

접착성 설탕시럽을 이용하여 탄소나노튜브의 얽힘을 푸는 새로운 접근방법

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A Novel Approach to Disentangle Carbon Nanotubes Using Viscous Sugar Syrup

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초록: 끈적끈적한 설탕시럽을 사용한 다중벽 탄소나노튜브(MWNT) 번들의 풀림이 연구되었다. 시럽은 수크로스, 글루코스, 프럭토스와 증류수를 1:1:1:0.8의 무게 비율로 혼합하여 제조되었다. 고점도의 물질을 위한 디스크형태의 믹서가 시럽과 MWNTs를 혼합하기 위하여 제작되었다. MWNT의 효과적인 풀림을 위한 최적의 혼합조건을 알기 위하여 MWNT/설탕시럽 함량 비율을 각 제조단계에서 다양하게 하였다. 설탕시럽에서 나노튜브의 분산상태를 정량적으로 평가하기 위해 디지털영상처리기술이 광학현미경 이미지에 사용되었다. 이것은 MWNT의 균일한 분산이 시럽을 한 번에 첨가하기보다는 각 단계에서 점차적으로 첨가함으로써 얻어진다는 것을 보여주었다. 혼합물의 동적점도가 MWNT의 전체적인 분산상태를 평가하기 위해서 측정되었다. MWNT 첨가가 시럽의 동적점도를 증가시켰고 분산정도가 증가하면서 동적점도가 감소함을 보였다. 이 새로운 분산방법을 고분자 복합체에 적용가능한지 입증하기 위해서 분산된 MWNT가 폴리비닐알콜과 폴리아크릴로니트릴에 옮겨졌고 각 매트릭스에서 재응집없이 균일하게 분산됨을 보였다.

Abstract: The disentanglement of multi-walled carbon nanotube (MWNT) bundles by using a sticky sugar syrup was explored for the first time. The syrup was prepared by mixing sucrose, glucose, fructose, and distilled water in a 1:1:1:0.8 weight ratio. A disk-type mixer suitable for high-viscosity materials was built to mix this syrup with MWNTs. To find out the optimum mixing conditions for effective disentanglement of MWNTs, the content ratio of MWNTs to sugar syrup was varied at each mixing step. Digital image processing technique was used with optical micrographs to quantitatively estimate the dispersion of nanotubes in sugar syrups. This revealed that the most homogeneous dispersion of MWNTs in the sugar syrup was achieved by gradually adding the syrup at each mixing step rather than all at once at the initial mixing step. The dynamic viscosity (η') of the mixtures was measured to evaluate the overall dispersion state of MWNTs. The incorporation of MWNTs increased the η' of sugar syrup, exhibiting a decreased η' with an increase in the degree of dispersion. To validate this novel dispersion method for polymer composites, disentangled MWNTs were transferred into poly(vinyl alcohol) (PVA) and polyacrylonitrile (PAN); they exhibited uniform dispersion in each polymer matrix, without reagglomeration occurred.

Keywords: sugar syrup, disentanglement, multi-walled carbon nanotube, dynamic viscosity, composite.

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Introduction

Carbon nanotubes (CNTs) have a fiber-like structure with diameters in the nanometer scale and lengths up to tens of microns. Due to their various benefits such as exceptional mechanical, electrical, magnetic, and thermal properties,¹⁻⁶ many researches have been devoted to exploring their potential applications in a large scale. Currently advances in the catalytic process have allowed the production of multi-walled carbon nanotubes (MWNTs) at the commercial scale. However, most of the manufacturing processes result in highly entangled and aggregated structures.⁷ CNTs tend to cluster together due to the strong van der Waals attraction between them, so it is extremely difficult to homogeneously disperse them in various media. This can prevent the achievement of their superior properties in applications such as reinforcement materials and membranes. Therefore, the homogeneous dispersion of CNTs in the desired medium is a prerequisite for their practical applicability. Previous dispersion works on CNTs in continuous phase were focused on the chemical modification of the nanotube surface by strong acids, gas plasma or functionalization, polymer dispersants, surfactant-assisted processing, etc.⁸⁻¹⁴ In addition, most of the dispersion methods operate through chemical treatments and strong, long-lasting sonication. These generate defects on the nanotube walls and makes the nanotubes short with open ends, which might worsen the electrical and mechanical properties.¹⁵

The full and easy dispersion method of CNTs with a little energy input and in a large scale is favored in the industrial field. Furthermore, noncovalent approaches appear more attractive than the covalent ones since they maximize the preservation of the intrinsic properties of CNTs.¹⁶ However, it does not seem that there is a simple way to obtain fully disentangle nanotubes with a little limit to their further applications. Thus, the present study proposes a novel method to conveniently disentangle nanotubes in their manufactured state without addition of chemicals nor functionalization of the nanotube surface. Further, fully dispersed nanotube suspensions were applied to the fabrication of CNT-reinforced polymer composites. MWNTs were mixed with a sticky sugar syrup, which was used as the dispersing medium to disentangle them prior to resuspending them in the desired solvents. To discover the effective mixing conditions to disentangle the MWNTs three different mixing ways were tested by varying the ratio of sugar syrup to MWNTs in each mixing step. The versatility of this method was clearly demonstrated by transferring disentangled

MWNTs into polyacrylonitrile (PAN) and poly(vinyl alcohol) (PVA) matrices, soluble in dimethylformamide (DMF) and water with very different degrees of affinity toward nanotubes, respectively.

Experimental

Materials. MWNTs (average diameter = 40–50 nm and length = ~500 μm) produced via a chemical vapor deposition (CVD) method were used for the experiments. As a dispersing medium, viscous sugar syrup was prepared by mixing sucrose, glucose, fructose, and distilled water in a 1:1:1:0.8 weight ratio. PVA (degree of hydrolysis = 99.5%, degree of polymerization = 1700) and PAN (molecular weight = 150000 g/mol) were purchased from DuPont and Sigma-Aldrich, respectively.

Disentanglement of MWNTs in Sugar Syrup. A disk-type mixer was designed to give high shear to viscous material. The gap distance between the mixing plates was fixed to 0.2 mm and one of them, having a diameter of 65 mm, was rotated at 20 rpm. The disentanglement of the MWNTs occurs by passing the mixture through between these two plates.

Dispersion of MWNTs in PAN and PVA. The sugar syrup was removed by washing with distilled water and the filtered MWNTs in a wet state were rinsed with DMF and water, (i.e., the solvents for PAN and PVA, respectively) prior to suspending them in each solvent. The so-obtained suspensions were gently sonicated for 30 min in the sonic bath, followed by the dissolution of PAN and PVA at 80 °C. The resulting PAN and PVA concentrations were 15 and 12 wt%, respectively. The spinnable PAN/MWNTs solutions were extruded into a coagulant bath containing distilled water at room temperature through a syringe needle (diameter = 0.65 mm). The PVA/MWNTs solutions were cast on glass plates at room temperature.

Measurement of the Physical Properties. After the mixing process of MWNTs with sugar syrup was completed, aliquots of the samples were collected to evaluate the dispersion status by using an optical microscope (Olympus BH-2) at 400 times magnification.

The viscosity of the MWNT/sugar syrup mixtures was measured at 30 °C in dynamic mode through an advanced rheometric expansion system (ARES; Rheometric Scientific Inc.). Parallel plate geometry in a diameter of 25 mm was employed, with a plate gap and a strain level of 1 mm and 5%, respectively.

The fractured surfaces of the prepared composites in liquid

nitrogen were observed via field emission scanning electron microscopy (FESEM; Philips JSM6330F) to examine the quality of nanotube dispersion in the polymer matrices.

Results and Discussion

As shown in Figure 1, the significant entanglement and bundling of CNTs in the bulk state, typical pattern of nanotubes when produced by CVD, gives rise to the extreme difficulty in their separation. The proper mixing with a sticky material is considered as one of the ways to debundle these CNTs. In addition, such a sticky medium should be removed with little difficulty for the successive usage of the as-debundled nanotubes. Thus, a sugar syrup prepared by mixing equal proportions of glucose, fructose, and sucrose with distilled water was chosen as the viscous medium. Using these three types of sugars in the same amount prevents crystallization, which is a crucial factor for a viscous medium since a crystallized sugar syrup could not wet the nanotubes effectively. In addition, the viscosity of sugar syrup can be easily controlled by regulating the water content. This enables viscosity optimization in relation to the mixing conditions.

Since the sugar syrup is highly viscous and should be added little by little over the mixing process, typical commercial thermoplastic fabrication equipment is not suitable for this procedure. Thus, a disk-type mixer was specially designed for a reproducible mixing, as shown in Figure 2. This mixer enables the shearing level to be adjustable via varying the gap distance and is very effective in treating even small sample quantities.

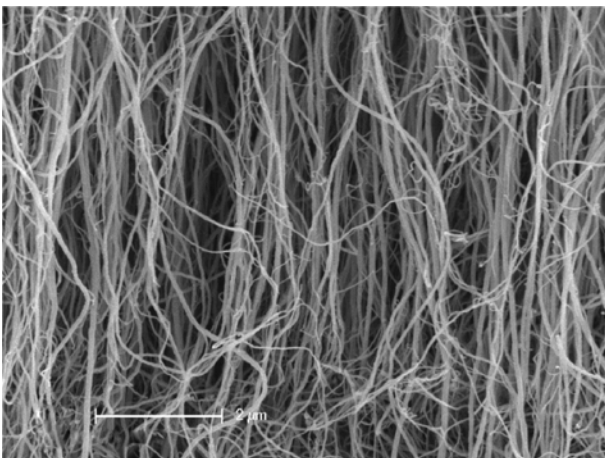


Figure 1. Field emission scanning electron microscopy image of highly entangled multi-walled carbon nanotubes produced by chemical vapor deposition.

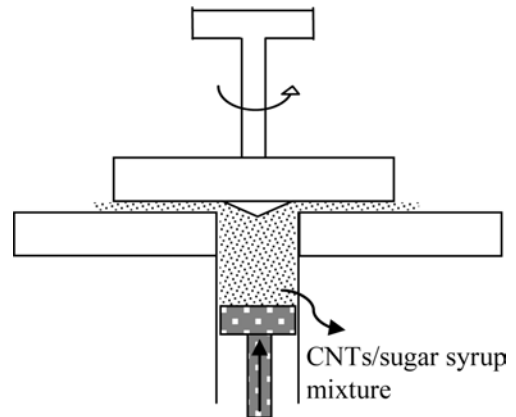


Figure 2. Schematic diagram of the automatic mixer designed for mixing multi-walled carbon nanotubes with the sugar syrup.

Due to the low flowability of the MWNT/sugar syrup mixtures and the consequent frequent occurrence of blocking between feeding zone and top plate, the cone-shaped attachment is placed on the top plate, facilitating its movement without retention.

Figure 3 illustrates the disentanglement process of the MWNTs in the sugar syrup during the mixing, showing how the nanotube bundles disappear in the dispersing medium with increasing the mixing time. At the initial stage, the high-viscosity syrup creates an appropriate interface among MWNTs bundles by drawing and opening the nanotube side-walls. Then, the further added syrup penetrates this interface, resulting in a single, disentangled nanotube. This phenomenon can be explained as follows. Shearing forces propagate via the viscous medium and pass through the nanotube bundles. In consequence, the shearing force not only diffuses between the nanotube bundles but also peels off the nanotubes located at their outer part, finally resulting in the exfoliation of individualized nanotubes. At this point, the sugar syrup also plays a role in preventing these dispersed nanotubes from returning to the initial bundle state by locking them with a segregated network. That is, the further added syrup fills the space between single nanotubes, leading to a fully debundled state.

When mixing nanotubes with sugar syrup, the dispersion quality is significantly affected by how the viscous medium is added. When kneading flour with water, a gradual addition rather than all at once is considered more effective for the preparation of well-mixed pastes. Therefore, adding sugar syrup divisionally over the mixing process is proposed to prove the superiority of step addition. Three different MWNT/sugar syrup mixtures are prepared by varying their ratio at each

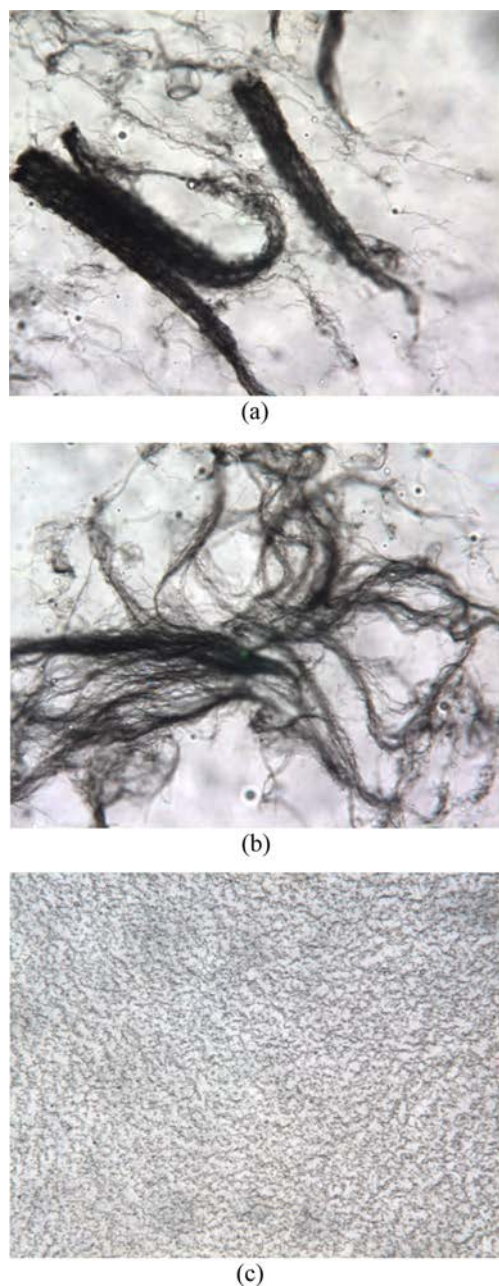


Figure 3. Optical micrographs showing the disentanglement of multi-walled carbon nanotube bundles in the sugar syrup during the mixing process: (a) bundle; (b) semi-disentangled; (c) fully disentangled states.

mixing step, as summarized in Table 1. The dispersion method entails a sequence of addition of sugar syrup in specified amounts and mixing with MWNTs. The Dispersion-1 sample is prepared by adding the sugar syrup all at once in the first step, while the Dispersion-2 and Dispersion-3 samples are obtained by gradual additions at each step; the final MWNT

Table 1. Different Concentrations of Multi-walled Carbon Nanotubes in the Sugar Syrup at Each Mixing Step

Sample	MWNTs concentrations in sugar syrups (wt%)			
	1st step	2nd step	3rd step	4th step
Dispersion – 1	1	1	1	1
Dispersion – 2	4	2	1.2	1
Dispersion – 3	4	3	2	1

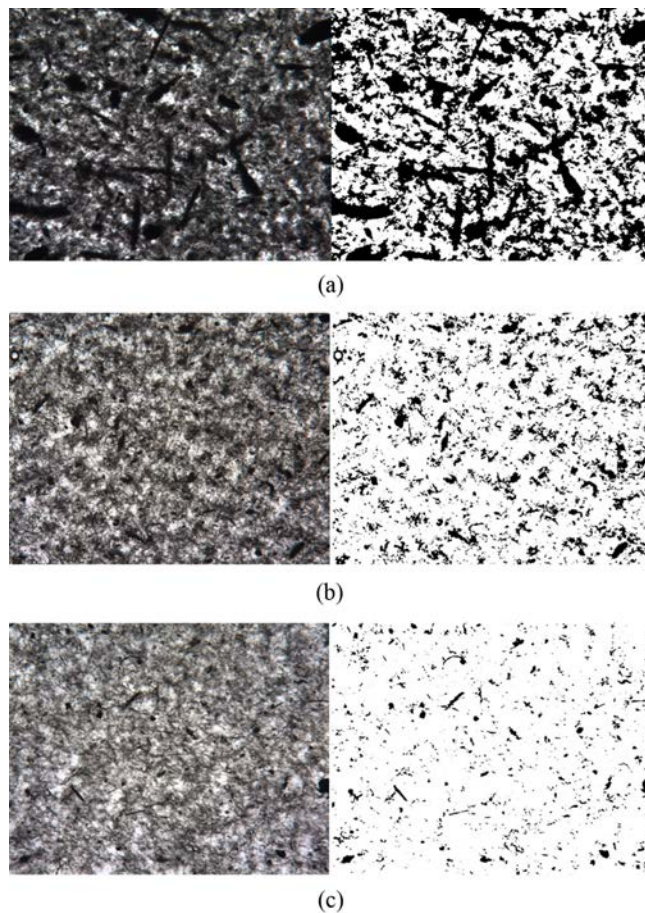


Figure 4. Optical micrographs (left column) and their binary images (right column) of multi-walled carbon nanotube bundles mixed with sugar syrup in different conditions (see Table 1): (a) Dispersion-1; (b) Dispersion-2; (c) Dispersion-3 samples.

concentration is identical (1 wt%) in the three samples.

Figure 4 shows the original optical micrographs and their binary images of the MWNTs mixed with sugar syrup. Digital image processing by using Matlab software is conducted to assess quantitatively the dispersion degree of nanotubes. The original microscope images are binarized by empirically setting the threshold to distinguish the black and white pixels. The ratio of black area to the entire area gives the value of 45,

17, and 5% for dispersion-1, dispersion-2 and dispersion-3, respectively. An increase in the ratio represents poor dispersion of nanotubes, still existing in such a large bundle state in the media. The step addition of sugar syrup gives rise to the effective disentanglement of nanotubes. Bigger bundles are frequently observed when adding more sugar at the initial step and the final degree of dispersion seems influenced by the initial dispersion state. When two immiscible components are mixed, the viscosity gap between them is an important criterion to determine the extent of mixing. That is the lower difference in viscosity the more effective mixing at the corresponding final concentration. The large viscosity mismatch between MWNTs and sugar syrup can lead to incompatibility and partial distribution of the minor phase in the major one. In addition, since the viscosity of solid MWNTs is extremely high, a relatively high-viscosity sugar syrup should be selected as the dispersing medium. At the first stage, the addition of the least amount of sugar syrup (i.e., only as much as the wetting nanotubes) results in the least viscosity mismatch. Both the increased stresses generated by the high viscosity of sugar syrup and the maximized distribution of mixing stresses due to viscosity matching of two components would give rise to the extensive break-up of the bundled phases. The Dispersion-3 sample exhibits better dispersion than the Dispersion-2 one, indicating that the MWNT disentanglement is maximized when adding the sugar syrup little by little over the mixing process. In other words, since the MWNTs are not completely disentangled in the medium at the first stage, the second stage of mixing still plays a significant role in determining the final degree of disentanglement.

The rheological properties of a mixture are directly correlated with the spatial and orientational distribution status of the nanotubes in the matrix.¹⁷ These can be used as a physical signal to monitor the overall quality of dispersion. Figure 5 shows the dynamic viscosity (η') curves of MWNT/sugar syrup mixtures at 30 °C. The pure sugar syrup sample exhibits Newtonian behavior in the low frequency range, followed by shear thinning; this is the typical pattern of pseudoplastic materials. However, the incorporation of MWNTs increases the η' of sugar syrup and produces notably yield behavior with the lower Newtonian flow region disappearing. This increase of η' suggests that there are a large number of contacts between MWNTs and the molecule of sugar syrup leading to restriction in its mobility. For MWNT/sugar syrup mixtures, the viscosity is inversely proportional to the degree of dispersion,^{17,18} therefore resulting in the following viscosity order in the tested fre-

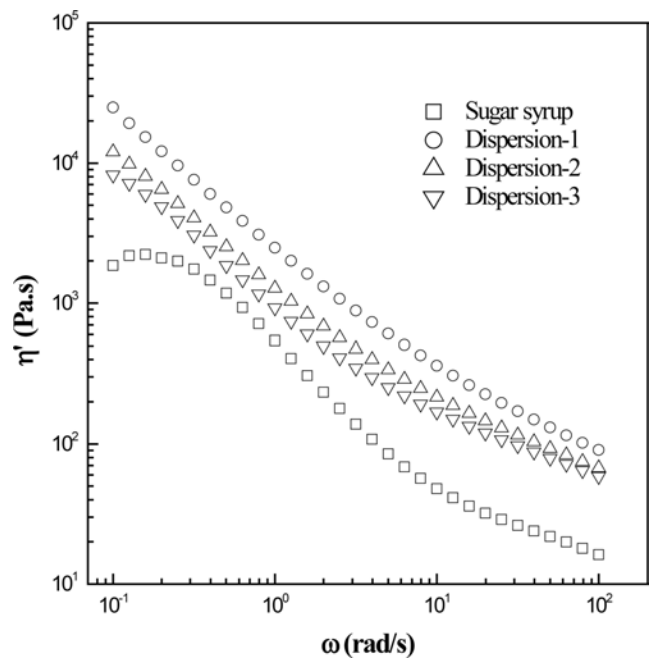
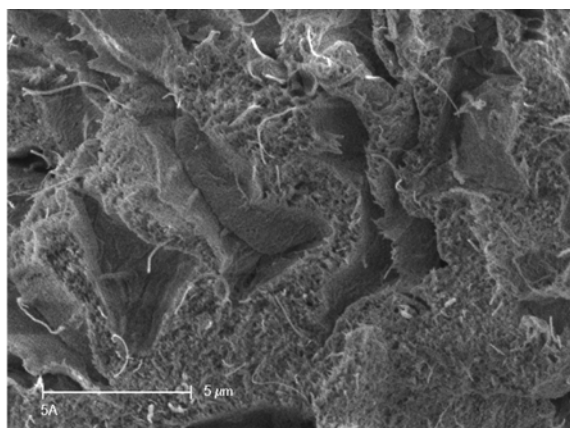


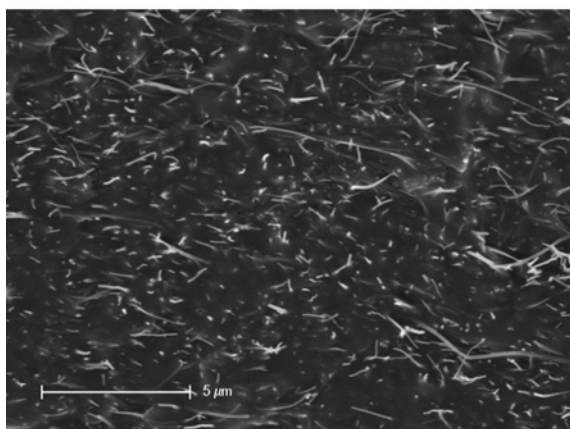
Figure 5. Dynamic viscosity (η') curve of multi-walled carbon nanotube/sugar syrup mixtures prepared with different mixing conditions.

quency range: Dispersion-1 > Dispersion-2 > Dispersion-3. The alignment of the nanotubes is expected to occur in the medium by shearing, favored by the degree of disentanglement. The individualized nanotubes react more easily to external stresses than the bundled ones, resulting in their alignment. This reduces the number of tube-tube contacts and, hence, the matrix motion was less hindered. Thus, the viscosity decreases with increasing the alignment of nanotubes.¹⁹ In addition, since the poorly dispersed suspensions contain many nanotubes in a bundled or semi-debundled state, some of the dispersing medium becomes immobilized within these aggregates. Therefore, the apparent volume of nanotube aggregates is larger than the true volume occupied by the sum of individualized nanotubes, resulting in increased viscosity. At the frequency of about 0.5–1 rad/s, the viscosity difference between the nanotube mixture and the pure sugar syrup decreases because of the aligned nanotubes or break-up of agglomerate under moderate shear. However, as the frequency further increases, the viscosity gap increases as well, suggesting that a higher shearing is not always more effective in terms of uniform dispersion since it may lead to rerandomization or reaggregation of the nanotubes.

To use the proposed method for the preparation of polymer composites, the disentangled state of the MWNTs in sugar



(a)



(b)

Figure 6. Field emission scanning electron microscopy images of the fractured surfaces of (a) a polyacrylonitrile fiber; (b) a poly(vinyl alcohol) film, both containing 5 wt% multi-walled carbon nanotube.

syrup is required to be maintained in the desired solvent for the polymer matrix after the syrup removal. To verify this possibility, PAN and PVA, whose composites with nanotubes have been deeply studied because of their potential applications, were selected as the polymer matrices.²⁰⁻²⁷ DMF and water, which have definitely different suspending power for nanotubes, are used for PAN and PVA, respectively. The sugar syrup is removed by repeated washing with water and then the filtered nanotubes are immediately transferred to each solvent to prevent reagglomeration, prior to the polymer dissolution. Figure 6 shows the FESEM images of freeze-fractured interfaces for both the 5 wt% PAN and PVA composites. The nanotubes are homogeneously dispersed with little agglomerates. This proves that the predispersed state is retained over the whole fabrication process of the composites. That is, once the

MWNTs are debundled by the sugar syrup, the solvent media also appear to have the ability to suspend the individualized nanotubes slightly depending on their suspending power. In addition, the dispersed state is maintained even during the fiber formation and the film casting processes, where the solvents are removed. This indicates that the polymer molecules replace the space previously occupied by the solvent ones, preventing the return to the entangled state. This method could be used not only for the fabrication of various polymer composites but also in CNT-matrix applications such as bucky papers and CNT fibers when considering that nanotube suspensions fully dispersed in various media are possibly prepared.

Conclusions

To the best of our knowledge, we explored for the first time the disentanglement of MWNTs by mixing with sugar syrup without chemical modification or additive incorporation, which is not expected to change their inherent properties. Sticky sugar syrup with crystal-inhibiting characteristics was used, allowing the disentanglement of the nanotubes. The disentanglement states of MWNTs in the medium affected by the type of mixing process are quantitatively evaluated by digital image processing. The key factor to effectively mix the nanotubes with this viscous medium is its divisional addition in a sense of viscosity matching method. At the initial mixing stage, the MWNTs should be debundled to some degree suitable for being further individualized by successive syrup addition at the next stage. Thus, we concluded that the initial mixing condition is crucial in determining the final dispersion state. Then, both PAN and PVA composites with uniformly dispersed nanotubes were successfully prepared, demonstrating that the disentangled state of the MWNTs resulting from the sugar syrup treatment was retained even in the successive fabrication processes. This versatile and environmentally benign method presents a little limitation in the preparation of polymer/CNTs composites. In addition, CNT-matrix related applications such as CNT fibers and membranes could be easily accessed through the preparation of stable and dispersed CNT suspensions.

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References

1. C. H. Liu, H. Huang, Y. Wu, and S. S. Fan, *Appl. Phys. Lett.*, **84**, 4248 (2004).
2. S. Subramoney, *Adv. Mater.*, **10**, 1157 (1998).
3. F. Du, R. C. Scogna, W. Zhou, S. Brand, J. E. Fischer, and K. I. Winey, *Macromolecules*, **37**, 9048 (2004).
4. F. Beguin and P. Ehrburger, *Carbon*, **40**, 1619 (2002).
5. Y. Breton, G. Desarmot, J. P. Salvetat, S. Delpeux, C. Sinturel, F. Beguin, and S. Bonnamy, *Carbon*, **42**, 1027 (2004).
6. J. Jyoti, S. Basu, B. P. Singh, and S. R. Dhakate, *Composites Part B*, **83**, 58 (2015).
7. Y. Yang, E. A. Grulke, Z. G. Zhang, and G. Wu, *J. Appl. Phys.*, **99**, 114307-1 (2006).
8. D. Qian, E. C. Dickey, R. Andrews, and T. Rantell, *Appl. Phys. Lett.*, **76**, 2868 (2000).
9. S. Kumar, T. D. Dang, F. E. Arnold, A. R. Bhattacharyya, B. G. Min, and X. Zhang, *Macromolecules*, **35**, 9039 (2002).
10. B. Vigolo, P. Poulin, M. Lucas, P. Launois, and P. Bernier, *Appl. Phys. Lett.*, **81**, 1210 (2002).
11. J. Zhu, J. Kim, H. Peng, J. L. Margrave, V. N. Khabashesku, and E. V. Barrera, *Nano Lett.*, **3**, 1107 (2003).
12. H. Xia and M. Song, *Soft Matter*, **1**, 386 (2005).
13. N. Grossiord, J. Loos, O. Regev, and C. E. Koning, *Chem. Mater.*, **18**, 1089 (2006).
14. V. C. Moore, M. S. Strano, E. H. Haroz, R. H. Hauge, R. E. Smalley, J. Schmidt, and Y. Talmon, *Nano Lett.*, **3**, 1379 (2003).
15. D. Tasis, N. Tagmatarchis, V. Georgakilas, and M. Prato, *Chem. Eur. J.*, **9**, 4000 (2003).
16. C. Richard, F. Balavoine, P. Schultz, T. W. Ebbesen, and C. Mioskowski, *Science*, **300**, 775 (2003).
17. P. Ma, N. A. Siddiqui, G. Marom, and J. Kim, *Composites Part A*, **41**, 1345 (2010).
18. Y. Song and J. Youn, *Carbon*, **43**, 1378 (2005).
19. F. Du, R. C. Scogna, W. Zhou, S. Brand, J. E. Fischer, and K. I. Winey, *Macromolecules*, **37**, 9048, (2004).
20. L. Liu, A. H. Barber, S. Nuriel, and H. D. Wagner, *Adv. Funct. Mater.*, **15**, 975 (2005).
21. S. Bhattacharyya, J. Salvetat, and M. Saboungi, *Appl. Phys. Lett.*, **88**, 233119 (2006).
22. C. Pirlot, I. Willems, A. Fonseca, J. B. Nagy, and J. Delhalle, *Adv. Eng. Mater.*, **4**, 109 (2002).
23. A. Koganemaru, Y. Bin, Y. Agari, and M. Matsuo, *Adv. Funct. Mater.*, **14**, 842 (2004).
24. J. Lin, Z. Lin, Y. Pan, C. Hsieh, C. Huang, and C. Lou, *J. Appl. Polym. Sci.*, **133**, 43474 (2016).
25. M. J. Yee, N. M. Mubarak, M. Khalid, E. C. Abdullah, and P. Jagadish, *Sci. Rep.*, **8**, 17295 (2018).
26. H. Zhang, L. Quan, A. Gao, Y. Tong, F. Shi, and L. Xu, *Polymers*, **11**, 422 (2019).
27. S. Palade, A. Pantazi, S. Vulpe, C. Berbecaru, V. Tucureanu, O. Oprea, R. F. Negrea, and D. Dragoman, *Polym. Compos.*, **38**, 1741 (2017).