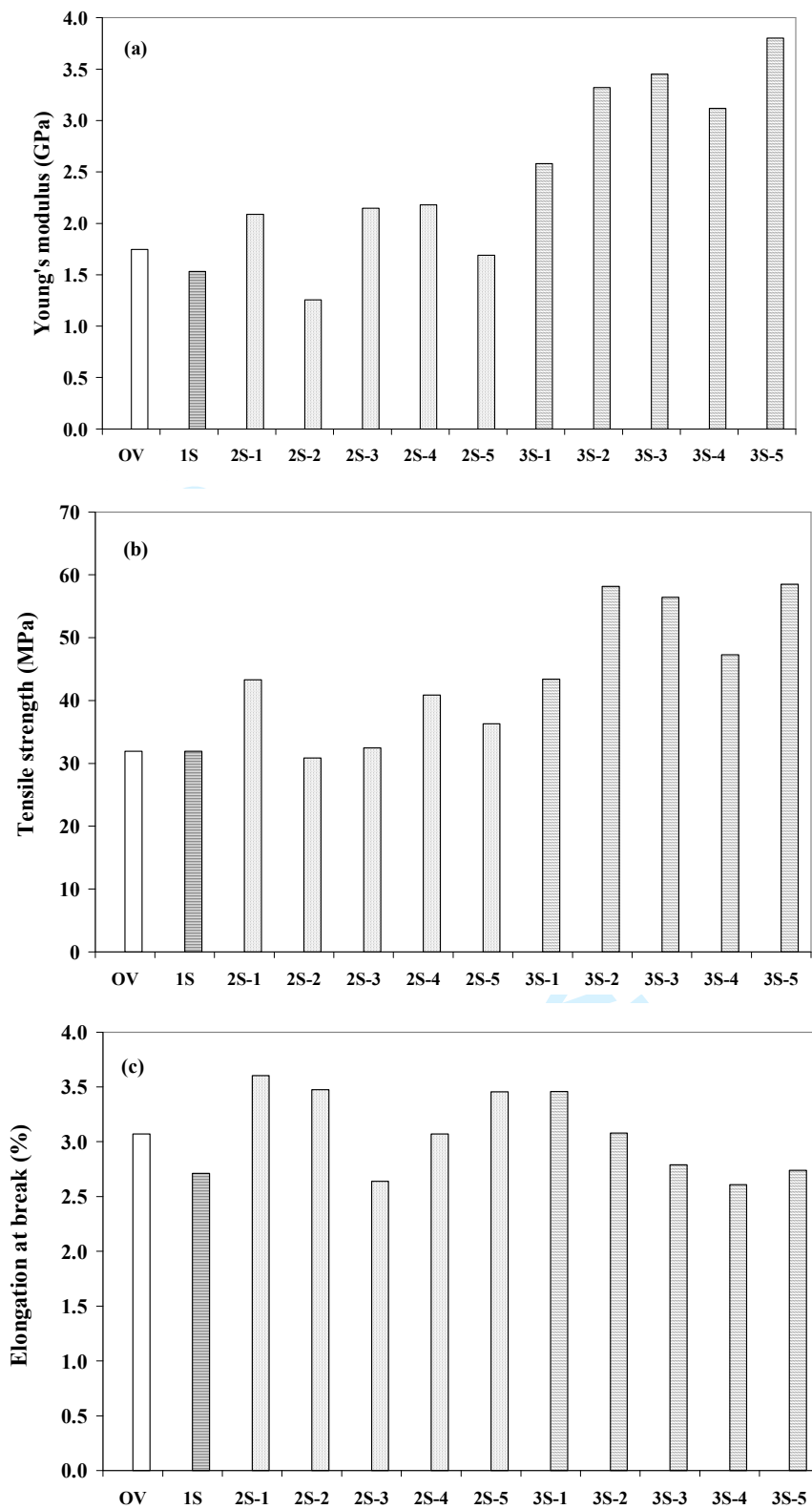


Figure 4 Tensile properties of composites II. (a) Young's modulus; (b) tensile strength; (c) elongation at break.

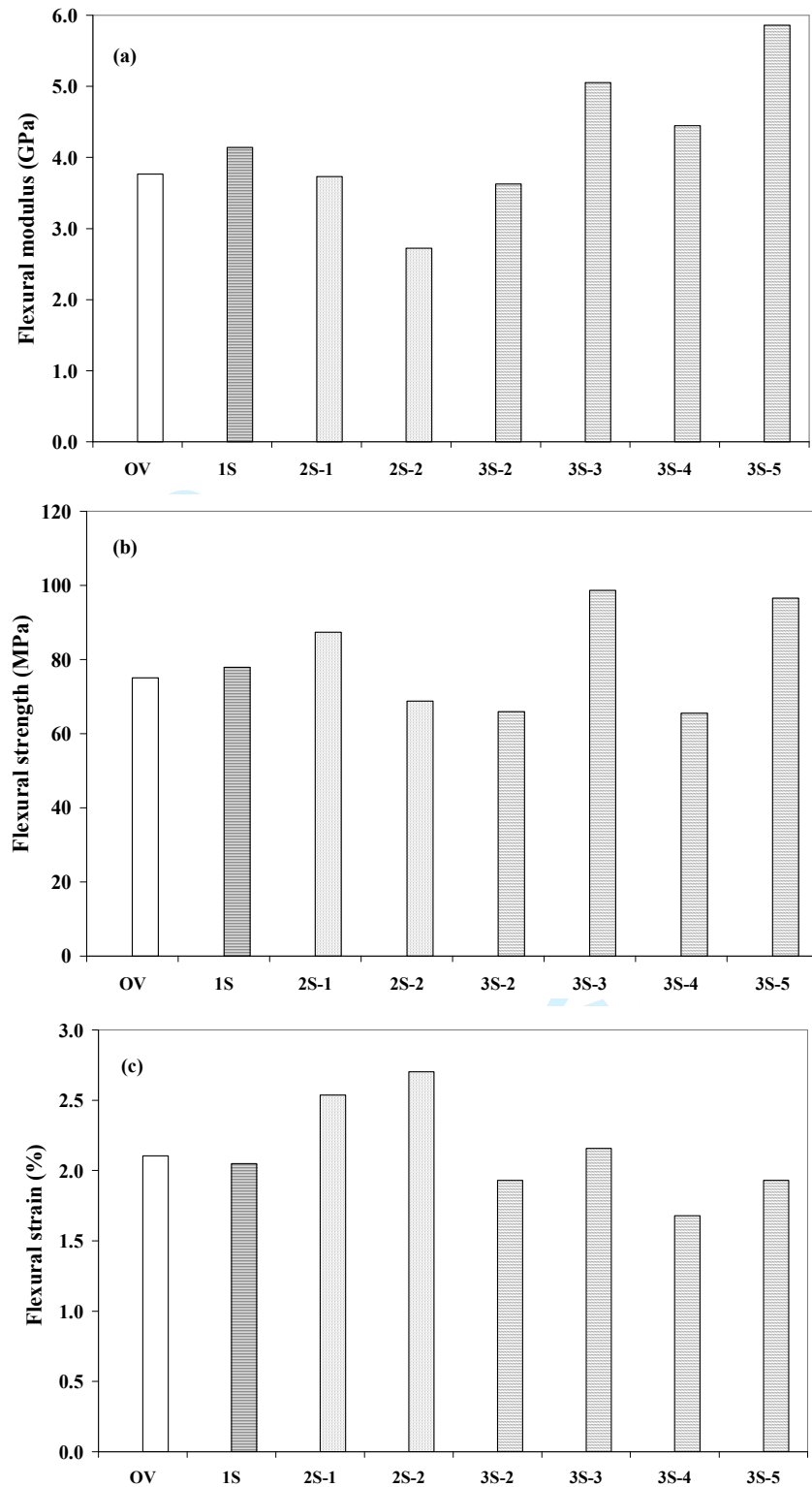


Figure 5 Flexural properties of composites II. (a) Flexural modulus; (b) flexural strength; (c) flexural strain.

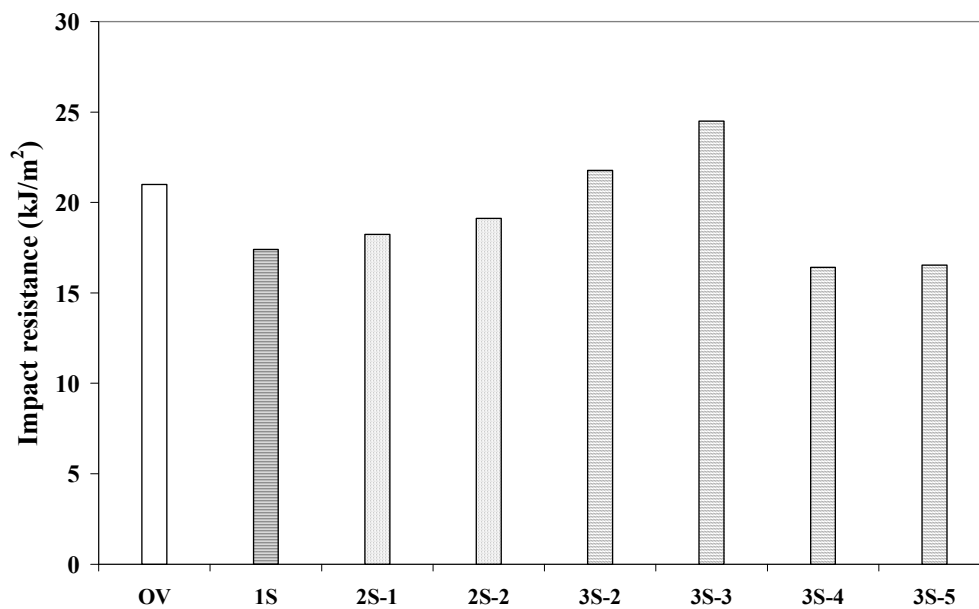


Figure 6 Impact strength of composites II.

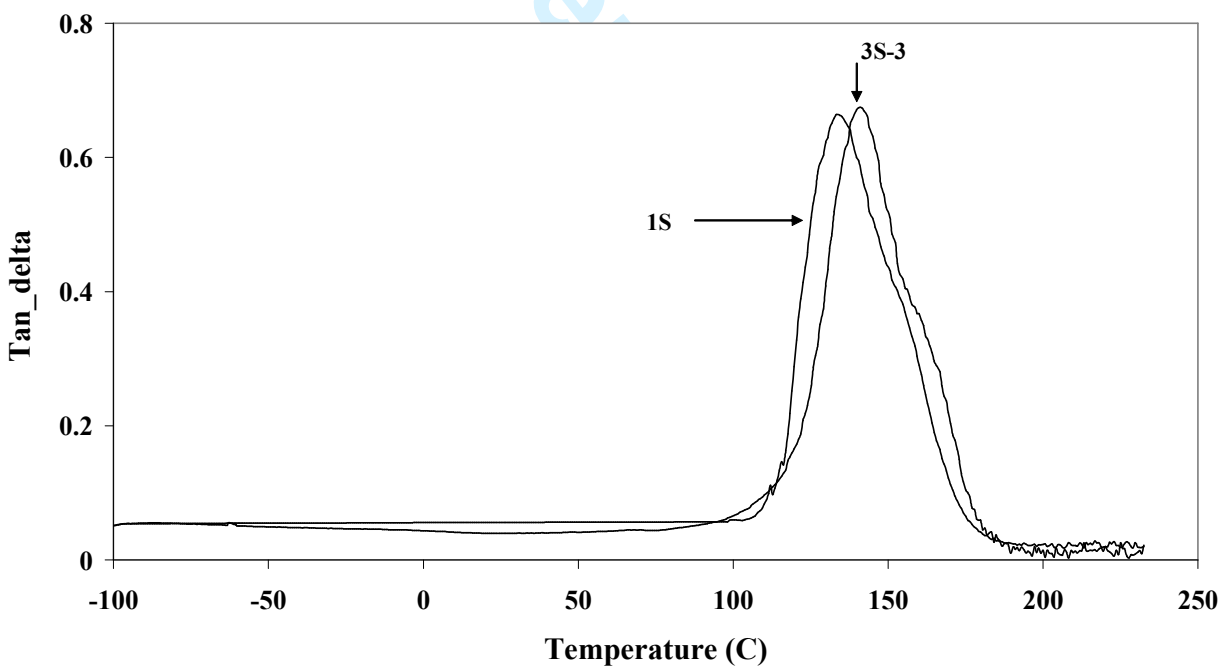


Figure 7 The α transition temperature of composites II. The 1S sample obtained from the 1-step heating process shows lower transition temperature than that obtained from the 3-step heating process.

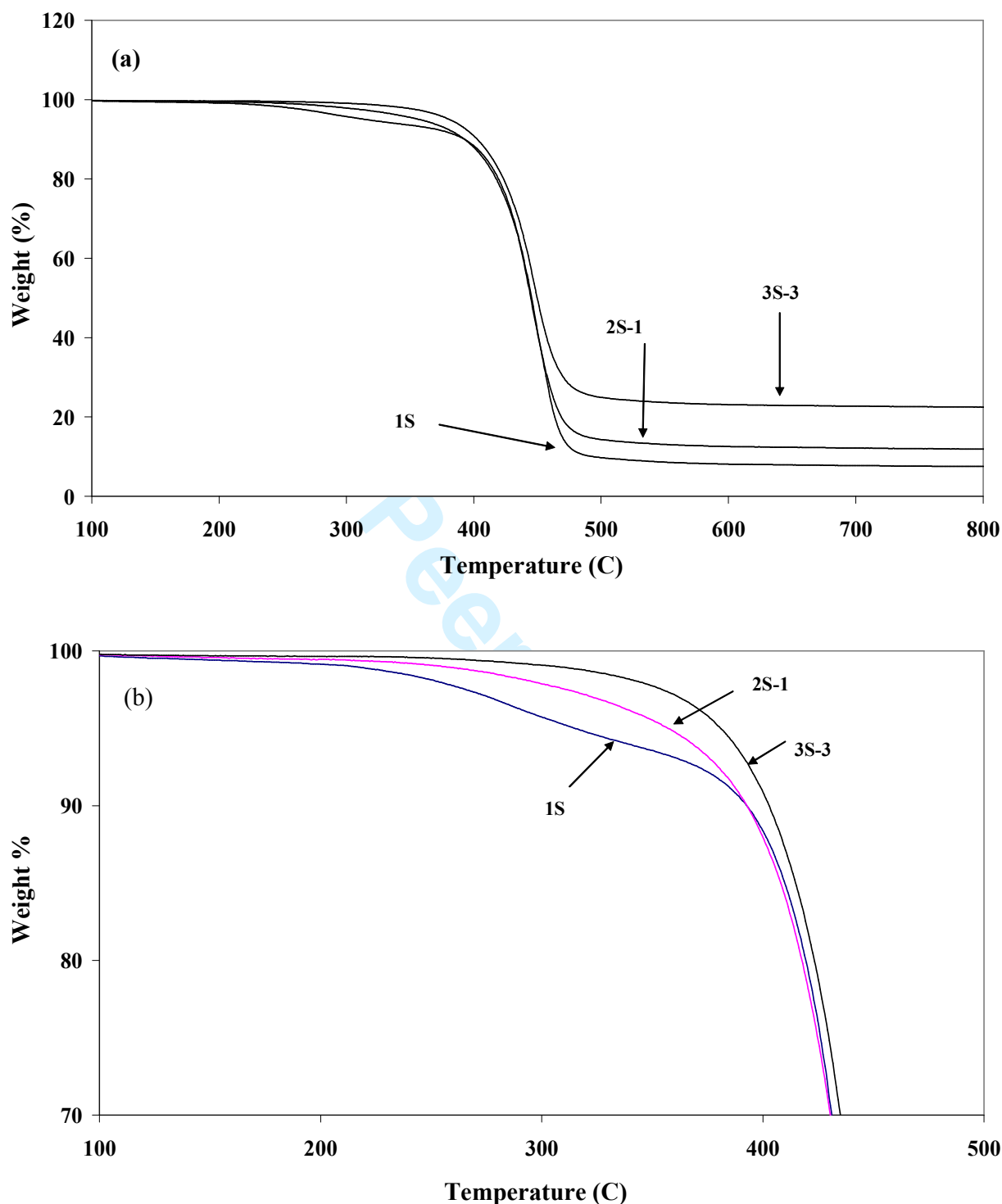


Figure 8 TGA thermograms of composites II. The 1S and 2S-1 samples (obtained from 1- and 2-step heating processes) show 2-step degradation process, indicating the entrapment of uncrosslinked epoxy in the network. The 3-step heating process offered highest crosslink density. Figure b is the enlarged scale of Figure a.

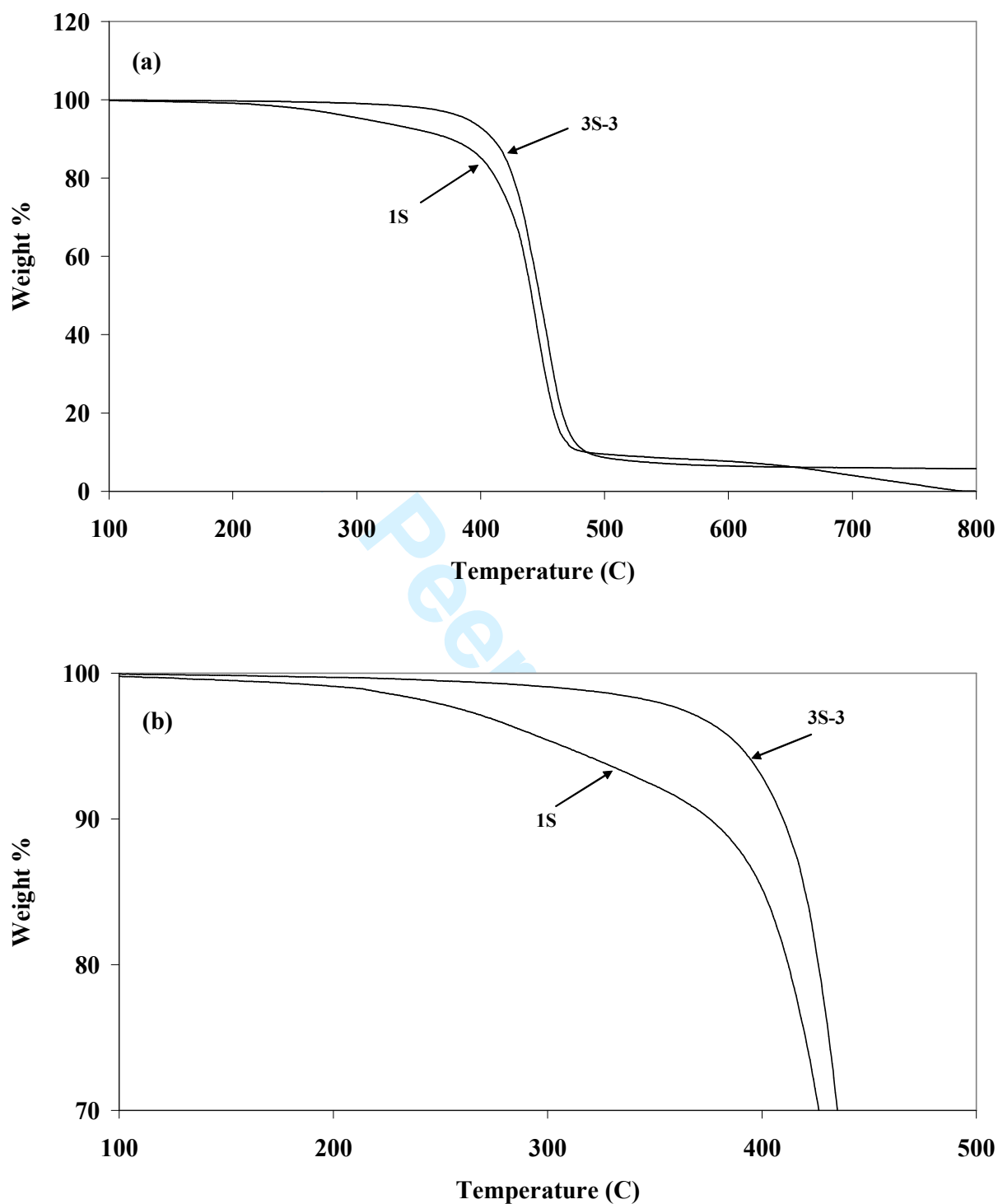


Figure 9 TGA thermograms of resins II. The 1S samples (1-step heating process) show 2-step degradation process, indicating the entrapment of uncrosslinked epoxy in the network. Figure b is the enlarged scale of Figure a.

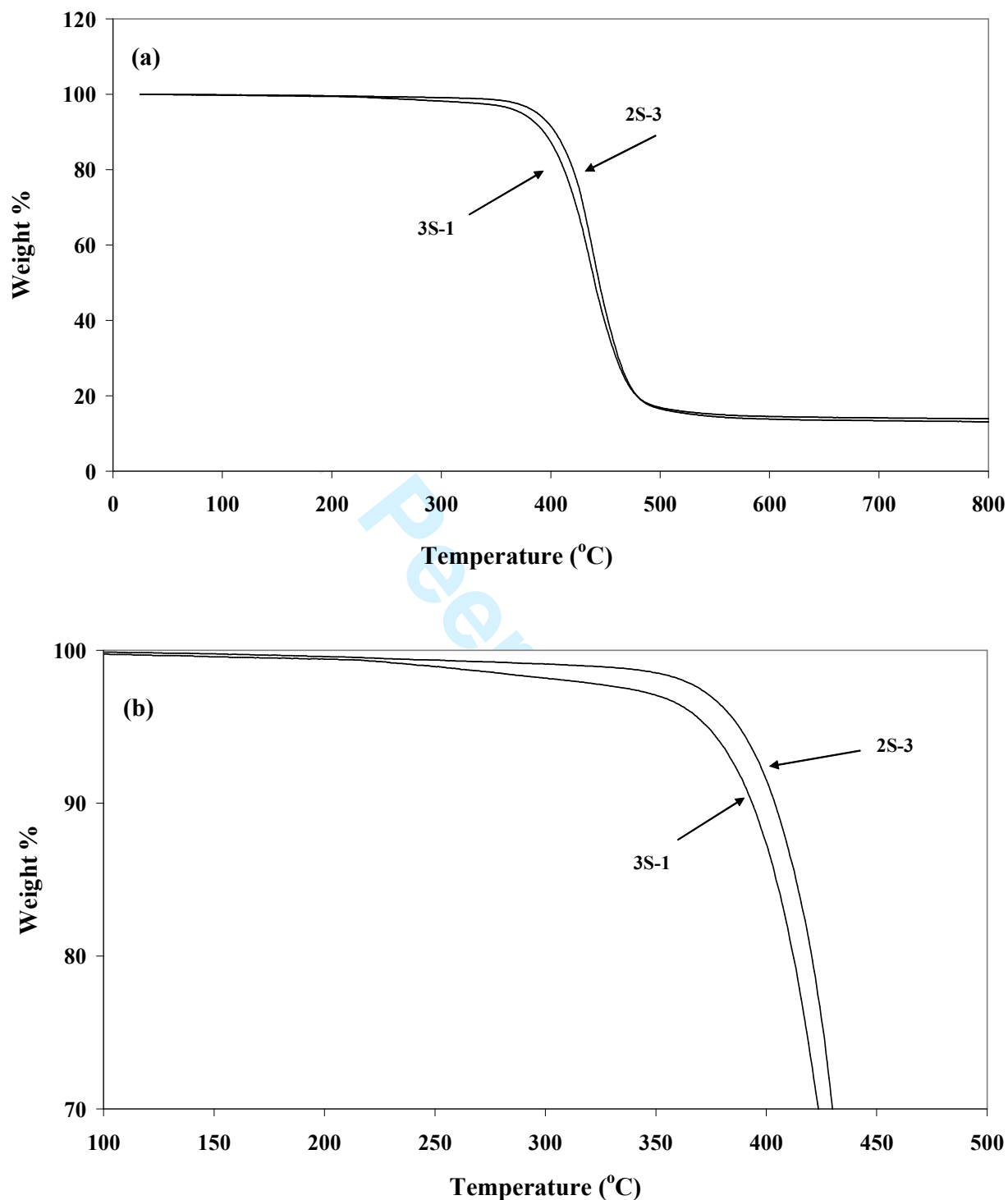


Figure 10 TGA thermograms of composites I. The 3S-1 sample degraded prior to the 2S-3 sample, indicating the higher crosslinking reaction in the 2S-3 sample. The entrapment of uncrosslinked epoxy in the network may occur in the 3S-1 sample. Figure b is the enlarged scale of Figure a.

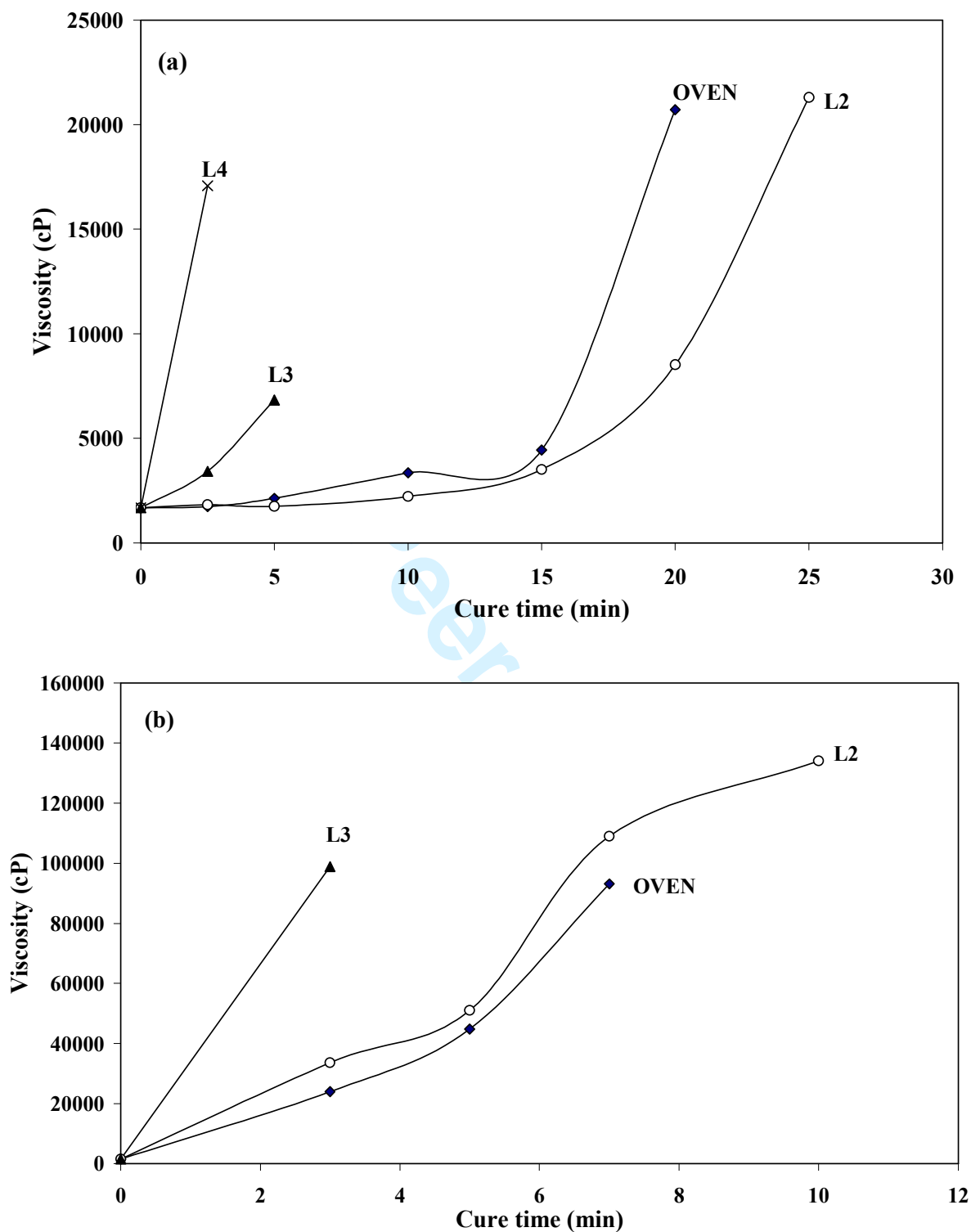


Figure 11 Viscosity of resin during curing in the thermal oven (OV) at 150°C and microwave oven at various power levels (L2 – L4) : (a) composite I; (b) composite II.

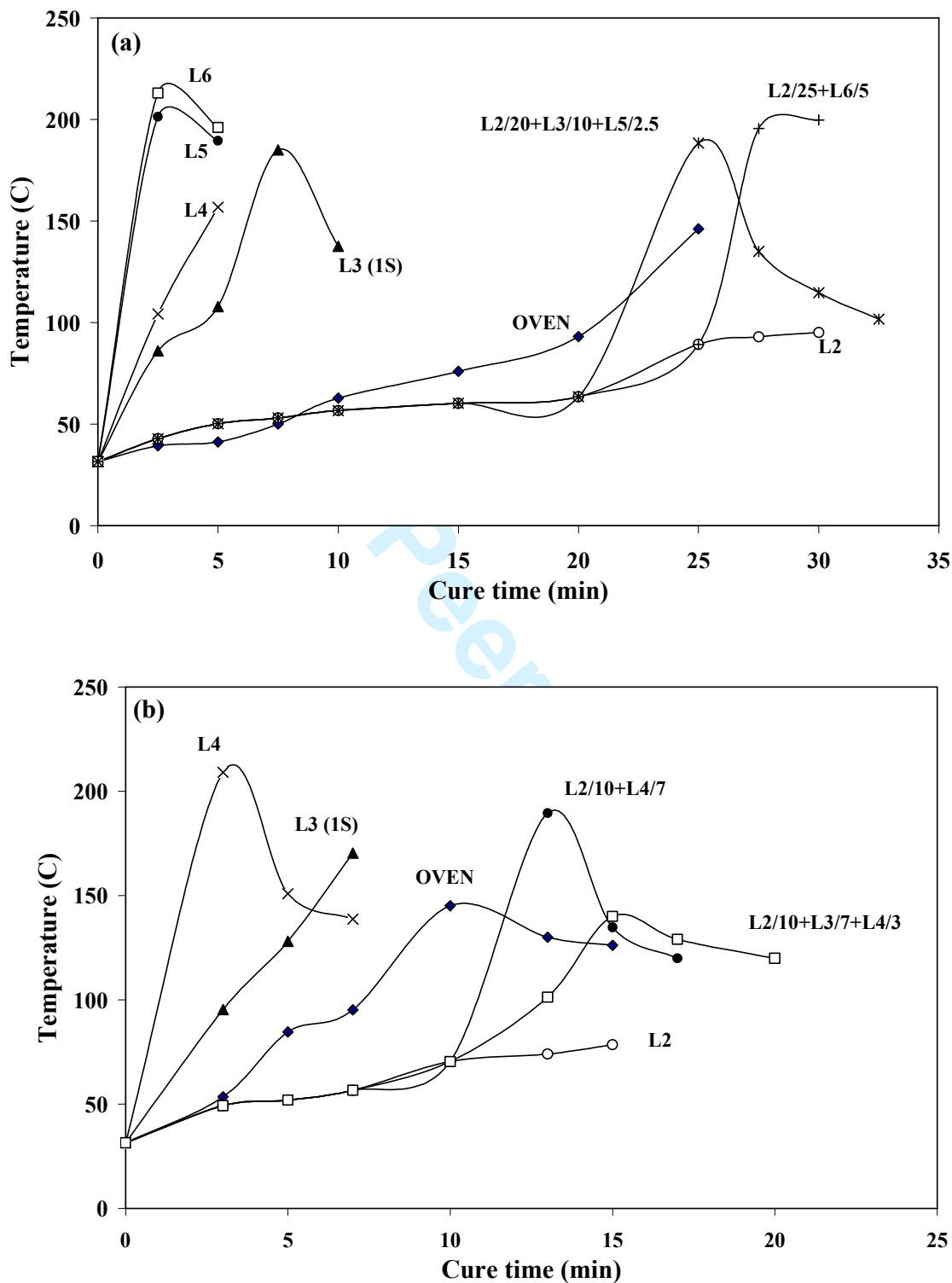


Figure 12 Temperature of resin during curing in the thermal oven (OV) at 150°C and microwave oven at various power levels : (a) composite I; (b) composite II.

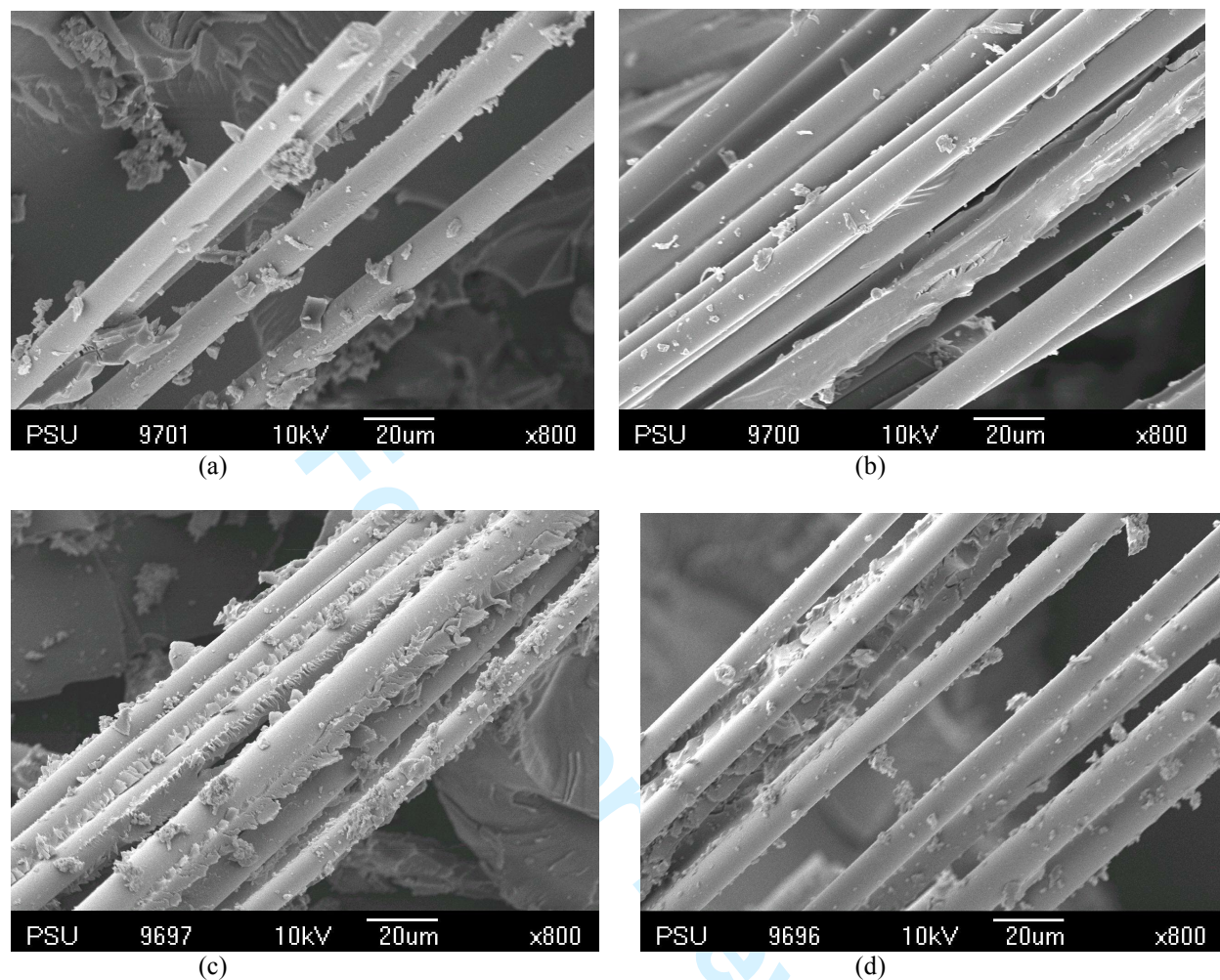


Figure 13 SEM micrographs of fractured surfaces of composites I : (a) the OV sample; (b) the 1S sample; (c) the 2S-3 sample; (d) the 3S-1 sample. The 2S-3 sample (c) showed most resin adhered on the fiber than other samples, indicating most interfacial adhesion in this sample.

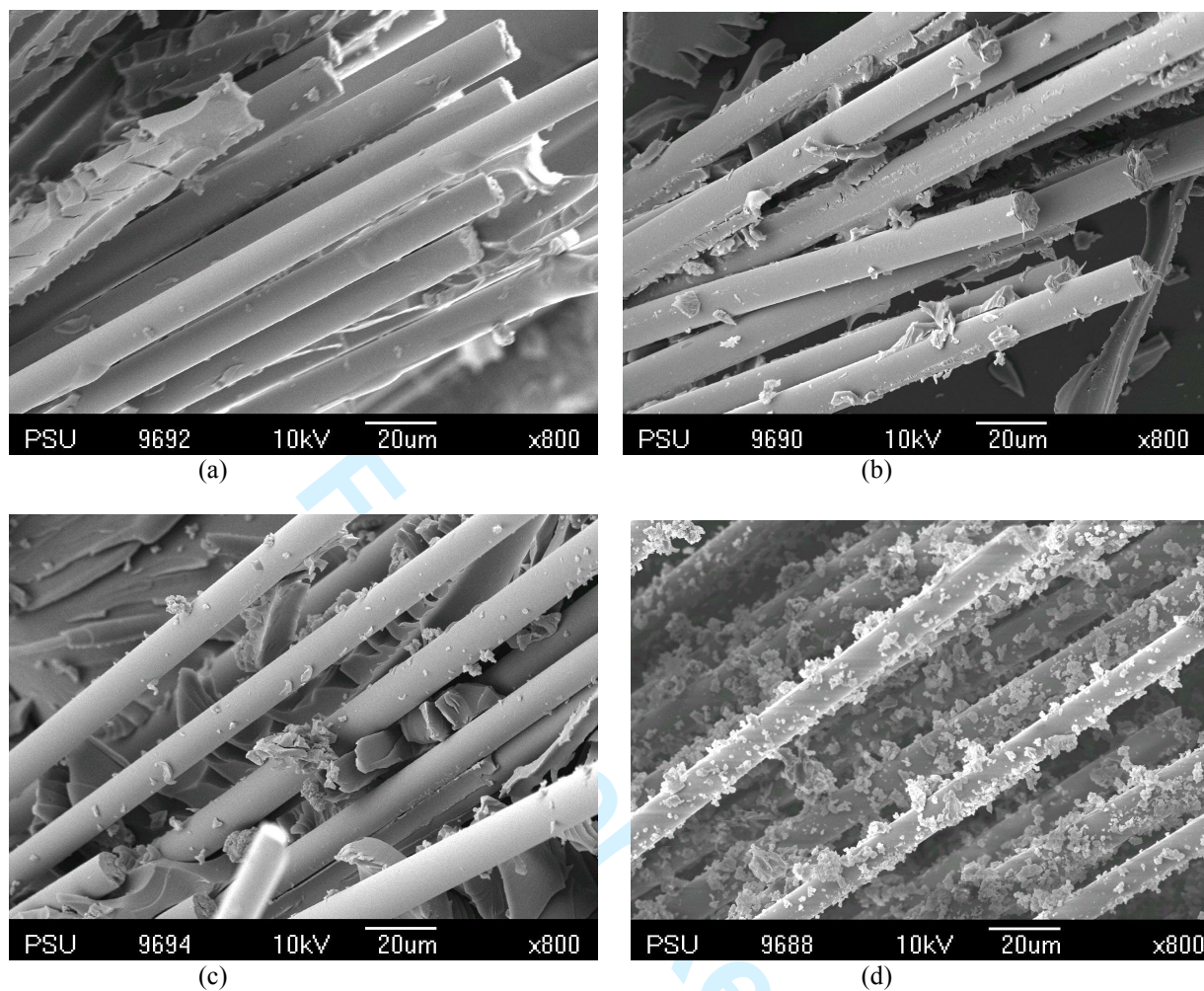


Figure 14 SEM micrographs of fractured surfaces of composites II : (a) the OV sample; (b) the 1S sample; (c) the 2S-1 sample; (d) the 3S-3 sample. The 3S-3 sample (d) showed most resin adhered on the fiber than other samples, indicating most interfacial adhesion in this sample.