

Thermal and Mechanical Properties of P(MAA-co-MMA)/PVP/MWNTs nanocomposites

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Introduction

The addition of nanoparticles has gained tremendous interest and become a well-established route to improve the basic thermal and mechanical properties, and toughness of polymers. Various types of nanoparticle have been chosen, including silica nanoparticles [1 ÷ 4], nanoclays [5 ÷ 8], and carbon nanotubes (CNTs) or nanofibres [9 ÷ 14]. Nanocomposites using CNTs have been intensively studied, since CNTs have excellent mechanical and electrical properties. For example, some researchers reported that the addition of CNTs led to a significant increase in the Young's modulus and tensile strength of polymeric nanocomposites [15 ÷ 18].

Poly(methacrylic acid) (PMMA) as a biocompatible polymer is typically used in the fabrication of contact lenses, etc. [19]. Polymethacrylic acid (PMAA) can be designed as a typical pH-responsive hydrogel, and has received considerable recognition in biomedical applications due to good biocompatibility [20, 21]. Poly(N-vinyl-2-pyrrolidone) (PVP) is a water-soluble, neutral, and biocompatible polymer widely employed in medicine and in other applications interfacing with biological systems because of its excellent biocompatibility with living tissues and extremely low cytotoxicity [22, 23].

In the present study, P(MAA-co-MMA)/PVP/MWNTs nanocomposites were prepared via ultrasonic assisted free radical polymerization technique, which can be designed as potential biomaterials for use in wound dressing. The addition of MWNTs to P(MAA-co-MMA)/PVP blends may improve the mechanical and thermal properties. The effect MWNTs on the thermal properties, and mechanical of P(MAA-co-MMA)/PVP/MWNTs nanocomposite have been investigated.

Materials

MWNTs were brought from Shenzhen Nano-Technologies Port Co. Ltd., China, with a purity of above 96%, average length of microns, and surface area of 4.26 m²/g. Methacrylic acid (MAA), methyl methacrylate (MMA), 2,2'-azobis(isobutyronitrile) (AIBN) and N,N'-methylenebis(acrylamide) (MBAA) were analytical grade from Chengdu Reagent Factory. Poly(N-vinyl-2-pyrrolidone) (PVP) with the Mw=58000 (Aldrich) were used as received. MAA and MMA were distilled under reduced pressure before use. AIBN, used as a radical initiator, was recrystallized from ethanol solution. MBAA was used as a cross-linker without further purification.

Preparation

MWNTs with dimethyl sulfoxide were sonicated in a two-necked flask for 20 min. Then, MAA and MMA monomer, and PVP were added into the flask and stirred for 10 min, which were further sonicated for 10 min. AIBN (0.01 mol/L) and MBAA (0.02 mol/L) were added and nitrogen gas was purged into the flask to remove oxygen. The mixtures were sonicated using a bath sonicator for 1 hour. Polymerization was carried out with constant stirring at 60°C for 10 min. Then, the reaction mixture was injected into the space

between two glass plates separated by polyethylene spacers (3mm thick) at 55°C for 24 hours. MAA (1.0 mol/L), MMA (1.0 mol/L), and PVP (25wt% of the entire monomers) were kept constant for variation of MWNTs. The prepared P(MAA-co-MMA)/PVP/MWNTs nanocomposites were quenched and then dried under vacuum at room temperature for 3 days to remove unreacted monomers.

Measurements

The thermal analyses were carried out with a differential scanning calorimeter (DSC, Du Pont 9900) over a temperature range from -70°C to 150°C at a heating rate of 10°C/min, purged with nitrogen gas, and quenched with liquid nitrogen. The cell was calibrated using an indium standard; the weight of the sample was 5-10 mg. The differential thermal analysis (DTA) and thermogravimetry analysis (TGA) were performed using a TA-50H thermal analyzer (Shimadzu) at a heating rate of 20°C/min under the stream of nitrogen. The microhardness of well-polished samples was determined using Vickers hardness tester (Future-Tech. Corp. FM-700, Tokyo, Japan) at a constant load of 100 g and dwell time of 15 s. Average values of six readings were reported as the microhardness of the samples. Since properties depend on the volume fraction of the reinforcing particles added to the matrix. Stress-strain properties of the nanocomposites were measured on an Instron testing machine (Model 4302).

Results and discussion

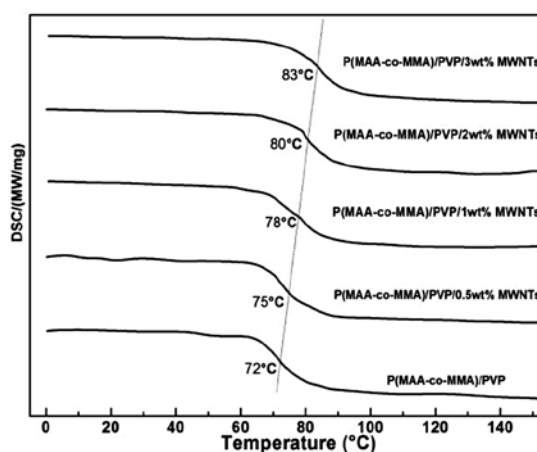


Fig. 1. DSC scans of P(MAA-co-MMA)/PVP and P(MAA-co-MMA)/PVP/MWNTs nanocomposites

DSC method is one of the most common techniques applied to study the transition in polymers and their composites. The α -transition is related to the Brownian motion of the main chains at the transition from the glassy to the rubbery state and the relaxation of dipoles associated with it. The thermograms of P(MAA-co-MMA)/PVP and P(MAA-co-MMA)/PVP/MWNTs nanocomposites are shown in Figure 1; it can be observed that P(MAA-co-MMA)/PVP blends exhibit glass transition temperatures (T_g) at about 72°C; Compared to P(MAA-co-MMA)/PVP blends, a shift of T_g to higher temperatures is observed in P(MAA-co-MMA)/PVP/MWNTs nanocomposite.

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The incorporation of MWNTs nanofillers into P(MAA-co-MMA)/PVP blends clearly increases the nanocomposites's T_g , as shown in Figure 1 by at most as much as 11°C. As an increase of T_g is an indication of good dispersion of the nanoparticles and attributed to a steric hindrance effect; steric hindrance increases with the ratio surface-to-volume of a nanoparticle and a correspondingly large amount of interfacial area with altered polymer chain mobility throughout P(MAA-co-MMA)/PVP/MWNTs nanocomposites.

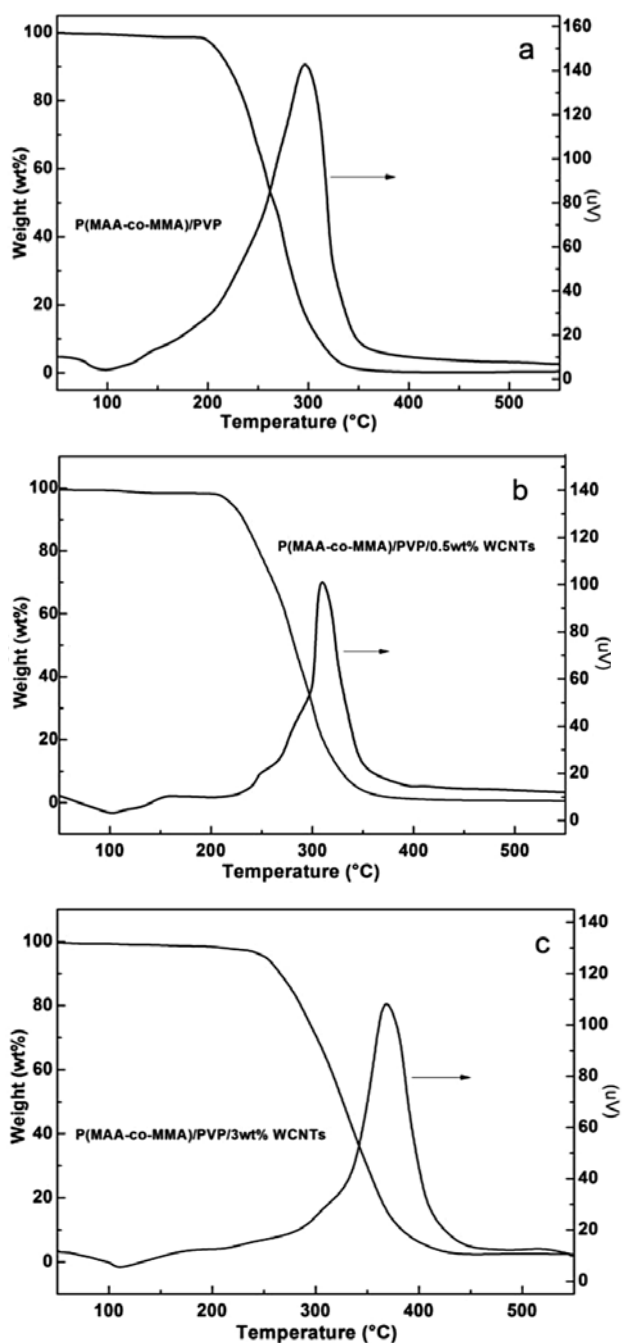


Fig. 2. TGA and DTA curves of P(MAA-co-MMA)/PVP and P(MAA-co-MMA)/PVP/MWNTs nanocomposites

It is usually well accepted that, in case of polymer-clay nanocomposites, the improved thermal stability of the polymer nanocomposites is mainly due to the formation of a char which hinders the out-diffusion of the volatile decomposition products, as a direct result of the decrease in permeability, usually observed in exfoliated nanocomposites [24].

Thermal stability of the P(MAA-co-MMA)/PVP and P(MAA-co-MMA)/PVP/MWNTs nanocomposites was assessed from analysis of the TGA and DTA curves (as shown in Figure 2). A more weak endothermic peak and a major exothermic one are observed in

the P(MAA-co-MMA)/PVP thermograms (Fig. 2a). The first peak occurs in the 50-130°C temperature range, is accompanied by a 2% weight loss and is related to the removal of the physically adsorbed water. The second major exothermic peak at $T_{max}=296^{\circ}\text{C}$ (maximum of the peak) with mass loss of 72%, corresponds to appearance of degradation process of the polymeric chains. For P(MAA-co-MMA)/PVP/MWNTs nanocomposites, as shown in Figure 2b and 2c, they also show a 2% weight loss in 50-130°C interval; the degradation of the nanocomposites takes place with peaks maximum temperature at 312°C and 369°C, separately. The decomposition temperature for P(MAA-co-MMA)/PVP blends is lower than those of its nanocomposites, indicating that the thermal stability of nanocomposites has been improved because of addition of MWNTs. Besides that, the residual weight of P(MAA-co-MMA)/PVP/MWNTs nanocomposites left increases steadily with the increase of MWNTs loading. This indicates that the thermal stability of P(MAA-co-MMA)/PVP blends is significantly improved on incorporation of MWNTs.

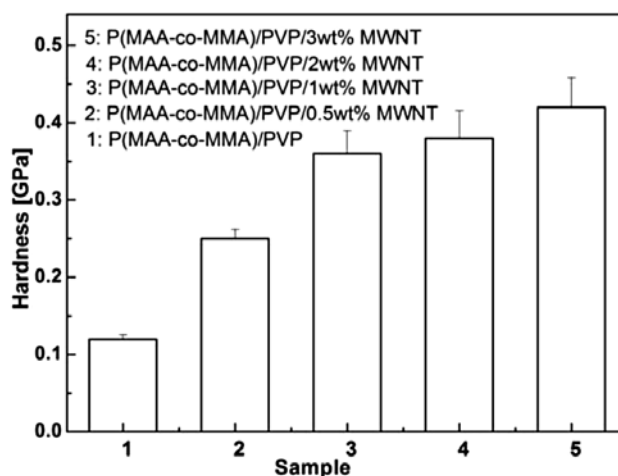


Fig. 3. Hardness of P(MAA-co-MMA)/PVP and P(MAA-co-MMA)/PVP/MWNTs nanocomposites

Figure 3 shows the microhardness of P(MAA-co-MMA)/PVP and P(MAA-co-MMA)/PVP/MWNTs nanocomposites as a function of MWNTs content, respectively. The hardness of nanocomposite at 0.5 wt% MWNTs increases from 0.12 GPa for the P(MAA-co-MMA)/PVP blends to 0.25 GPa. The hardness of nanocomposite at 3wt% MWNTs increases to 0.42 GPa. More importantly, for low CNT contents, a remarkable increase in hardness is clearly visible; for the WCNTs reinforced polymer nanocomposites, the hardness increases at least 2 times in comparison to the P(MAA-co-MMA)/PVP blends; these data suggest a good dispersion of the nanofiller component in the polymer matrix. The increase in microhardness might be attributed to higher microhardness of MWNTs compared to P(MAA-co-MMA)/PVP networks. Moreover, relatively uniform distribution of MWNTs particles and decrease in interparticle distance with increasing particle loading in the matrix results in increase of resistance to indentation of P(MAA-co-MMA)/PVP blends; nanoparticles are much closer to each other in the matrix, and hence, nanoparticles will resist more strongly the penetration of the indentation in the matrix.

There are many researches on the effectiveness of nanoparticles to improve the mechanical properties of polymer. Tensile tests were carried out in order to determine the mechanical properties of P(MAA-co-MMA)/PVP blends and P(MAA-co-MMA)/PVP/MWNTs nanocomposites. Five measurements on five different strips were performed on each sample for statistical accuracy. Shown in Figure 4 are representative stress-strain curves for P(MAA-co-MMA)/PVP and P(MAA-co-MMA)/PVP/MWNTs nanocomposites with different

MWNTs loading. The strain, ϵ represents the fractional elongation while the stress, δ , is the force divided by the cross-sectional area of the unloaded sample.

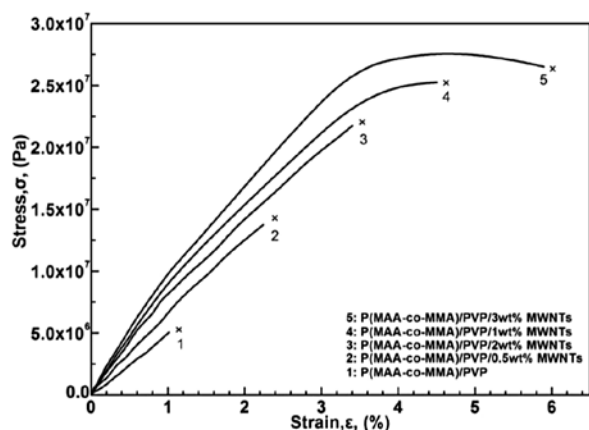


Fig. 4. Representative stress–strain curves for P(MAA-co-MMA)/PVP and P(MAA-co-MMA)/PVP/MWNTs nanocomposites

The P(MAA-co-MMA)/PVP blends shows elastic behavior up to a yield point of $\epsilon = 0.41\%$, followed by a small deformation before fracture occurs at a strain-to-break of $\epsilon_b = 1.02\%$. This low value of strain-to-break is typical for low-molecular-weight polymers.

Dramatic changes in the stress-strain curves can be observed on the addition of MWNTs. As the MWNTs content is increased, the yield point increases to approximately $\epsilon = 1.66\%$ for the sample with a weight fraction (w_f) of 3%. In addition, significant plastic deformation is observed. The strain-to-break increases steadily with weight fraction reaching $\epsilon_b = 5.9\%$ for the $w_f = 3\%$ sample. This is unusual, as most polymer-nanotube composites become brittle on the addition of even small amounts of nanotubes. However, under this weight fraction the strain-to-break does not indeed fall off and the material becomes more flexible as more nanotubes are added.

Sternstein et al. have mainly ascribed the reinforcement mechanism of nano-filled polymer, to trapped entanglements that existed in the temporary bonding between polymer chains and the filler surface [25], which has both near- and far-field effects on matrix chain motion, and plays the role of physical cross-linking network, thus leading to greatly enhanced modulus of matrix [26]; when load is transferred to the physical cross-linking network, the debonding (disentanglement) of chain segments from the nano-filler surface facilitates the relaxation of the matrix entanglement structure, leading to the higher toughness. On the other hand, the choice of suitable filler, as well as a suitable quantity, grain size and high compatibility with the polymer matrix, is a key factor for efficient toughening, which can accomplish improvement of polymer's mechanical properties, except elongation at break and toughness. On the addition of nano-filler, the interface conditions for the brittle-ductile transition of matrix should be in accordance with the following requirements: (1) a strong adhesion should exist between the matrix and nano-filler so that the stress is transferred through the interfacial area; and (2) the interfacial area should be a lower stiffness than the matrix and deform, thereby yielding prior to the matrix and inducing matrix yielding [27]. In our experiment, due to the poor interfacial bonding between P(MAA-co-MMA)/PVP blends and MWNTs, the interface stiffness is lower.

Conclusion

DSC, TGA and DTA tests showed that the incorporation of MWNTs nanofillers into P(MAA-co-MMA)/PVP blends clearly increases the nanocomposites's T_g more than 10°C and improves the thermal stability of P(MAA-co-MMA)/PVP blends; the hardness of P(MAA-

co-MMA)/PVP/MWNTs nanocomposites increases at least 2 times in comparison to the P(MAA-co-MMA)/PVP blends. The strain-to-break increases steadily with weight fraction, which means P(MAA-co-MMA)/PVP/MWNTs nanocomposites becomes more flexible as more nanotubes are added.

Literature

- Li Z., Barnes J. C., Bosoy A., et al.: Mesoporous silica nanoparticles in biomedical applications. *Chem. Soc. Rev.* 2012, **41**, 2590-2605.
- Wittmar A., Ruiz-Abad D., Ulbricht M.: Dispersions of silica nanoparticles in ionic liquids investigated with advanced rheology. *J. Nanopart. Res. J.* 2012, **14**, 1-10.
- Tang F., Li L., Chen D.: Mesoporous silica nanoparticles: synthesis, biocompatibility and drug delivery. *Adv. Mater.* 2012, **24**, 1504-1534.
- Ambrogio M. W., Thomas C. R., Zhao Y. L., et al.: Mechanized silica nanoparticles: a new frontier in theranostic nanomedicine. *Accounts chem. Res.* 2011, **44**, 903-913.
- Papoulis D., Komarneni S., Panagiotaras D., et al.: Three-phase nanocomposites of two nanoclays and TiO_2 : Synthesis, characterization and photocatalytic activities. *Appl. Catal. B-Environ.* 2014, **147**, 526-533.
- Huttunen-Saarivirta E., Vaganov G. V., Yudin V. E., et al.: Characterization and corrosion protection properties of epoxy powder coatings containing nanoclays. *Prog. Org. Coat.* 2013, **76**, 757-767.
- Aulin C., Salazar-Alvarez G., Lindström T.: High strength, flexible and transparent nanofibrillated cellulose-nanoclay biohybrid films with tunable oxygen and water vapor permeability. *Nanoscale* 2012, **4**, 6622-6628.
- Sánchez-Jiménez P. E., Pérez-Maqueda L. A., Perejón A., et al.: Nanoclay nucleation effect in the thermal stabilization of a polymer nanocomposite: a kinetic mechanism change. *J. Phys. Chem. C* 2012, **116**, 11797-11807.
- Juan-Alcaniz J., Gascon J., Kapteijn, F.: Metal-organic frameworks as scaffolds for the encapsulation of active species: state of the art and future perspectives. *J. Mater. Chem.* 2012, **22**, 10102-10118.
- Dreyer D. R., Jarvis K. A.; Ferreira P. J.: Graphite oxide as a carbocatalyst for the preparation of fullerene-reinforced polyester and polyamide nanocomposites. *Polym. Chem-UK* 2012, **3**, 757-766.
- Gu H., Huang Y., Zhang X., etc.: Magneto-resistive polyaniline-magnetite nanocomposites with negative dielectrical properties. *Polymer* 2012, **53**, 801-809.
- Coleman J.N., Khan U., Blau J., Gun'ko Y.: Small but strong: A review of the mechanical properties of carbon nanotube-polymer composites. *Carbon* 2006, **44**, 1624-1652.
- Jeon J. H., Lim J. H., Kim K. M.: Fabrication of hybrid nanocomposites with polystyrene and multiwalled carbon nanotubes with well-defined polystyrene via multiple atom transfer radical polymerization. *Polymer* 2009, **50**, 4488-4495.
- Lee W. I., Kim S. H., Park J. M.: Assessment of dispersion in carbon nanotube reinforced composites using differential scanning calorimetry. *Carbon* 2009, **47**, 2699-2703.
- Zhang Q., Mochalin V. N., Neitzel I., et al.: Fluorescent PLLA-nano-diamond composites for bone tissue engineering. *Biomaterials* 2011, **32**, 87-94.
- Deng L., Eichhorn S. J., Kao C. C., et al.: The effective young's modulus of carbon nanotubes in composites. *ACS Appl. Mater. Inter.* 2011, **3**, 433-440.
- Naffakh M., Díez-Pascual A. M., Remškar M., et al.: New inorganic nanotube polymer nanocomposites: improved thermal, mechanical and tribological properties in isotactic polypropylene incorporating INT-MoS_2 . *J. MATER. CHEM.* 2012, **22**, 17002-17010.
- Gkikas G., Barkoula N. M., Paipetis A. S.: Effect of dispersion conditions on the thermo-mechanical and toughness properties of multi walled carbon nanotubes-reinforced epoxy. *Compos. Part. B-Eng.* 2012, **43**, 2697-2705.

19. Dhandayuthapani B., Yoshida Y., Maekawa T., Kumar D. S.: Polymeric Scaffolds in Tissue Engineering Application: A Review. *Int. J. Polym. Sci.* 2011, **2011**, 89–108.
20. Donini C., Robinson D. N., Colombo P., Giordano F., Peppas N. A.: Preparation of poly(methacrylic acid-g-poly(ethylene glycol)) nanospheres from methacrylic monomers for pharmaceutical applications. *Int. J. Pharm.* 2002, **245**, 83–91.
21. Gan Z., Ju J., Zhang T., Wu D.: Preparation of Rhodamine B Fluorescent Poly(methacrylic acid) Coated Gelatin Nanoparticles. *J. Nanomater* 2011, **2011**, 231–238.
22. Inal M., Yigitoglu M.: Improvement of Bioethanol Productivity of Immobilized *Saccharomyces Bayanus* with Using Sodium Alginate-Graft-Poly(N-Vinyl-2-Pyrrolidone) Matrix. *Appl. Biochem. Biotech.* 2012, **168**, 266–278.
23. Aldana A. A., Gonzalez A., Strumia M. C., Martinelli M.: Preparation and characterization of chitosan/genipin/poly(N-vinyl-2-pyrrolidone) films for controlled release drugs. *Mater. Chem. Phys.* 2012, **134**, 317–324.
24. Leszczynska A., Njuguna J., Pielichowski K., Banerjee J. R.: Polymer/montmorillonite nanocomposites with improved thermal properties: Part I. Factors influencing thermal stability and mechanisms of thermal stability improvement. *Thermochim. Acta* 2007, **453**, 75–96.
25. Sternstein S., and Zhu A. J.: Reinforcement mechanism of nanofilled polymer melts as elucidated by nonlinear viscoelastic behavior. *Macromolecules* 2002, **35**, 7262–7273.
26. Vacatello M.: Chain dimension in filled polymers: an intriguing problem. *Macromolecules* 2002, **35**, 8191–8193.
27. Fu Q., Wang G., Liu C.: Polyethylene toughened by CaCO₃ particles: The interface behaviour and fracture mechanism in high density polyethylene/CaCO₃ blends. *Polymer* 1995, **36**, 2397–2401.

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Aktualności z firm

News from the Companies

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ODKRYCIA

Superchłonna technologia BASF

26 listopada 2014 r. firma BASF ogłosiła swoje plany dużej inwestycji w pionierską platformę dla superchłonnej technologii w pionie środków do pielęgnacji i higieny osobistej. W ciągu następnych 2–3 lat BASF zainwestuje do 500 mln EUR w moce produkcyjne – dla procesu polimeryzacji kropeł – na całym świecie poprzez reorganizację istniejących zakładów. Superchłonne polimery, to związki, które są w stanie wchłonąć i zatrzymać niezwykle dużą ilość płynu w stosunku do ich własnej masy. Są stosowane do produkcji pieluch dla niemowląt oraz środków higienicznych dla kobiet. Przez 10 lat naukowcy BASF intensywnie pracowali nad nową technologią i optymalizacją związanych z nią procesów produkcyjnych. Firma BASF wprowadzi na rynek nową generację wysoce innowacyjnych superchłonnych polimerów pod nazwą SAVIVA™. Produkty te będą pojawiały się na rynku stopniowo, począwszy od końca 2016 r. (kk) (em)

(BASF, 26.11.2014)

KONKURSY, NAGRODY, WYRÓŻNIENIA

BayLab w ścisłym finale „Popularyzatora Nauki”

Program edukacyjny „Making Science Make Sense”, realizowany w salonie multimedialnym BayLab, a także jego partnerzy, zostali finalistami najstarszego konkursu popularyzacji nauki w Polsce. BayLab to multimedialny salon, w którym firma Bayer – zatrudniająca na całym świecie 14 000 naukowców – dzieli się innowacjami i wiedzą z pasjonatami nauki. Wyboru finalistów dokonała kapituła pod przewodnictwem prof. Michała Kleibera, prezesa Polskiej Akademii Nauk. Do tegorocznej edycji konkursu nadesłano blisko 70 zgłoszeń. Bayer Sp. z o.o. został nominowany w kategorii „Sponsor popularyzacji”. Do ścisłego finału jury zakwalifikowało również dwa współpracujące z BayLabem koła studenckie: Chemiczne Koło Naukowe Flogiston z Politechniki Warszawskiej oraz Studenckie Koło Naukowe przy I Katedrze i Klinice Kardiologii WUM. (kk) (em)

(Bayer, 3.12.2014)

Młodzi liderzy nauki nagrodzeni

Minister Nauki i Szkolnictwa Wyższego prof. Lena Kolarska-Bobińska spotkała się 16 grudnia 2014 r. z laureatami V edycji programu LIDER Narodowego Centrum Badań i Rozwoju. Wraz z dyrektorem NCBR, prof. Krzysztofem Janem Kurzydłowskim, przekazała 36 młodym liderom nauki symboliczne czeki na łączną kwotę ponad 40 mln PLN. Wśród nagrodzonych projektów badawczych najwyższej oceny został projekt dr n. med. Anny Wójcickiej z Centrum Nowych Technologii Uniwersytetu Warszawskiego. Jej badania dotyczą wykorzystania sekwencjonowania nowej generacji do opracowania czulego i specyficznego panelu molekularnego do diagnostyki nowotworów tarczycy. Ponadto dofinansowanie otrzymały m.in. następujące projekty: nowy system automatycznego szacowania ekwiwalentu wodnego śniegu z zastosowaniem bezzałogowego statku powietrznego, opracowanie nieinwazyjnej metody doboru i optymalizacji protez wewnątrzczyniowych, nowatorskie konstrukcje wnęki rezonansowej kwantowego lasera kaskadowego oraz analiza obrazu w klasyfikacji uszkodzeń łożysk sprężarki silników lotniczych i prognozowanie ich żywotności. (kk)

(<http://www.ncbir.pl>, 16.12.2014)

Złoty Laur „Super Biznesu” dla PGE

Działania na rzecz ochrony środowiska naturalnego podejmowane przez PGE Polską Grupę Energetyczną zostały docenione przez redakcję Super Expressu. Podczas uroczystej gali 8 grudnia ub. r., nagrodę Złoty Laur „Super Biznesu” odebrał przedstawiciel PGE z rąk Stanisława Gawłowskiego, Sekretarza Stanu w Ministerstwie Środowiska.

Patronat honorowy nad konkursem Złoty Laur „Super Biznesu” objęło Ministerstwo Skarbu Państwa i Ministerstwo Środowiska. (kk)

(<http://www.gkpgpe.pl/>, 9.12.2014)

Społeczny raport TAURON

Raport zrównoważonego rozwoju Grupy TAURON za rok 2013 zdobył największe uznanie wśród internautów, którzy oddali swój głos w konkursie, zorganizowanym przez Forum Odpowiedzialnego Biznesu, PwC oraz SGS. Warto podkreślić, że TAURON, jako jedyna spółka, otrzymała równolegle wyróżnienie jury za odważne wykorzystywanie Internetu. (kk)

(<http://media.tauron-pe.pl>, 10.12.2014)

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