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Electrospinning of cellulose acetate fibers from a ternary solvent system

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In this study, cellulose acetate fibers (CA) were prepared by the technique of electrospinning. A new ternary solvent mixture consisting of acetone / dichloromethane (DCM)/*N,N*-dimethylformamide (DMF) at the ratio of 2/1/1 (v/v/v) was used in the electrospinning process. The suggested composition of solvents ensured continuous electrospinning of CA fibers, while other compositions of the same solvent system were not suitable to produce fibers. Smooth fibers with the mean diameter of 241 ± 92 nm were obtained by the solvent system containing more than 11% (w/v) of CA. The morphology and diameter of electrospun CA fibers were highly dependent on the concentration of CA solution.

Key words: electrospinning, cellulose acetate, nanofibers, ternary solvent system

INTRODUCTION

Currently, there are three main techniques for nanofiber based material production: multi-component fiber spinning, modular melt-blowing and electrospinning [1]. The latter is the most popular technique due to its simplicity and inexpensive instrumental setup [2–4]. Fibers produced from electrospinning have unique characteristics such as a large surface area to volume ratio, low basis weight, a nanoporous structure and a relatively uniform fiber size. Due to these characteristics application areas of electrospun fibers include filters, tissue engineering and protective clothing [2, 5–7].

Cellulose acetate (CA) is a biodegradable plastic, which is manufactured from purified natural cellulose [8]. Electrospun CA fibers are characterized by good thermal stability and chemical resistance [9]. It have been demonstrated that the solvent systems used for CA fiber production have a significant influence on the morphology and diameter of fibers [10−12]. Traditional single solvent systems are not suitable for uniform CA fiber formation. Single solvent systems such as *N,N*-dimethylformamide (DMF), dichlormethane (DCM), formic acid, methanol, chloroform and pyridine mainly produce discrete beads while an acetone solvent in electrospinning forms short and beaded fibers [12]. As a result, binary solvent systems are used in CA electrospinning to obtain uniform fibers below the diameter of 1 000 nm. The most appropriate solvent system for electrospinning of CA fibers was shown to be a mixture of acetone / *N,N*-dimethylacetamide (DMAc) [13−16]. Greish et al. [9] performed detailed research on this solvent system with respect to chemical and thermal treatment of CA fibers. Binary solvent systems of successful uniform CA fibers electrospinning are mixtures of acetone/DMAc [9, 12], acetone/DCM [11], methanol/DCM [12], and acetic acid / water [10]. In most cases successful electrospinnability of CA fibers from binary solvent systems was defined by the difference in the boiling points and dielectric constants of both solvents. Prolonged utilization of the solvent system containing volatile compounds causes clogging of the spinneret during the electrospinning process, especially in low humidity environment [3, 17]. A binary system of acetone/DCM (boiling points 40 °C and 56 °C, respectively) is a typical example of such solvent system.

We have developed a new ternary solvent system for continuous electrospinning of CA nanofibers introducing DMF (boiling point 154 °C) as a widely used solvent to the mixture to reduce overall volatility of the system. It was

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found that the solvent system consisting of acetone/DCM/DMF with the ratio of 2/1/1 (v/v/v) results in the optimized nanofiber production process with high-quality fibers of low average diameter. The influence of the CA concentration on the average diameter and morphology of the electrospun nanofibers were investigated. In the present study, the effect of the acetone/DCM/DMF solvent composition on the electrospinnability and diameter of CA nanofibers was systematically investigated. The proposed composition of the solvent system allows a stable electrospinning process.

EXPERIMENTAL

CA flakes (Rhodia SA, France) having a molecular mass of 50,000 were utilized in this study. The solvents of the ternary system used in this work were acetone (min. assay 99.8%, Sigma-Aldrich, USA), DMF and DCM (min. assays of 99.8%, Eurochemicals S. p. A, Italy). All materials were used without any purification.

Homogeneous solutions were obtained by dissolving CA in an acetone/DCM/DMF ternary solvent mixture in room temperature. A full-factorial experiment design was applied, including acetone/DCM/DMF ratios of 1/1/1 and 2/1/1 (v/v/v) as well as CA concentrations of 9%, 10%, 11%, 12% (w/v).

The conductivity measurements of solutions were performed before electrospinning by using a conductivity meter (HI 8733, Hanna Instruments, USA) at 20 °C.

A single-needle system was used in electrospinning experiments (Fig. 1). The electrospinning device consisted of a high voltage DC power supply based on the "Flyback" principle. The grounded electrode was connected to the collector and the high voltage electrode was connected to the needle of the syringe. The CA solutions were loaded to the syringe with the needle, which was fixed horizontally on the syringe pump (LSP01-1A, Baoding Longer Precision Pump Co., Ltd., China). Electrospun fibers were collected on the vertically positioned cylindrical-collector coated with aluminum foil and rotating at the linear speed of 150 cm/min. The electrospinning parameters were as follows: voltage = 18 kV, feed rate = 2.8 ml/h and tip-to-collector distance = 11 cm. The electrospinning process was carried out in an enclosed Plexiglas box at ambient conditions (at 20 °C and 40% relative humidity). The collected samples of electrospun nanofibers were dried in vacuum at room temperature for 12 h.

The morphology and diameter of the CA fibers were investigated by using a scanning electron microscope (Quanta 200 FEG, FEI Company, USA). The average fiber diameters were determined by analyzing SEM images with the ImageJ (NIH, USA) [18] image analysis software. For each sample fiber diameters were measured at 100 different points.

RESULTS AND DISCUSSION

In the case of the ternary solvent system of acetone/DCM/DMF at the ratio of 1/1/1 (v/v/v) the electrospun fibers showed beaded fibers with droplets and stick-together morphology. This ternary mixture contained 1/3 by volume of DMF solvent, which is characterized by a high boiling point (154 °C), while the ternary solvent system at the ratio 2/1/1 (v/v/v) had 1/4 part by volume of the DMF solvent. The increased amount of the DMF solvent in the ternary system of 1/1/1 (v/v/v) had an impact on the overall boiling point of the mixture. When electrospinning is performed from solvents with higher boiling point value, the ejected charged jet does not have enough time to dry during its time of flight. As a result, droplets and stick-together morphology of fibers were fabricated.

Using the solvent system of acetone/DCM/DMF 2/1/1 the electrospinning was possible starting with CA concentration higher than 9% (w/v). In case of concentration lower than 9% (w/v), fibers were not formed due to the jet breaking up into droplets. Electrospinning of the 9 and 10% (w/v) CA (Fig. 2A and B) resulted in the formation of beaded fibers. The electrospun mat of the 11% (w/v) CA showed rather uniform structure with exceptions of several splayed out fibers (Fig. 2C). The smooth fibers were obtained from 12% w/v solution (Fig. 2D).

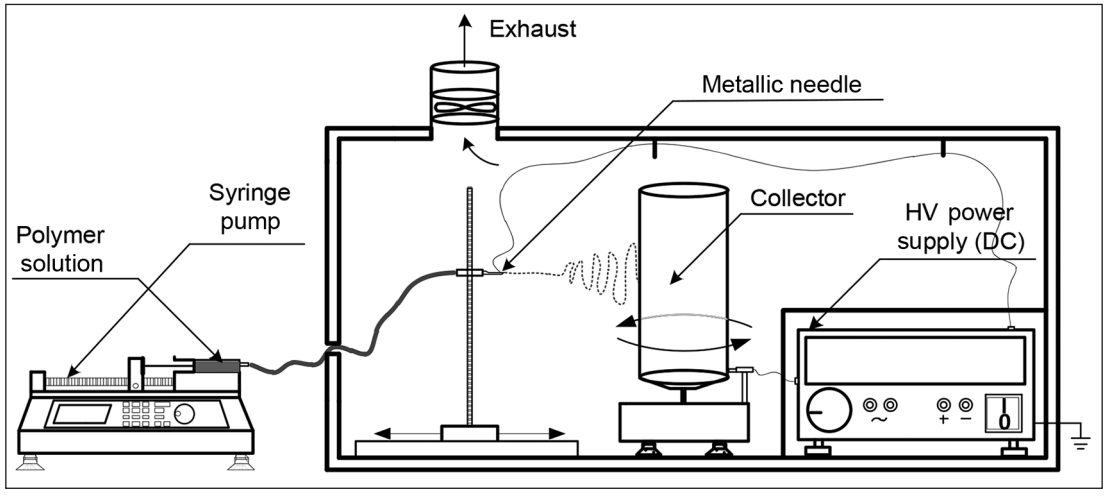

Fig. 1. Scheme of the used electrospinning system

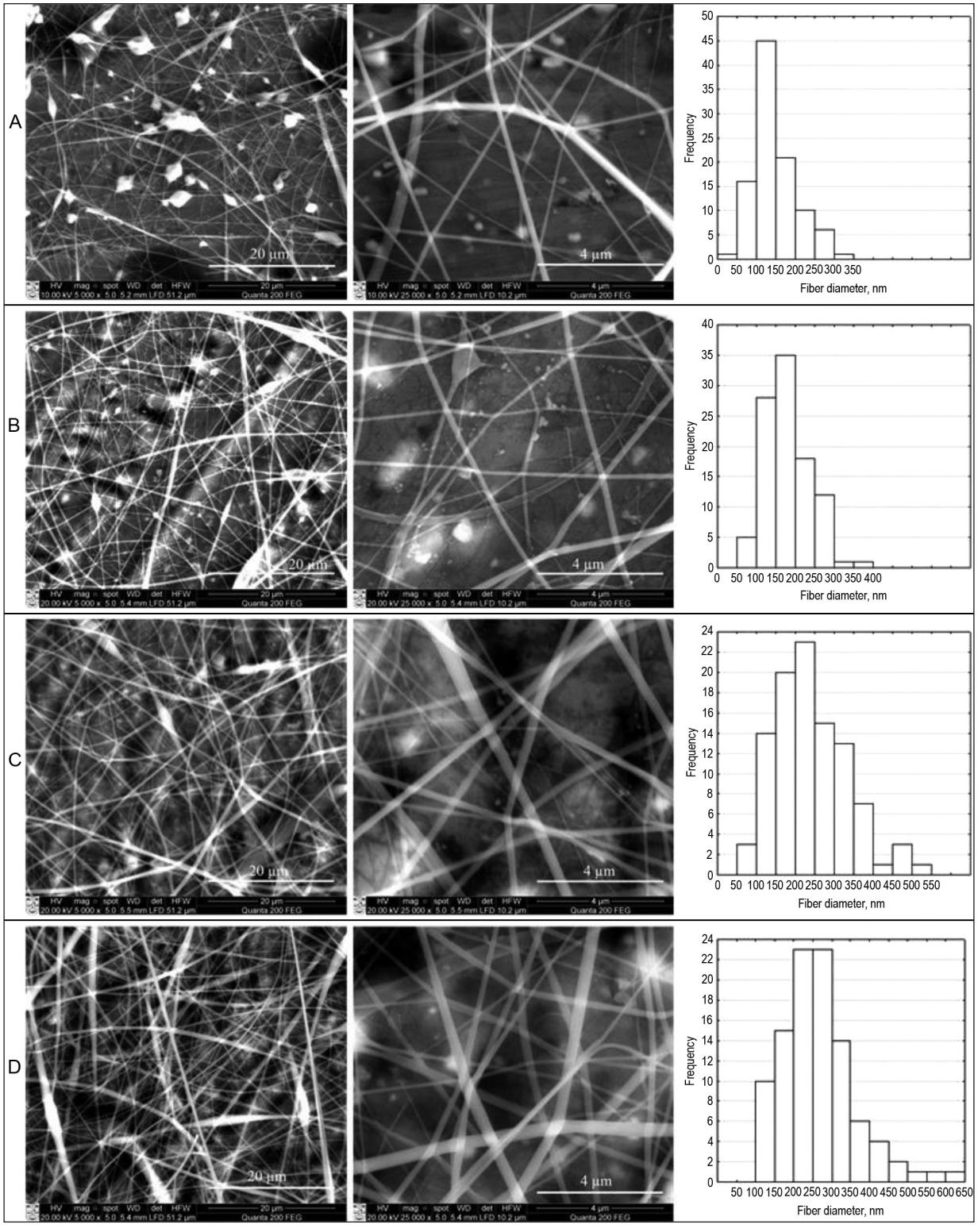

Fig. 2. SEM images of the electrospun CA nanofibers obtained from the acetone/DCM/DMF ternary solvent system and fiber diameter distribution histograms: CA concentrations – (A) 9% w/v, (B) 10% w/v, (C) 11% w/v, (D) 12% w/v

The respective diameter distributions of fibers are presented in the right side of Fig. 2. Properties of the electrospun CA fibers obtained from the ternary solvent mixture are presented in Table 1.

The comparative analysis of electropsun CA fiber diameters showed that CA solution concentrations have effect on the fiber diameter range. It was determined that diameters of fibers did not follow normal (Gaussian) distribution (Statistica, StatSoft Inc., USA) ($p < 0.05$ based on Shapiro-Wilk's W test) (see histograms in Fig. 2). Also, the analysis has clearly showed that the increase of CA solution concentration has direct influence on the diameter of electrospun

Table 1. **Properties of the electrospun CA fibers obtained from acetone/DCM/DMF ternary solvent system**

Parameter	Concentration of CA in ternary solution, % w/v			
	9%	10%	11%	12%
Conductivity of solution, μS/cm	3.50	3.40	3.35	3.30
Mean fiber diameter, nm	152	179	241	264
Standard deviation of diameter, nm	57	62	92	97
Median fiber diameter, nm	143	165	232	251
25th percentile diameter, nm	116	127	172	199
75th percentile diameter, nm	178	214	299	319

Table 2. **Comparison of various CA solution parameters and the resulting electrospun fibers**

Research	Electrospinning parameters	Concentration of CA and solvent system	Fiber diameter, nm
Celebioglu and Uyar 2011 [11]	Voltage (V) = 15 kV, feed rate (fr) = 1 ml/h, tip-to-collector distance (toc) = 10 cm (22 °C and 30% relative humidity (RH))	10% w/v in DCM/acetone 1/1 v/v	300–1 000
		7.5% w/v in DCM/acetone 2/1 v/v	500–1 500
		10% w/v in DCM/acetone 2/1 v/v	750–1 350
		7.5% w/v in DCM/acetone 3/1 v/v	750–2 500
		10% w/v in DCM/acetone 3/1 v/v	1 000–2 500
		5% w/v in DCM/acetone 9/1 v/v	1 500–3 500
		7.5% w/v in DCM/acetone 9/1 v/v	3 500–7 000
Han et al. 2008 [10]	V = 25 kV, fr = 3 ml/h, toc = 10 cm (25 °C)	17 wt.% in acetic acid/water 70/30 w/w	160
		17 wt.% in acetic acid/water 75/25 w/w	180
		17 wt.% in acetic acid/water 80/20 w/w	~350
		17 wt.% in acetic acid/water 85/15 w/w	~400
		17 wt.% in acetic acid/water 90/10 w/w	~600
		17 wt.% in acetic acid/water 95/5 w/w	1 280
Tungprapa et al. 2007 [12]	V = 12 kV, toc = 15 cm	16% w/v in acetone/DMAc 1/1 v/v	160
		16% w/w in acetone/DMAc 3/1 v/v	260
		14% w/v in acetone/DMAc 2/1 v/v	230
		16% w/v in acetone/DMAc 2/1 v/v	260
		18% w/v in acetone/DMAc 2/1 v/v	330
		20% w/v in acetone/DMAc 2/1 v/v	370
		8% w/v in DCM/methanol 4/1 v/v	1 100
		10% w/v in DCM/methanol 4/1 v/v	1 580
		12% w/v in DCM/methanol 4/1 v/v	1 230
Present study	V = 18 kV, fr = 2.8 ml/h, toc = 11 cm (20 °C and 40% RH)	11% w/v in acetone/DCM/DMF 2/1/1 v/v/v	241
		12% w/v in acetone/DCM/DMF 2/1/1 v/v/v	264

fibers (linear $R^2 = 0.966$) whereas the concentration increase has indicated the decline of CA solution conductivity (linear $R^2 = 0.965$) (see Table 1).

The findings from other studies, using various solvent systems, for electrospinning CA fibers are presented in Table 2. Han et al. [10] reported that low diameter (up to 200 nm) smooth CA fibers could be formed from the acetic acid / water solvent system (ratio of 70/30 and 75/25 w/w). Accordingly, Tungprapa et al. [12] found that low diameter CA fibers could also be formed from the acetone/DMAc solvent system (ratio of 1/1 v/v). While the largest smooth fibers of CA by a diameter over 1 000 nm could be obtained using higher amount of the DCM solvent part in solvent systems. Despite the broader diameter of CA fibers from the DCM/acetone solvent system (ratio of 3/1 and 9/1) these fibers are practically important because of its porous structure inside the fibers [11]. These properties would be useful for filtration application due to the high surface to volume ratio. On the other hand, the morphology of beaded fibers of CA shown in Fig. 2 (A–B) also would be useful for filtration application, as beaded fiber mats decrease the volume fraction and increase the effective fiber surface area [19].

The present study shows that smooth CA fibers could be obtained from the acetone/DCM/DMF solvent system (ratio 2/1/1 v/v/v) with comparatively low concentrations of CA solutions resulting in a mean fiber diameter of 241–264 nm. It should be pointed out that in all described solvent systems acetone is an essential component in electrospinning of CA fibers.

CONCLUSIONS

The current study demonstrated that continuous electrospun CA fibers could be obtained from a new ternary acetone/DCM/DMF solvent system (ratio 2/1/1 v/v/v). The developed solvent system ensured a stable CA electrospinning process

(without needle clogging) in case of using very volatile solvents. It also allowed avoiding stick-together morphology in case of using solvents with a high boiling point. Electrospinning of the 11 and 12% (w/v) CA solutions have resulted in uniform morphology of the mat of the mean fiber diameter 241 ± 92 and 264 ± 97 nm, respectively.

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References

1. G. Ward, *Filtr. Sep.,* **42**, 22 (2005).
2. P. Q. Pham, U. Sharma, G. A. Mikos, *Tissue Eng.*, **12**, 1197 (2006).
3. X. Wang, H. Niu, X. Wang, T. Lin, *J. Nanomater.*, **2012**, Article ID 785920, http://dx.doi.org/10.1155/2012/785920 (2012).
4. S. Petrik, M. Maly, *Proceedings of 2009 Fall MRS Symposium*, Boston (2009).
5. R. S. Barhate, S. Ramakrishna, *J. Membr. Sci.*, **296**, 1 (2007).
6. W. W. F. Leung, C. H. Hung, P. T. Yuen, *Sep. Purif. Technol.*, **71**, 30 (2010).
7. N. A. M. Barakata, M. F. Abadir, F. A. Sheikh, M. A. Kanjwal, S. J. Park, H. Y. Kim, *Chem. Eng. J.*, **156(2)**, 487 (2010).
8. K. Y. Lee, L. Jeong, Y. O. Kang, S. J. Lee, W. H. Park, *Adv. Drug Delivery Rev.*, **61(12)**, 1020 (2009).
9. E. Y. Greish, M. A. Meetani, E. A. Al Matroushi, B. Al Shamsi, *Carbohydr. Polym.*, **82**, 569 (2010).
10. S. O. Han, J. H. Youk, K. D. Min, Y. O. Kang, W. H. Park, *Mater. Lett.*, **62**, 759 (2008).
11. A. Celebioglu, T. Uyar, *Mater. Lett.*, **65**, 2291 (2011).
12. S. Tungprapa, T. Puangparn, M. Weerasombut, et al., *Cellulose*, **14**, 563 (2007).
13. C. H. Hong, S. J. Ki, J. H. Jeon, et al., *Compos. Sci. Technol.*, **87**, 135 (2013).
14. Y. Tian, M. Wu, R. Liu, et al., *Carbohydr. Polym.*, **83**, 743 (2011).
15. C. Tsioptsias, K. G. Sakellariou, I. Tsivintzelis, L. Papadopoulou, C. Panayiotoua, *Carbohydr. Polym.*, **81**, 925 (2010).
16. H. Liu, Y. Hsieh, *J. Polym. Sci., Part B: Polym. Phys.*, **40(18)**, 2119 (2002).
17. N. Bhardwaj, S. C. Kundu, *Biotechnol. Adv.*, **28**, 325 (2010).
18. W. Rasband. *ImageJ. Version 1.45s*, National Institutes of Health, Bethesda, MD, USA [http://rsb.info.nih.gov/ij/index.html].
19. K. M. Yun, A. B. Suryamas. F. Iskandar, L. Bao, H. Niinuma, K. Okuyama, *Sep. Purif. Technol.*, **75**, 340 (2010).

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CELIULIOZĖS ACETATO PLUOŠTŲ FORMAVIMAS ELEKTRINIO VERPIMO BŪDU IŠ TRINARIO TIRPIKLIŲ MIŠINIO

S a n t r a u k a

Celiuliozės acetatas (CA) yra biologiškai skaidus polimeras, plačiai taikomas įvairiose žmogaus veiklos srityse. Tyrimo tikslas – elektrinio verpimo būdu suformuoti vientisą CA pluoštą. Tačiau silpnas CA tirpumas tradiciniuose vienanariuose tirpikliuose bei nevientisos struktūros pluošto formavimasis naudojant dvinarius tirpiklius riboja CA pluoštų gamybą. Tyrimo autoriai pasiūlė naują trinarį tirpiklių mišinį, tinkamą išgauti nenutrūkstamą (be adatos užsikimšimo) elektrinio verpimo būdu formuojamą CA pluoštą. Mažesnio nei 300 nm vidutinio skersmens CA pluoštai buvo išverpti panaudojus acetono / dichlormetano / dimetilformamido tirpiklių mišinį santykiu 2/1/1 (pagal tūrį). Nustatyta, kad CA polimero koncentracija tirpale lemia išverpto CA pluošto morfologiją bei pluošto gijų skersmenį. Vientisi 241 ± 92 nm vidutinio skersmens pluoštai buvo išverpti iš didesnės nei 11 % koncentracijos CA tirpalo. Didelis poringumas ir pluošto gijų susijungimas sudaro prielaidas CA pluoštus panaudoti specifinėse srityse (pvz., filtravimui). CA formuojant pluoštus užtikrina, kad bus naudojamos aplinkai draugiškesnės medžiagos.