

The Morphology and Properties of Poly(methyl methacrylate)-Cellulose Nanocomposites Prepared by Immersion Precipitation Method

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ABSTRACT: Poly(methyl methacrylate) (PMMA)-cellulose nanofibers nanocomposite were prepared by an immersion precipitation method using various nanofiber contents. Solvent exchange was used to disperse the cellulose nanofibers in dimethylacetamide (DMAc) so that they could be easily mixed with PMMA solution. Atomic force microscopy images show that the thickness of the nanofibers dispersed in DMAc is around 2–3 nm. The nanocomposites obtained were translucent. The thermogravimetric and differential scanning calorimetry analyses show that with increasing cellulose nanofiber content the thermal stability and the glass transition temperature (T_g) of polymer matrix shift to higher temperature. The tensile modulus and strength increased with increasing nanofiber content. Dynamic mechanical analysis profiles show that the presence of cellulose nanofibers affects the storage modulus of PMMA nanocomposites over the whole range of temperatures studied. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Cellulose nanofibers as reinforcement in nanocomposites are a relatively new area of interest. This is because the use of cellulosic fibers as reinforcing phase in nanocomposites has attracted the attention of many researchers around the world, such as low cost of the raw material, renewable nature, low density, wide variety of sources available in the world, high specific properties, modest abrasivity during processing, and biodegradability. The main drawback of cellulose fibers for reinforcement applications is incompatibility with non-polar polymer matrices due to their hydrophilic nature.¹ Agglomeration is a common problem when hydrophobic polymers are filled with cellulose nanofibers. This phenomenon causes the worse adhesion between cellulose nanofibers and polymer matrix. Agglomeration usually occurs during the blending.

Among available natural fibers, oil palm empty-fruit-bunch (OPEFB) is a very abundant, inexpensive, and renewable resource. OPEFBs are considered as waste after the extraction of oil palm fruits. With production reaching around 20 million tons of crude palm oil (CPO) in 2010, Indonesia is the major producer of CPO in the world. Each ton of CPO produces 1.1 ton of OPEFBs and causes a serious impact on the environment.² In our previous work, we succeeded to isolate cellulose

nanofibers from OPEFB which was highly dispersed in water.³ Therefore, it is a major challenge how to obtain good cellulose nanofibers dispersion in hydrophobic polymer matrix.

Some researchers have improved the dispersion of cellulose nanofibers in polymer matrix such as coating of the surface of cellulose nanofibers with surfactants^{4,5} and dispersing cellulose nanofibers in non-water solvent without any surface chemical modification or coating surfactant.^{6–8}

Kim et al.⁴ coated cellulose nanofibers obtained by HCl hydrolysis of Whatman cellulose filter paper with the non-ionic surfactant (sorbitan monostearate) in order to improve the adhesion of cellulose nanoparticles to the hydrophobic polymer matrix (polystyrene, PS). The surfactant appeared to enhance the dispersion of nanofibers within a PS matrix. Moreover, differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) provided evidence of the plasticizing effect of surfactant on the composite films, reducing the glass transition temperature (T_g). Sequeira et al.¹ argued that this strategy is not promising because high quantities of surfactant are required to obtain highly dispersed nanofiber suspensions in polymer matrix (in general, several times higher than the quantity of cellulose nanofibers).

Poly(methyl methacrylate) (PMMA) is hydrophobic, hard glassy amorphous plastic, and has low water sorption ability. PMMA

is commonly used in lenses, ideal replacement for glass, special application windows (such as helicopters and buses), and body implants.⁹

In a previous study, Agrawal et al.⁹ reported that ZnO nanoparticles were mixed into the PMMA matrix by solution mixing using *N,N*-dimethylacetamide (DMAc) as a solvent and PMMA nanocomposites were obtained via film casting. Their method offered a good dispersion of filler particles into the host matrix. A significant improvement in mechanical properties was observed with the incorporation of 0.5 wt % ZnO particles. Liu et al.⁷ reported that freeze-dried cellulose nanocrystal powder was incorporated into dimethylformamide (DMF) to obtain a stable suspension, and then compounded with PMMA, and the nanocomposite sheets were prepared by solution casting and thermal curing. The storage modulus of the nanocomposite sheets from DMA showed significantly enhanced property in comparison with that of the neat PMMA sheets. Deficiency of the methods of both papers lies in the remaining solvent (DMAc or DMF) in the composite films. These were shown by the shift of T_g value to lower temperature with respect to the neat PMMA material due to the solvent residues.

In this article, we report the preparation and characterization of PMMA-cellulose nanofibers nanocomposites by immersion precipitation method. In the first step, cellulose nanofibers were treated with DMAc using a solvent exchange method in an attempt to facilitate the mixing with the PMMA solution. Thereafter, PMMA-cellulose nanofibers nanocomposites were prepared by immersion precipitation method. With this method besides the good compatibility and homogenous dispersion of cellulose nanofibers in a polymer matrix could be achieved, DMAc residues also could be removed effectively. A series of PMMA nanocomposites with various cellulose nanofiber contents were produced and characterized by several analyses.

EXPERIMENTAL

Materials

OPEFBs supplied by PT Perkebunan Nusantara VIII Kertajaya, Lebak, Indonesia were used for obtaining nanofibers. Sulfuric acid (95%), PMMA ($M_w = 100,000$), DMAc, methanol, and other chemicals such as ethanol, benzene, sodium chlorite, acetic acid, and potassium hydroxide were supplied by WAKO Pure Chemical Industries (Japan).

Preparation of Highly Dispersed Cellulose Nanofibers in DMAc by Solvent Exchange

Cellulose fibers from OPEFB were prepared as described in our previous works.^{3,10} The cellulose fibers were hydrolyzed in sulfuric acid solution (64 wt %) under strong agitation at 45°C for 60 min. Hydrolysis was terminated by adding cold water. The diluted suspension was centrifuged at 11,000 rpm for 10 min to obtain a precipitate. The precipitate was re-suspended in water with strong agitation, followed by centrifugation. This process was repeated until the pH of the suspension reached 5 then dialysis was carried out for 3 days until the pH became constant. The water of the suspension was replaced by DMAc in the same manner as the acid was removed post hydrolysis. Subsequently, the suspension was sonicated for several minutes to disperse the

nanofibers in DMAc using an ultrasonic homogenizer at 200 W output power (26 mm probe tip diameter, UD-201, Tomy Ultrasonic Disruptor, Japan), then stored in a refrigerator. The nanofiber suspensions were coded as NF.

Preparation of the PMMA-Cellulose Nanofiber Nanocomposite

PMMA solution and cellulose nanofiber suspensions in DMAc (0.5 wt % of fibers) with various nanofiber contents (0, 0.5, 1, and 3 wt %; based on the dry weight of the nanocomposites) were mixed together at room temperature with strong agitation overnight. The mixtures were cast on glass plates and immersed into non-solvent (water, methanol) for several days. Subsequently, the composites obtained were hot-pressed between sheets of Teflon at 100°C and 5 MPa for 1 h to prepare the translucent nanocomposite sheets. Several codes were used, such as PMMA-NF0.5%-water and PMMA-NF0.5%-MeOH. Thus PMMA-NF0.5%-MeOH, for example, signifies PMMA nanocomposite with 0.5 wt % cellulose nanofibers immersed in methanol.

Characterization

Scanning Electron Microscopy Observation. The morphology of a PMMA nanocomposite sheet before hot-press as reference was observed by scanning electron microscopy (SEM, JEOL S4000, operating at 10 kV).

Atomic Force Microscopy Observation. The morphology of dispersed cellulose nanofibers in DMAc was examined with an atomic force microscopy (AFM) scanning probe system comprising SPA-300 and SN-3800 units and an SI-AF-01 cantilever (SII NanoTechnology, Japan). The sample was prepared by placing a drop of diluted nanofibers suspension (0.001 wt % of fibers) onto freshly cleaved mica and drying in ambient conditions. The thickness of cellulose nanofibers were measured on AFM images using specialized software (Spis32). About 50 measurements were used to determine average and standard deviation values.

Thermogravimetric and Derivative Thermogravimetric Analyses. Thermogravimetric (TG) and derivative Thermogravimetric (DTG) analyses were carried out using a Thermo Plus TG 8120 instrument. Thermograms were acquired between 30 and 500°C at heating rate 10 K min⁻¹, with nitrogen as purge gas at flow rate 110 mL min⁻¹. An empty pan was used as reference.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) analysis was performed on a Thermo Plus DSC 8230 at heating rate of 10 K min⁻¹ under a nitrogen atmosphere. The thermograms were acquired between 40 and 200°C with approximately 7 mg samples. The glass transition temperature (T_g) was determined from the heating scan of the samples.

Tensile Test. The tensile tests for all samples were performed using EZ Test machine (Shimadzu, Japan). The samples were prepared by cutting rectangular strips from the films with width of 3 mm and length of 10 mm.

Dynamic Mechanical Analysis. DMA was performed using DVA-200S analyzer. The specimens were scanned over a

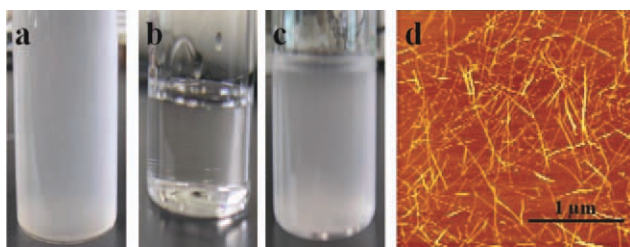


Figure 1. Photograph of dispersed cellulose nanofiber suspension in DMAc (0.5 wt % of fibers) (a); PMMA solution (b); mixture of PMMA solution and cellulose nanofiber suspension (c); AFM image of dispersed cellulose nanofibers in DMAc (d). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperature range of -30 to 150°C . The frequency of the oscillations was fixed at 1 Hz and the strain amplitude was 0.05% . The heating rate was $1^{\circ}\text{C min}^{-1}$ for all temperature scan tests. The tests were conducted in tensile mode.

RESULT AND DISCUSSION

Morphology of Dispersed Cellulose Nanofibers in DMAc and PMMA Nanocomposites

Figure 1 shows the photographs of dispersed cellulose nanofiber suspension in DMAc (0.5 wt % of fibers), PMMA solution, mixture of PMMA solution and cellulose nanofiber suspension in DMAc and its AFM image. A good dispersion of cellulose nanofibers in the PMMA solution could be seen in this figure [Figure 1(c)], i.e., no aggregates were present. The AFM image showed that the average thickness of cellulose nanofibers dispersed in DMAc was $2.01 \pm 0.42\text{ nm}$, while the length of all nanofibers was difficult to measure due to the difficulty in locating the ends of the nanofibers [Figure 1(d)].

In this study, two non-solvents (water and methanol) were used for immersion of mixture of PMMA solution and cellulose nanofiber suspension to make nanocomposite sheets. Figure 2 shows the change of sheet appearance after immersion in non-solvents, before and after hot press 5 MPa at 100°C for 1 h . Af-

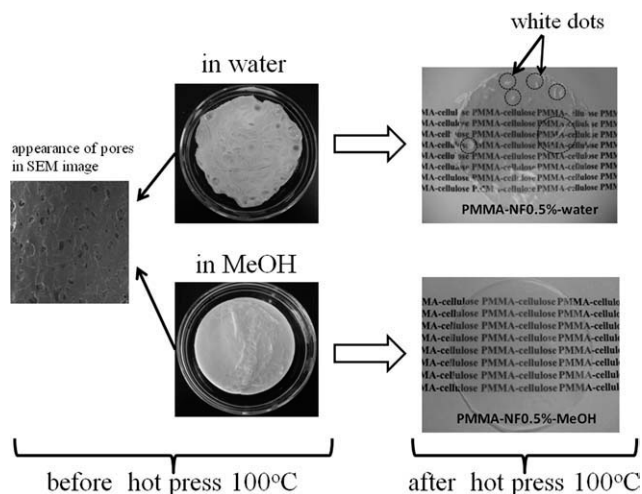


Figure 2. Change of sheet appearance after immersion in non-solvents, before and after hot press 5 MPa at 100°C .

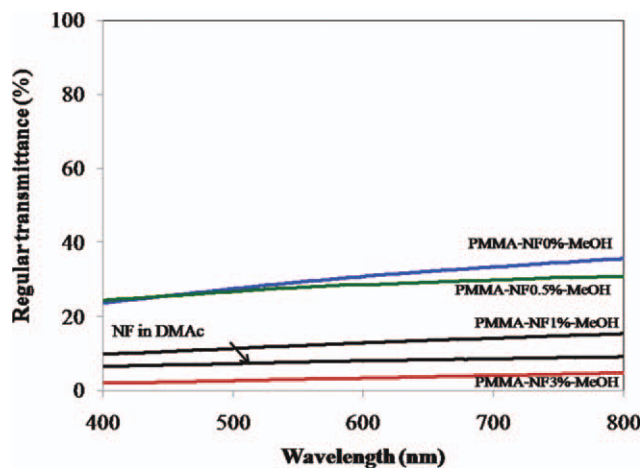


Figure 3. UV-vis transmittance spectra of neat PMMA and its nanocomposites obtained by immersion precipitation method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ter immersion and before hot press, the opaque precipitates were formed and there were many pores inside the sheets (shown by SEM micrograph in Figure 2 as reference). After immersion and hot press, PMMA nanocomposite sheets seemed translucent. The 5 MPa of hot press at 100°C for 1 h was high enough to remove the trapped gases inside the films and made them translucent. This behavior corresponds to the reduction in the density of pores and content of trapped gases in nanocomposite sheets.¹¹ Fang et al.¹² argued that extending the hot-pressing time might help further improve the transparency. Full densification is necessary to achieve transparent film.

The sheets immersed in water had several white dots corresponding to trapped gases. This is because the surface of the sheets immersed in water was not flat so the difficulty of removal trapped gases by hot press occurred.

The UV-vis transmittance spectra at visible wavelength range of $400\text{--}800\text{ nm}$ of the neat PMMA and its nanocomposites are shown in Figure 3. The transmittance of PMMA nanocomposite sheets were decreased with increasing cellulose nanofiber content, because of the nature color of cellulose nanofibers dispersed in DMAc [Figure 1(a)].

Thermal Properties

In order to evaluate the effect of cellulose nanofibers on the morphology and properties of PMMA nanocomposite sheets independently, the DMAc residues were removed as much as possible. TG analysis was performed to evaluate the DMAc residues inside the nanocomposite sheets and to determine the changes in weight in relation to change in temperature. Based on the information from TG analysis, the content of DMAc residues at the temperature range $150\text{--}300^{\circ}\text{C}$ is summarized in Table I. As shown in Table I, immersion in methanol for several days was more effective to remove DMAc residues than immersion in water.

TG and DTG curves of PMMA sheets incorporated with different amounts of cellulose nanofibers immersed in water and methanol are shown in Figures 4 and 5, respectively. With

Table I. The Weight of DMAc Residues (in wt %) (Based on TG Analysis Results), Glass Transition Temperature (T_g), Onset Temperature, and T_{max} (Degradation Temperature) of Neat PMMA and its Nanocomposites

	$\Delta(150-300^\circ\text{C})^a =$ DMAc residues	Onset temperature ($^\circ\text{C}$)	T_{max} ($^\circ\text{C}$)	T_g ($^\circ\text{C}$)
PMMA-NF0%-water	1.54	281	330	94.7
PMMA-NF0.5%-water	1.95	299	342	97.8
PMMA-NF1%-water	2.02	305	352	98.7
PMMA-NF3%-water	3.13	315	379	99.7
PMMA-NF0%-MeOH	1.06	289	333	98.0
PMMA-NF0.5%-MeOH	1.22	304	332	101.4
PMMA-NF1%-MeOH	1.23	315	345	103.2
PMMA-NF3%-MeOH	1.51	316	351	104.9

^a $\Delta(150-300^\circ\text{C}) =$ the weight loss at 300°C - the weight loss at 150°C .

increasing cellulose nanofiber content, the thermal stability of polymer matrix shifted to higher temperature, indicating that cellulose nanofibers cause the delay in the thermal degradation of the polymer matrix. This enhancement of the thermal stability might be attributed to the nanofibers preventing out-diffu-

sion of the volatile decomposition products. Well dispersed cellulose nanofibers can act as a barrier for diffusing vapor as vapors cannot pass through the crystal structure.^{9,13} According to the DTG curves, the degradation of the nanocomposites has only one process which is ascribed to the decomposition of

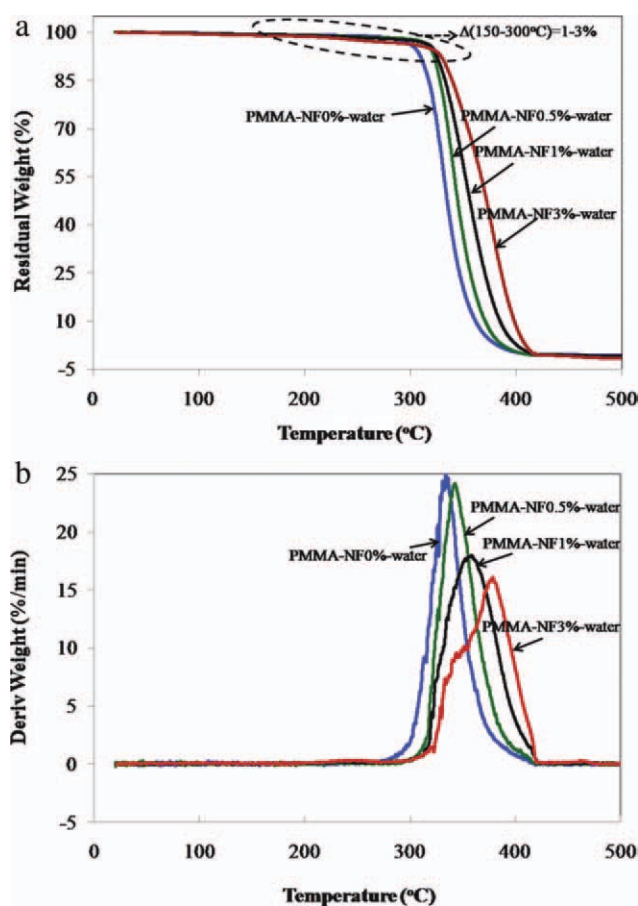


Figure 4. TG and DTG curves of neat PMMA and its nanocomposites after several days' immersion in water. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

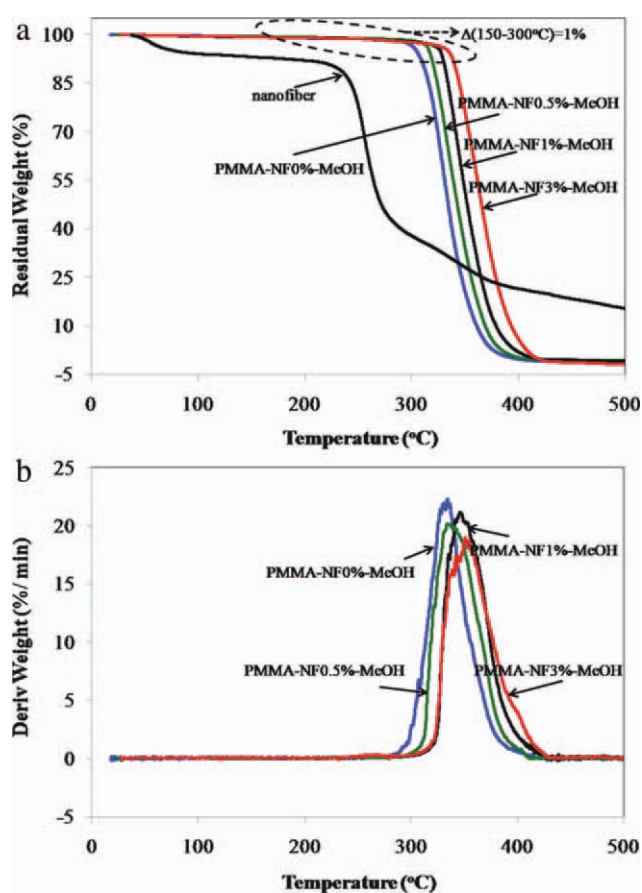


Figure 5. TG and DTG curves of neat PMMA and its nanocomposites after several days' immersion in methanol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

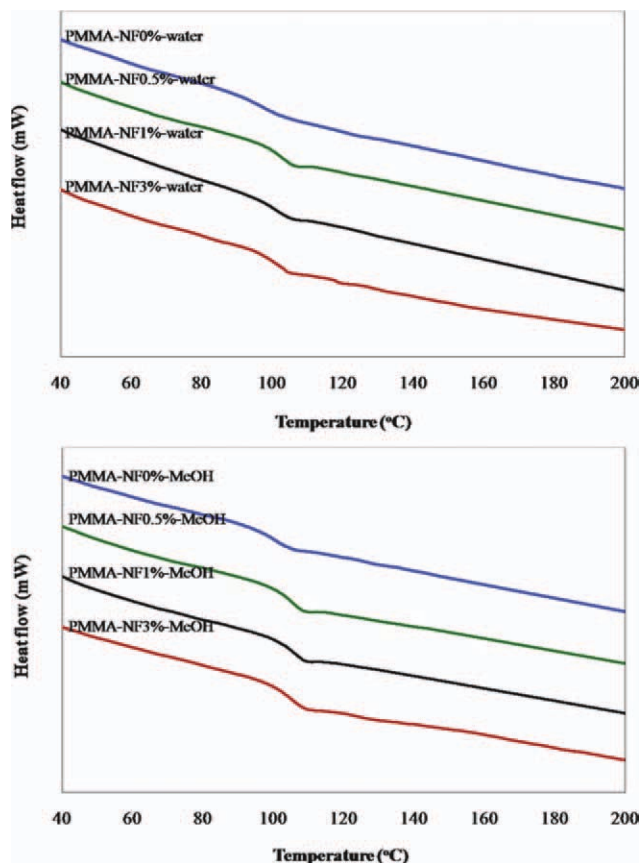


Figure 6. DSC curves of neat PMMA and its nanocomposites after several days' immersion in water and in methanol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PMMA. Figures 4 and 5 show that the degradation of neat PMMA and its nanocomposites started at around 281–316°C. As listed in Table I, with increasing cellulose nanofiber content, the temperature at which the rates of the thermal degradation processes are the highest (T_{max}) also increased.

Figure 6 shows DSC curves of neat PMMA and its nanocomposite sheets with different content of cellulose nanofibers taken at 10 K min⁻¹ heating rate in nitrogen atmosphere. The DSC curves only show a glass transition temperature (T_g) without melting temperature (T_m). With increasing cellulose nanofiber content, the T_g of the PMMA nanocomposite sheets also increased. The T_g of neat PMMA immersed in water and in methanol was around 94.7°C and 98.0°C, respectively. The T_g of PMMA-cellulose nanocomposite with addition of 0.5, 1, and

3 wt % of cellulose nanofibers immersed in methanol was 101.4, 103.2, and 104.9°C, respectively. Meanwhile, the T_g of PMMA nanocomposites immersed in water with addition of 0.5, 1, and 3 wt % of cellulose nanofibers was 97.8, 98.7, and 99.7°C, respectively. One can observe that incorporation of cellulose nanofibers led to an increase in the T_g of the PMMA matrix. This might be due to the restrictions in chain movement by interactions between PMMA with cellulose nanofibers. From Figure 6, the T_g of nanocomposite sheets immersed in methanol was higher than those of in water. This might be because DMAc residues in the sheets immersed in water were higher than that of in methanol. The DMAc could act as plasticizer and made the T_g decrease.

Mechanical Properties of PMMA Nanocomposites

The tensile modulus and strength of neat PMMA and its nanocomposites reinforced with cellulose nanofibers with 0.5, 1, and 3 wt % are shown in Table II. Both the tensile modulus and strength of PMMA increased with the addition of cellulose nanofiber content, while the strain at break was decreased. The 3 wt % nanofibers improved the modulus of PMMA from 761.6 MPa to 843.2 MPa and the tensile strength from 34.6 MPa to 38.6 MPa, while it reduced the strain at break from 7.5% to 5.9%. The tensile modulus of neat PMMA was increased due to not only the geometry and stiffness of cellulose nanofibers but also the formation of hydrogen bonded nanofibers network.¹⁴ Meanwhile, the increase of tensile strength indicates interfacial adhesion between the polymer matrix and cellulose nanofibers occurred.

Thermo-Mechanical Properties of PMMA Nanocomposites

Compared to PMMA nanocomposite sheets immersed in water, PMMA nanocomposite sheets immersed in methanol has better removal process of DMAc residues. To study the effect of cellulose nanofiber reinforcement on the thermal-mechanical properties of PMMA, we performed DMA on PMMA nanocomposite sheets immersed in methanol only.

Figure 7 shows the temperature dependence of the storage modulus (E') of neat PMMA and its nanocomposite sheets. The figures show that the storage modulus of neat PMMA below T_g (−30°C) was almost constant at around 4.8 GPa. Above T_g , the modulus of neat PMMA dropped to 0.4 MPa at around 150°C. The addition of cellulose nanofibers improved the storage modulus of neat PMMA. The values of storage modulus of neat PMMA and its nanocomposites are summarized in Table II. The addition of 3 wt % nanofibers improved the modulus of neat PMMA from 4.8 GPa to 7.9 GPa at −30°C (glassy state),

Table II. Mechanical Properties and Storage Modulus (E') of Neat PMMA and its Nanocomposites

Sample	Tensile modulus (MPa)	Tensile strength (MPa)	Strain at break (%)	$E'_{-30^\circ\text{C}}$ (GPa)	$E'_{150^\circ\text{C}}$ (MPa)
PMMA-NF0%-MeOH	761.6	34.6	7.5	4.8	0.4
PMMA-NF0.5%-MeOH	823.1	35.9	7.6	4.9	1.6
PMMA-NF1%-MeOH	835.2	38.2	6.8	5.0	2.0
PMMA-NF3%-MeOH	843.2	38.6	5.9	7.9	21.1

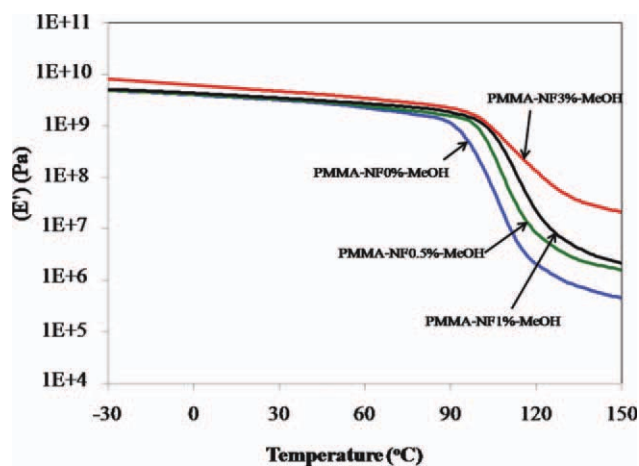


Figure 7. Effect of cellulose nanofiber content on the storage modulus of neat PMMA and its nanocomposites after immersion in methanol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and interestingly, from 0.4 MPa to 21.1 MPa at rubbery plateau. This difference in modulus improvement at rubbery plateau compared to that of at glassy state is explained by the fact that the matrix becomes extremely soft in the rubbery plateau and the reinforcement with cellulose nanofibers becomes more noticeable at high temperatures. This is also ascribed to the presence of strong interactions between hydrogen bonds of cellulose nanofibers which lead to the formation of a rigid network governed by the percolation threshold.¹⁵ With increasing nanofiber content the possible entanglement between nanofibers and polymer matrix also increased.

From DMA figures we noticed that above T_g , storage modulus of nanocomposite sheets due to the addition of cellulose nanofibers into polymer matrix increased significantly while from tensile test results their tensile strengths increased slightly. We supposed that entanglements had occurred between partly nanofibers and polymer matrix. Only a good dispersion of cellulose nanofibers in polymer matrix is not enough to reach a good interfacial adhesion between nanofibers and the polymer matrix. Therefore, the further research is still needed to enhance the interfacial adhesion, such as using compatibilizer.

CONCLUSION

PMMA nanocomposite sheets were successfully prepared by immersion precipitation method with the reinforcement of

cellulose nanofibers obtained by sulfuric acid hydrolysis. The described method offered a good dispersion of cellulose nanofibers into the PMMA matrix. An increase in thermal and mechanical properties of PMMA matrix was observed after the addition of 0.5, 1, and 3 wt % nanofibers. DMA measurements showed that the storage modulus of the nanocomposites increased with increasing nanofiber content.

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