

Electrical Conductivity of Single Walled and Multiwalled Carbon Nanotube Containing Wool Fibers

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Received 21 July 2010; accepted 13 December 2010

DOI 10.1002/app.33979

Published online 11 April 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The main purpose of this study was producing conductive wool fabric applying carbon nanotubes. Raw and oxidized wool samples were treated with carbon nanotubes in the impregnating bath in the presence of citric acid as a crosslinking agent and sodium hypophosphite as a catalyst while sonicating them in the ultrasonic bath. Electrical resistance, washing durability, and color variation of treated samples were assessed. Through SEM images, the surface morphology of treated samples was studied confirming the surface coating through carbon

nanotubes. According to the results, the electrical resistance of treated wool with carbon nanotubes reduced substantially. However, the single-walled carbon nanotubes are more useful to increase the conductivity. In addition, the wool color changed into gray after the treatment. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 3353–3358, 2011

Key words: carbon nanotube; wool; citric acid; electrical resistance

INTRODUCTION

Textile industry is always under the pressure of introducing new finishing approaches due to improving textiles applications. Through these new methods, textiles not only meet their conventional features but also new functional properties can be created to enable them to be used in diverse fields such as military and medicine.¹ Carbon nanotubes (CNTs) were discovered in 1991 and due to their significant physical and mechanical features their applications have been developed.² High flexibility, fully reversible bending, semiconducting character, and high electrical conductivity are examples of their remarkable mechanical and physical properties.^{3–7} On the basis of the number of walls, carbon nanotubes can be divided into two various kinds; multiwalled carbon nanotubes (MWCNT) and single-walled carbon nanotubes (SWCNT).⁸ It has been proved that tensile strength of a layer of MWCNT is 100 times higher than that of steel resulting from their graphitic and tubular structure.^{10,11} Basically, they are fullerene-related structures composed of graphite cylinders, which are closed at either end with caps consisting of pentagonal rings.¹ The chemical stability of CNTs is high because of their covalent

bonds between the carbon atoms.¹² It has been confirmed that chemical activity of CNTs is lower than that of carbon fibers and graphite.¹² Through CNTs, advanced composites can be achieved, and several pieces of research have been conducted to study the features of diverse matrix materials, polymers, ceramics, and metals.^{13–15}

Through the application of CNT particles on the textile surface fabric, the conductivity changes.¹⁶ Producing the conductive clothes has attracted a great attention during last years and various approaches were used to this end.¹⁶ Although in previous studies, it has been reported that the electronic textiles (e-textiles) can be produced through weaving and knitting of metal electrodes, there were a lot of disadvantages for this method. For instance, stiffness and elasticity of achieved samples increased and reduced, respectively.¹⁷ Polymerization of electrically conductive polymers on the surface of fibers is a method through which the conductive fibers with improved physical and mechanical properties are produced.^{17–20} Panhuis studied the conductivity of CNT coated wool-nylon-lycra fabric, through analyzing the variation of that and it was observed that the conductivity of fabrics increased after CNT treatment.¹⁷ CNTs have been used in some form of matrix producing composite structures and this field is now a rapidly growing research field.²¹ The yield strength of the produced sintered materials improved by increasing the CNTs volume fraction except in case of 20 vol % CNT/Cu composite where

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the nanocomposite was fractured at a lower strength value.⁸ It was also confirmed that the density and electrical conductivity of CNT/Cu nanocomposites diminished by increasing the CNTs volume fraction while hardness and Young's modulus were boosted by increasing the CNTs volume fraction.⁸

Wool is one of the most important animal fibers in textile industry.^{22,23} Wool fibers have a large surface area in relation to their bulk, and the surface structure plays a prominent role in wool properties including felting, appearance, soiling, dyeing, and the water absorption, to name but a few.²⁴ Understanding the exact configuration of wool can be effective in finding new ways to promote its properties.²⁴ Unwanted effects such as felting and the barrier of diffusion are most probably due to the presence of wool scales.²⁵ It has been recognized that oxidation process by potassium permanganate is effective in increasing the water absorption of wool.²⁶ The impacts of potassium permanganate on wool, increased with time, temperature and concentration of KMnO_4 in the treatment bath.^{27,28} It has been reported that through an oxidation process, the sharp edges of wool scales can be removed.^{27,28} Carboxylic acid treatments are known to introduce carboxylic and hydroxyl functional groups on the surface of wool. As a result, CNTs tendency towards the surface of wool increases.²⁹

This study has focused on distinctive impacts of CNTs on wool fabrics. Two oxidized and nonoxidized wool samples were used. This can reveal the role of oxidation process on the adsorption of CNTs on the surface of wool. Oxidation process was carried out in an acidic solution ($\text{pH} = 4$) in the presence of sodium chloride (NaCl).

EXPERIMENTAL AND METHODS

Materials

The 100% raw wool fabric with twill structure, warp, and weft density 16 and 18 per cm, respectively; with fineness 30 (Nm); fabric mass 350 gr/m^2 was used. Carbon nanotubes, with two distinctive structures (MWCNTs and SWCNTs) from Iran Petrol Research Center, Citric acid (CA) as a crosslinking agent from Merck Company (Germany), and sodium hypophosphite (SHP) as a catalyst from Riedel-dehean (Germany) were used. The wool samples were scoured by colorless nonionic detergent from Intersac Company (Canada).

Apparatuses

A Spectrophotometer (CM-3600d) from KONIKA MINOLTA Company (Japan) was employed to detect the color variation of treated samples, and an

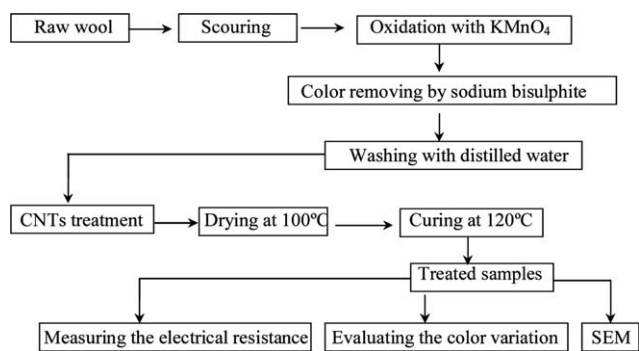


Figure 1 The order of treatments on wool samples.

ultrasonic bath (CD-4800) from China was used to mix the components of the impregnating bath. A high voltage insulation tester model 3125 from Japan was employed to measure the electrical resistance of treated samples. The SEM images were taken by Philips-XL30 (Netherlands). For the purpose of curing the treated samples, a thermal oven was used.

The order of various treatments on the wool samples is proposed in Figure 1.

Scouring

the wool samples were washed, in L: R→50 : 1 (liquor to good ratio) with 2 g/L nonionic detergent, at 40–45°C for 20 min, and then were rinsed thoroughly with distilled water. The samples were then dried at room temperature for at least 24 h.

Oxidation process

the washed wool samples were oxidized with 3% (%w/w) KMnO_4 in an acidic solution ($\text{pH} = 4$) in the presence of 10 g/L NaCl in L : R → 40 : 1 at 30°C for 20 min. The pH of the solution was adjusted by 4N sulfuric acid. To remove the brown color from the samples, the oxidized fabrics were treated with sodium bisulphite and sulfuric acid and then were washed with distilled water.^{22,23}

CNTs treatment

The impregnating bath consisted of diverse concentrations of carbon nanotubes, 20% (%w/w) CA, and 13% (%w/w) SHP (Table I). The samples were treated for 30 min. Before placing the wool samples into the impregnating bath, its compounds had been sonicated for several minutes to disperse the nanoparticles. Treated samples were dried at 100°C for 10 min and then cured at 120°C for three minutes. There might have been some additional nanoparticles of CNTs that had not linked with the fabric and just were adsorbed physically on the surface of wool, to remove them, treated samples were located

TABLE I
Contents of the Impregnating Bath

CNTs (SWCNT, MWCNT) (g/L)	CA (%)	SHP (%)
0.5	20	13
1.5	20	13
2.5	20	13
3.5	20	13
4.5	20	13
5.5	20	13

in distilled water in the ultrasonic bath and were sonicated for 5 min; subsequently, they were dried at 100°C for 10 min.

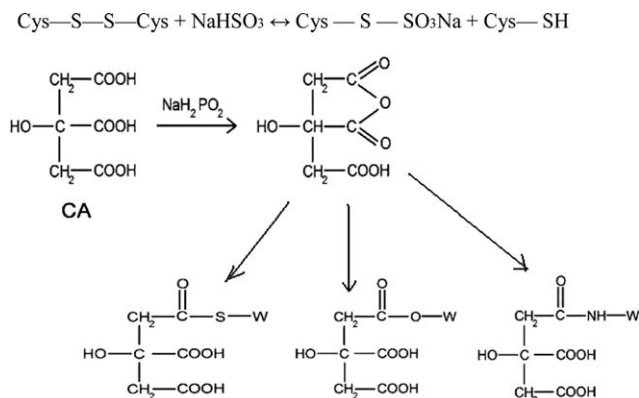
Measuring the electrical resistance

According to AATCC- 76 standard the electrical resistance of treated samples was measured. The dimension of samples was 8 cm × 2 cm. In this method, the fabrics were fixed using two cooper electrodes of high voltage insulation tester and then the electrical resistance was measured at 2500 V. All samples were tested in constant conditions namely all of them were located in room temperature for at least 24 h and then were tested in 65% r.h. The electrical resistance was measured at least five times for each sample and an average number was registered.

RESULTS AND DISCUSSIONS

The variation of electrical resistance

Treated samples with diverse concentrations of carbon nanotubes were evaluated in terms of their conductivity and electrical resistance. It can be reasonable that through oxidation process, the higher amounts of CNTs can be adsorbed on the wool surface. Montazer and Pakdel in their previous research proved quantitatively that oxidation process with KMnO_4 has positive effects on the adsorption of nanoparticles specifically titanium dioxide particles on the surface of wool.^{22,23} The remarkable electrical



Scheme 1 Mechanism of crosslinking formation between citric acid and wool.

properties of carbon nanotubes make them ideal candidates for producing fabrics with higher conductivity.³⁰ It is worth mentioning that the wool contains several main functional groups as follows: carboxyl ($-\text{COOH}$), amino ($-\text{NH}_2$), and hydroxyl ($-\text{OH}$); therefore, it is chemically extremely active.³¹ Application of crosslinking agent was necessary to introduce additional sites for creation of linkages.³¹⁻³³ Martel et al., observed that usage of sodium hypophosphite (SHP) can catalyze the reaction between citric acid and wool.³² Oxidized samples were reduced by sodium bisulphite. The suggested mechanism for crosslinking reactions was proposed in Scheme 1.

It was observed that through increasing the amount of carbon nanotubes in the impregnating bath, a higher amount of nanoparticles was adsorbed on the surface of wool. Consequently, its electrical resistance decreased, in other words, its electrical conductivity increased. The electrical resistance variation of treated samples with both MWCNTs and SWCNTs are proposed in Tables II and III, respectively. On the basis of the results of Tables II and III, it was confirmed that increasing the amount of CNTs up to 4.5 g/L in the impregnating bath can be effective in boosting the conductivity

TABLE II
The Variation of Electrical Resistance for MWCNT Treated Samples for Raw and Oxidized Wool Before and After Washing Process

MWCNTs (g/L)	Electrical resistance of raw treated wool (Ω/square)	Electrical resistance of raw treated wool after washing (Ω/square)	Electrical resistance of oxidized treated wool before washing (Ω/square)	Electrical resistance of oxidized treated wool after washing (Ω/square)
0.5	5.61×10^{10}	5.87×10^7	4.3×10^8	3.84×10^7
1.5	4.68×10^9	2.93×10^7	1.2×10^7	8.5×10^6
2.5	3.16×10^7	4.8×10^6	9.1×10^6	4.95×10^6
3.5	1.08×10^7	2.1×10^6	7.9×10^6	3.6×10^5
4.5	1.35×10^7	2.2×10^6	7.78×10^6	2.00×10^5
5.5	1.07×10^7	1.5×10^6	5.59×10^6	3.00×10^5

TABLE III
The Variation of Electrical Resistance for SWCNT Treated Samples for Oxidized Wool Before and After Washing Process

SWCNTs (g/L)	Electrical resistance of oxidized wool before washing (Ω /square)	Electrical resistance of oxidized wool after washing (Ω /square)
0.5	2.7×10^6	3.02×10^7
1.5	7.4×10^5	2.19×10^6
2.5	1.2×10^5	2.21×10^5
3.5	2.5×10^4	1.73×10^5
4.5	1.2×10^4	6.48×10^4
5.5	1.0×10^4	5.3×10^4

of treated wool samples. Above this point, its still increasing rate proceeds at a lower pace, which can be explained due to the fact that the surface of wool was saturated by CNTs; therefore, the amount of adsorption of nanoparticles on the surface of wool reduced. In addition, the conductivity of treated samples with SWCNTs was higher than that of MWCNTs treated ones. The electrical resistance of nonoxidized-treated samples decreased from $5.61 \times 10^{10}(\Omega)$ to $1.07 \times 10^7(\Omega)$ by increasing the amount of carbon nanotubes from 0.5 g/L to 5.5 g/L in the impregnating bath. As for the oxidized treated samples, the highest and lowest amount of the electrical resistance were $4.3 \times 10^8 (\Omega)$ and $5.59 \times 10^6 (\Omega)$, respectively, (Table II). It was observed that in oxidized-treated samples the electrical resistance was lower in comparison with that of nonoxidized treated samples due to a higher amount of CNTs adsorption (Tables II and III).

The variation of color indices

The color variation of treated samples was evaluated using a spectrophotometer (KONIKA MINOLTA-CM-3600d). It was assumed that through application of carboxylic acids in the impregnating bath, the adsorption speed of nanoparticles on the fabric surface can be increased.^{22,23} In the previous research,

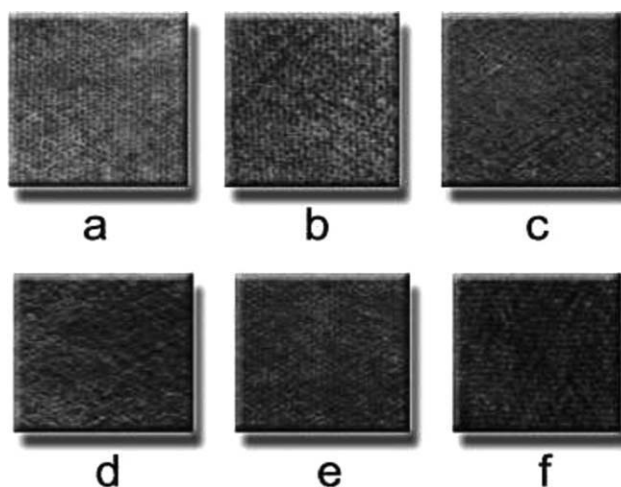


Figure 2 Treated wool samples with diverse concentrations of CNT.

nanoparticles of titanium dioxide were anchored on to the surface of wool using this method.^{22,23,26} Wool samples were immersed in the impregnating bath, and then cured to create linkages between wool and citric acid.^{22,23,31} It has been reported that curing process plays a prominent role in the creation and stabilization of crosslinks between the functional groups of wool and carboxylic acids.³¹ Montazer and Pakdel compared the whiteness and yellowness of raw and oxidized wool samples and it was confirmed that through an oxidation process the surface of wool seems whiter thanks to destroying some parts of yellow chromophores.^{22,23} In addition, they confirmed the presence of nanoparticles on the surface of wool both qualitatively and quantitatively through XRD patterns and EDS analysis.^{22,23} In their research, the reactions between the functional groups of wool and carboxylic acid, which was used as a crosslinking agent, as well as the occurred alterations of the wool structure, were evaluated using both FT-IR and Raman spectra.^{22,23} There is a general consensus among scientist that several amino acids such as cystine, tyrosine, and tryptophan are affected in an oxidation process.^{27,28} The mechanism

TABLE IV
Color Indices of Wool Samples

h^*	C^*	b^*	a^*	L^*	MWCNT (g/L)	Wool samples
94.89	11.61	11.56	-0.99	79.62	0	Raw wool
94.78	9.88	9.85	-0.82	78.88	0	Raw wool + CA
94.9	11.71	11.6	-0.1	80.06	0	Oxidized wool
94.78	9.88	9.85	-0.82	78.88	0	Oxidized wool + CA
90.04	2.44	2.44	0.0	34.9	0.5	Oxidized wool + CA
88.23	2.16	2.16	0.07	30.8	1.5	Oxidized wool + CA
84.95	1.33	1.33	0.12	26.46	2.5	Oxidized wool + CA
83.9	1.32	1.32	0.13	25.64	3.5	Oxidized wool + CA
81.36	1.2	1.29	0.15	24.18	4.5	Oxidized wool + CA
81.19	1.13	1.33	0.15	23.9	5.5	Oxidized wool + CA

TABLE V
Color Indices of Wool Samples Treated with MWCNTs After Washing Process

Gray scale	ΔE^*	Δh^*	ΔC^*	ΔL^*	MWCNT (g/L)	Wool sample
4.83	0.1	-0.60	-0.09	-0.18	0	Raw wool
4.66	0.12	0.1	0.69	-0.22	0	Raw wool + CA
4.91	0.09	0.12	-0.11	-0.17	0	Oxidized wool
4.75	0.11	0.12	0.33	-0.22	0	Oxidized wool + CA
3.91	0.2	-0.60	0.2	-0.11	0.5	Oxidized wool + CA
3.9	0.25	-0.80	0.31	-0.23	1.5	Oxidized wool + CA
3.89	0.4	-0.1	0.43	-0.32	2.5	Oxidized wool + CA
4.87	0.41	-0.11	0.48	-0.35	3.5	Oxidized wool + CA
3.61	0.5	-0.13	0.5	-0.41	4.5	Oxidized wool + CA
3.33	0.85	-0.15	0.51	-0.45	5.5	Oxidized wool + CA

of degradation of cystine amino acid is proposed in Scheme 1.

In this study, through the oxidation process, wool samples seem whiter in comparison with raw wool and this result was consistent with the previous findings.^{22,23} To make a scientific comparison among treated samples color, several indices were employed. L^* shows lightness of the fabric (lighter if positive; darker if negative), a^* and b^* are the signs for evaluating the red-green color (redder if positive; greener if negative) and the yellow-blue color (yellow if positive; bluer if negative), respectively.²⁶ In addition, C^* is metric chroma and h^* is metric hue angle. ΔE was calculated based on eqs. (1)–(3).³⁴ The

results of Table IV showed that generally through applying nano CNT particles on the surface of oxidized wool, on the one hand, their L^* (lightness) and b^* have decreased, from 78.88 and 9.85 to 34.9 and 2.44, respectively, and on the other hand a^* increased from -0.82 in untreated oxidized samples to 0.0 in treated oxidized fabrics (Table IV). Adsorbing of CNTs on the surface of wool altered the color fabrics into gray (Fig. 2) which proved the existence of CNTs on fabric (Table V) and their color variation described based on gray scale. The Grey Scale is for assessing the degree of change in shade caused to a dyed Textile fabric and yarn in color fastness tests. The scale consists of nine pairs of gray color chips

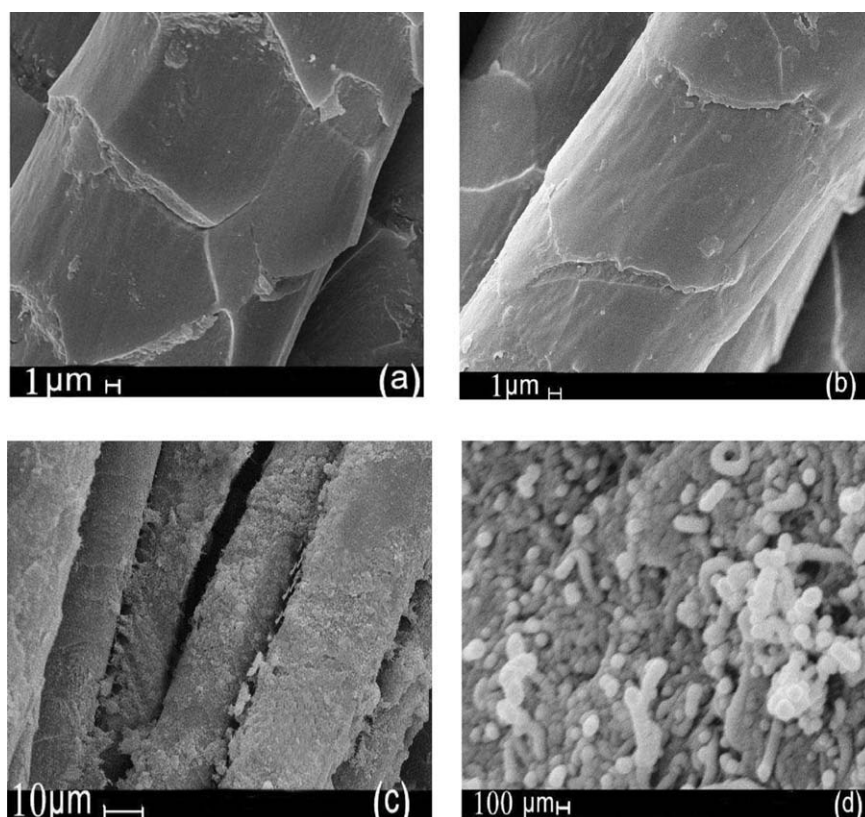


Figure 3 SEM images of wool samples (a) Raw wool ($\times 3000$), (b) Oxidized wool ($\times 3000$), (c) treated sample with 5.5 g/L CNT ($\times 1000$), (d) CNT particles on the surface of treated sample with 5.5 g/L CNT ($\times 30,000$).

each representing a visual difference and contrast. The fastness rating goes step-wise from: Note 5: no visual change to Note 1: a large visual change.

$$\Delta E = [\Delta L^* + \Delta a^* + \Delta b^*]^{0.5} \quad (1)$$

$$\Delta C^* = [(\Delta a^*)^2 + (\Delta b^*)^2]^{0.5} \quad (2)$$

$$\Delta E = [(\Delta C^*)^2 + (\Delta L^*)^2]^{0.5} \quad (3)$$

SEM images

Through Philips- XL30 (Netherlands) the SEM images were taken. The surface of wool fiber consists of cuticle cells overlapping to form a structure like tiles on a roof.³⁵ They account for major properties of wool such as dyeability, felting shrinkage, and frictional coefficient.³⁶ In general, oxidation process changes the pattern of wool surface. It was observed that through the oxidation process the height of sharp edges of wool scales have reduced (Fig. 3). CNT particles covered the surface of wool and the aggregation of nanoparticles can be seen in Figure 3.

CONCLUSION

It has been confirmed that the electrical resistance of wool fabric can be reduced significantly through using carbon nanotubes in the simple exhaustion method. Using citric acid and sodium hypophosphite helped to improve carbon nanotubes adsorption on wool fabric surface. Single wall carbon nanotubes are more efficient than multi wall carbon nanotubes to produce lower electrical resistance wool fabrics. Also preparation of wool fabric through oxidation with potassium permanganate helped to obtain improved results and better conductivity. Finally the color of the treated wool is gray.

References

- Karthik, L.; Jalili, N. *Tex Res J* 2005, 75, 670.
- Schlittler, R. R.; Seo, J. W.; Gimzewski, J. K.; Durkan, C.; Saifullah, M. S. M.; Welland, M. E. *Sci* 2001, 292, 1136.
- Robertson, D. H.; Brenner, D. W.; Mintmire, J. W. *Phys Rev B* 1992, 45, 12592.
- Yakobson, B. I.; Brabec, C. J.; Bernholc, J. *Phys Rev Lett* 1996, 76, 2511.
- Lu, J. P. *Phys Rev Lett* 1997, 79, 297.
- Wong, E. W.; Sheehan P. E.; Lieber, C. M. *Sci* 1997, 277, 1971.
- Cornwell, C. F.; Wille, L. T. *Solid State Commun* 1997, 101, 555.
- Daoush, W. M.; Lima, B. K.; Mo, C. B.; Nam, D. H.; Hong, S. H. *Mater Sci Eng A* 2009, 513 and 514, 247.
- Che, J.; Cagin, T.; Goddard W. A., III. *Nanotechnol* 2000, 11, 65–69.
- Yu, M. F.; Files, B. S.; Arepalli, S.; Ruoff, R. S. *Phys Rev Lett* 2000, 84, 5552.
- Mintmire, J. W.; White, C. T. *Carbon* 1995, 33, 893.
- Tans, S. J.; Verschueren, A. R. M.; Dekker, C. *Nature* 1998, 393, 49.
- Terrones, M. *Annu Rev Mater Sci* 2003, 33, 419.
- Peigney, A.; Laurent, C. H.; Flahaut, E.; Rousset, A. *Ceram Int* 2000, 26, 677.
- Flahaut, E.; Peigney, A.; Laurent, C. H.; Marliere, C. H.; Chastel, F.; Rousset, A. *Acta Materialia* 2000, 48, 3803.
- Baughman, R. H.; Zakhidov, A. A.; De Heer, W. A. *Science* 2002, 297, 787.
- Panhuis, M.; Jian, W.; Syed, A.; Ashraf, G.; Wallace, G. *Synth Met* 2007, 157, 358.
- Xue, P.; Tao, X. M. *J Appl Polym Sci* 2005, 98, 1844.
- Gregory, R. V.; Kimbrell, W. C.; Kuhn, H. H. *Synth Met* 1989, 28, 823.
- Varesano, A.; Acqua, L. D.; Tonin, C. *Polym Degrad Stab* 2005, 89, 125.
- Qian, D.; Dickey, E. C. *Appl Phys Lett* 2000, 76, 2868.
- Montazer, M.; Pakdel, E. *Photochem Photobiol* 2010, 86, 255.
- Montazer, M.; Pakdel, E.; Bameni, Moghadam, M. *Fibers Polym* 2010, 11, 967.
- Huson, M.; Evans, D.; Church, J.; Hutchinson, S.; Maxwell, J.; Corino, G. *J Struct Biol* 2008, 163, 127.
- Kan, C. W.; Chan, K.; Yuen, C. W. M.; Miao, M. H. *J Mater Process Technol* 1998, 82, 122.
- Montazer, M.; Pakdel, E. *J Text Inst*, DOI: 10.1080/00405001003771242, Published online.
- Ma, B.; Zheng, C.; Sun, R. *Tex Res J* 2003, 100, 73.
- Kantouch, A.; Bendak, A.; Sadek, M. *Tex Res J* 1978, 48, 619.
- Kim, H.; Park, B. H.; Yoon, J. S.; Jin, H. J. *Polym Int* 2007, 56, 1035.
- Nygaard, J.; Cobden, C. H.; Bockrath, M.; McEuen, P. L.; Lindelof, P. E. *Appl Phys A* 1999, 69, 297.
- Hsieh, S. H.; Huang, Z. K.; Huang, Z. Z.; Tseng, Z. S. *J Appl Polym Sci* 2004, 94, 1999.
- Martel, B.; Weltrowski, M.; Morcellet, M. *J Appl Polym Sci* 2002, 83, 1449.
- Nazari A.; Montazer, M.; Rashidi, A.; Yazdanshenas, M. E.; Anari, M. *Appl Catal A Gen* 2009, 371, 10.
- Kuehni, R. G. *Color Space and Its Divisions*; New Jersey USA: Wiley, 2003, p 234.
- Montazer, M.; Zolfaghari, A. R.; Toliati, T.; Bameni Moghadam, M. *J Liposome Res* 2009, 19, 173.
- Hocker, H. In *Wool: Science and Technology*; Simpson, W. S.; Crawshaw, G. H., Eds.; Cambridge: Woodhead, 2002, p 60.