



Contributions of polystyrene to the mechanical properties of blended mixture of old newspaper and wood pulp

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ABSTRACT

Composites from recycled newspaper would result in the effective use of the waste product which is currently burned or land-filled, as well as potential reduction in the cost of manufactured composite. In this work, old newspaper (ONP) together with yellowish wood pulp and waste polystyrene from packaging were used to produce composite. The technique studied in this work is an alternative to the conventional melt compounding and was expected to provide efficient wetting of fibers by the polymer. Polystyrene was grafted with acrylonitrile, ethylmethacrylate and butylmethacrylate, respectively, using benzoyl peroxide as an initiator. The amount of polystyrene to monomer is 1:0.75 and to initiator is 1:1. The grafted copolymers were characterized using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Different ratios of waste polystyrene or grafted waste polystyrene were mixed with a blend of old newsprint and wood pulp to form composites. The mechanical properties of these composites as well as water uptake were studied. The tensile properties of the prepared composites did not show essential improvement, except for the modulus of elasticity. Scanning electron microscopy indicate that composites with grafted polystyrene showed more homogeneity than the composite with polystyrene and also than blank, so the grafted polymer is distributed very well improving the mechanical properties of the composites. Strong adhesion between the fiber and grafted polymer was found.

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1. Introduction

Technology has brought many benefits to the world. Along with these benefits come problems, one of which is the disposal of solid waste materials. Approximately 60% of the volume of solid waste in an average municipal waste stream consists of agro based resources such as paper and paper based products, wood, and yard wastes. Recycling paper products back into paper requires wet processing and removal of inks, inorganic, and adhesives (Rowell, Young, & Rowell, 1997). Recycling these same products into composites can be done using dry processing and all co-existing resources can be incorporated into the composite. As an effort to reuse old newspaper, a newspaper fiber reinforced polypropylene composite was made (Schneider, Myers, & Clemons, 1995; Sanadi, Young, & Rowell, 1994; Ren & Hon, 1993; Maldas & Kokta, 1994). Recycled newspaper cellulose fiber (RNCF) reinforced poly(lactic acid) (PLA) biocomposites were fabricated by a microcompounding and molding system. The mechanical and thermomechanical properties of these composites have been studied and compared to PLA/talc composites. These composites possess similar mechanical

properties to talc-filled composites as a result of reinforcement by RNCF. The thermogravimetric analysis (TGA) thermograms reveal the thermal stability of the biocomposites to nearly 350 °C. These findings illustrate that RNCF possesses good thermal properties (Huda, Drazl, & Misra, 2005). Pehanich (2004) determined the effect of sodium silicate, potassium silicate, and silane treatment levels on newspaper and unbleached kraft fibers for enhancing selected mechanical properties of wood fiber–cement composites compared to untreated wood fiber–cement composites. Palm leaves, as a woody lignocellulose, together with polystyrene, were used to produce composites (Olfate, Samir, & Mona, 1998). Madani, Basta, Abdo, and El-Saied (2004) intended to use old newsprint paper (ONP) as filler in radiation shielding rubber composite. In this respect, the treatment of ONP with magnetite was carried out. The effect of incorporating untreated and treated newsprint in the rubber matrix on the swelling, electrical and mechanical properties, as well as gamma and neutron-shielding power has been investigated. Also, newsprint reinforced polystyrene was prepared and the effect of processing conditions on viscosity (in terms of torque) and molecular weight of polystyrene was studied. Polystyrene was melted in an intensive mixer. The influence of processing temperature, time, and roller speed (Hon & Sean, 1991). The morphological and rheological properties of poly(tert-butylacrylate-g-

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styrene) were studied (Chuan, Anika, Julius, & Holger, 2006; Dan, Xiaohuan, & Xiao, 2006; Fuente, Fernandez, Cerrada, Spiess, & Wilhelm, 2006). Poly(methylmethacrylate) and poly(ethylacrylate) were grafted in high yields from 2-bromo, 2-methyl propionyl groups on crosslinked poly(styrene beads), using copper mediated atom transfer radical polymerization (ATRP) methodology (Hayal & Niyazi, 2004). Polyethylene glycol grafted polystyrene resins with different polyethylene glycol levels were prepared and their swelling properties were examined (Byeong & Yoon, 2000). Photografting of glycidymethacrylate onto commercially available polystyrenemicrotitre plates was carried out in methanol as well as butanol with benzophenone as photoinitiator (Alexander, Daniel, & Ulrich, 2000).

Polystyrene, as a package material, is used in the manufacture of plastic cups for dairy products such as ice cream or yogurt cups, cups for marmalade, dry foods and other food products. It is also widely used as a package material in home delivery restaurants, because of the good heat-insulating properties (Bikales & Overberger, 1985; Brown, 1992; Jenkins & Harrington, 1991). According to the US Environmental Protection Agency (EPA), about 0.6% of solid wastes in the USA is polystyrene packaging—including both food service packaging (cups, plates, bowls, trays, clamshells, meat trays, egg cartons, yogurt and cottage cheese containers and protective packaging).

To the contrary, paper does not protect from moisture, spoilage and can damage its shape as well. Recycled paper for packaging is a lightweight material, but its wet strength is so low that it cannot qualify for many food packaging applications unless it is reinforced and waterproofed (Mathlouthi, 1998). Plastics' ability to provide light weighted packages is probably the largest single driving force behind the penetration of plastics in the market for food container (American Plastics Council, 1998). Paper recycling industry quotes for typical energy savings from producing recycled paper range from about 28% to 70% (Virtanen & Nilsson, 1983). The amount of energy saved will depend on paper grade, processing, mill operation and proximity to a waste paper source and markets. A key issue in paper recycling is the impact of energy use in manufacturing, which is usually derived from oil or coal. The benefit of paper recycling is generally assumed to be desirable and necessary and waste management policy in many countries considers, in its hierarchy, reuse and recycling to be preferable for energy recovery, and superior to landfill. The disposal and recycling of the already recycled paper in the form of paper egg packages (degree of recycling), which depends on fiber quality, is another key research issue in paper recycling (MacGuire 1997).

The aim of the present work was to prepare graft copolymers of polystyrene with acrylonitrile, ethylmethacrylate and butylmethacrylate and to make composites of these graft copolymers with old newsprint to reinforce these copolymers. The mechanical properties of these composites were studied.

2. Materials and methods

2.1. Raw material and chemicals

Old Newsprint (ONP) and yellowish wood pulp delivered from RAKTA Company for Pulp and Paper, Alexandria, Egypt were used as raw materials. Waste polystyrene, from packaging, was used as the polymer matrix. Acrylonitrile, ethylmethacrylate, and butylmethacrylate, were products of Aldrich and used as monomers. Benzoyl peroxide was used as initiator and benzene was used as solvent.

2.2. Preparation of grafted polystyrene

Polystyrene was grafted with acrylonitrile, ethylmethacrylate and butylmethacrylate monomers to produce grafted polystyrene in a procedure described as follows:

In 250 ml three necked round flask place 15.9 gm of polystyrene dissolved in 50 ml of benzene. The solution was mechanically stirred until complete dissolution then 7.5 ml of the monomer, i.e. acrylonitrile or ethylmethacrylate or butylmethacrylate, was added. 0.24 gm of benzoyl peroxide was dissolved in 20 ml of benzene and then added dropwise to the stirred solution. The reaction was carried out under inert atmosphere for 4 h. The grafted copolymer was filtered and purified then dried.

2.3. Characterization of grafted copolymer

The thermal stability of polystyrene-g-polyacrylonitrile, polystyrene-g-poly(ethylmethacrylate) and polystyrene-g-(polybutylmethacrylate) was measured on a thermal gravimetric analyzer (TGA), Perkin-Elmer using about 20 mg of the samples at a heating rate of 10 °C/min in nitrogen atmosphere. Glass transition, crystallization and melting temperatures were determined using shima-dzu differential scanning calorimeter (DSC-50). The samples were heated to 200 °C for 5 min at a rate of 10 °C to remove any thermal history, followed by controlled cooling at the same rate.

2.4. Treatment of raw material

ONP was cut and soaked in warm water treated by 2% NaOH for 3 h, then mechanically stirred using mechanical stirrer (1500 rpm) to obtain a pulp slurry. The pulp was washed properly and pressed to release the water and dried in air. The dry pulp was then ground. Yellowish wood pulp was cut and soaked in water for 24 h, then mechanically stirred. The pulp was pressed and dried in air and the dry pulp was then dried.

2.5. Preparation and measurements of the composite samples

X number grams of waste polystyrene (depending on the needed polymer percentage) was placed in a certain amount of benzene in a beaker. A specific amount of ground samples (50% ONP and 50% wood pulp) were impregnated in polymer solution and kept covered for 24 h at room temperature. The solvent was evaporated and dried and the homogeneous mixture was then processed as follows: 70 g dry sample was placed in a disc form, diameter 15 cm heated to 150 °C and then pressed under 50 KN disc for 5 min. Modulus of rupture (MOR), modulus of elasticity (MOE), and tensile strength were calculated on the basis of initial sample dimensions. The composite was tested for water absorption according to American Society for testing (1990) in which the samples were immersed in water for 24 h and 7 days. After excess water drains off, the weights and thickness were measured. The following equations are applied,

$$\text{Thickness swelling (\%)} = (T_w - T_i) / T_i \times 100$$

where T_w is the wet thickness and T_i is the initial thickness. (1)

$$\text{Water absorption (\%)} = (W_w - W_i) / W_i \times 100$$

where W_w is the wet weight and W_i is the initial weight. (2)

2.6. Scanning electron microscopy (SEM)

The microstructure of the composite samples was analyzed by scanning electron microscopy (SEM) using JEOL JXA-840A Electron

Probe Microanalyzer on gold-palladium coated specimens. The SEM observation was carried out with secondary electrons imaging and acceleration of the electron beam at 10 kV.

3. Results and discussions

3.1. Thermal gravimetric analysis (TGA) of the grafted copolymers

The TGA of the grafted copolymer of St-g-PAN, St-g-PEMA and St-g-PBMA is shown in (Figs. 1–3). The TGA curves show good thermal stability. The initial decomposition temperatures of the grafted copolymers are 80, 180 and 170 °C, respectively. The previously mentioned grafted copolymers retained about 79%, 96% and 95% of their initial masses, respectively. The data show higher thermal stability for St-g-PEMA copolymer due to its higher glass temperature.

3.2. Differential scanning calorimetric (DSC) analysis

The DSC graphs for waste polystyrene and its grafted form with ethyl methacrylate are shown in (Figs. 4 and 5). The results show that the Tg of polystyrene is 98.57 °C and that of its grafted form is 74.61 °C. This noticeable shift in the Tg of the grafted polystyrene was attributed to grafting with ethylmethacrylate monomer and it

confirms grafting process (OKarakasi, Pappa, Tarantili, Economides, & Magoulas, 2006).

3.3. Characteristics of raw materials

Preliminary experiments were performed using waste polystyrene or grafted waste polystyrene as the plastic matrix, which was reinforced with mechanical pulp from chopped post-used newspapers and yellowish wood pulp.

ONP is preferred over other wastepaper for making composites, since the pulp of the newsprint is a mechanical pulp, i.e. neutral and has nonbulky fibers. The nonbulky fibers lead to the formation of trapped air pockets as the number of hydrogen bonds is few. The presence of these air pockets allows the polymer solution to form bonds between the interfaces (Bikales & Overberger, 1985). As known chemical wood pulp fibers tend to be longer and stronger since they were not finely ground down as mechanical wood pulp papers are. The high acidity of bleached wood pulp can lead to brittleness and discoloration of paper. Fibers made of cellulose chains degrade when exposed to an acidic environment in the presence of moisture. In this acid hydrolysis reaction, cellulose chains are repeatedly split into smaller fragments as long as the source of acid remains in paper. This acid hydrolysis reaction produces more acid in the process, and the degradation accelerates are downward spiral.

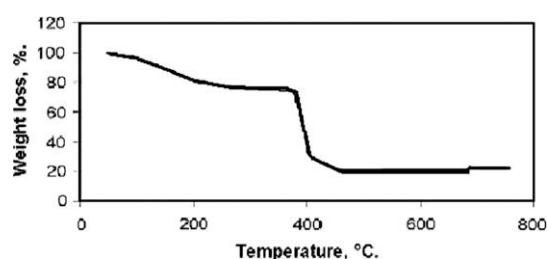


Fig. 1. TGA of polystyrene-g-acrylonitrile.

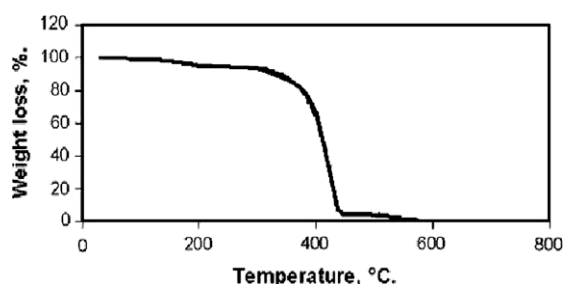


Fig. 2. TGA of polystyrene-g-ethylmethacrylate.

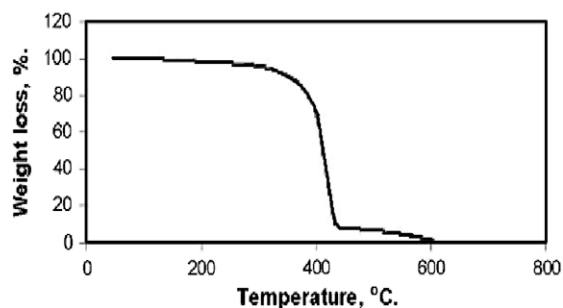


Fig. 3. TGA of polystyrene-g-butylmethacrylate.

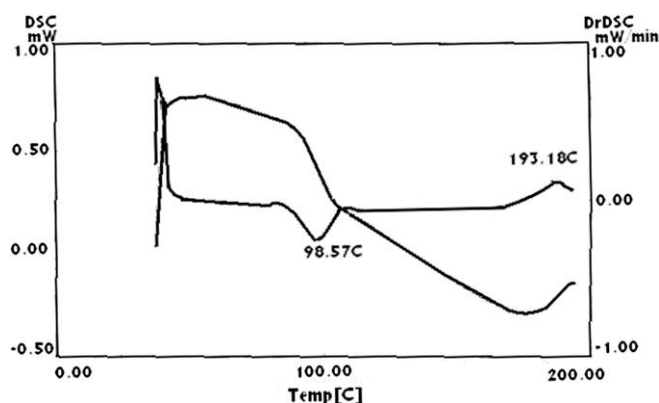


Fig. 4. DSC of polystyrene.

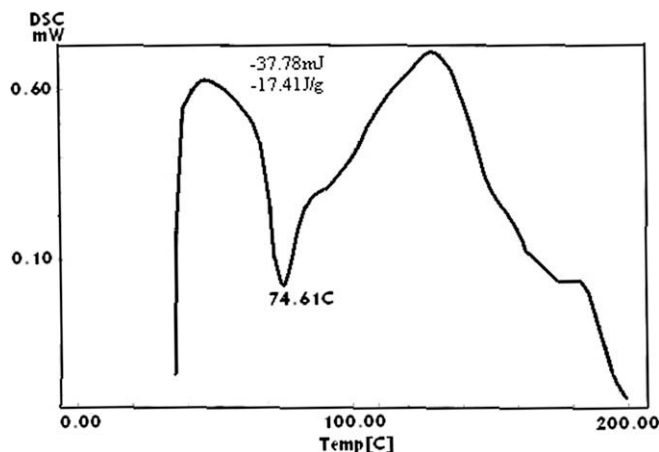


Fig. 5. DSC of polystyrene-g-ethylmethacrylate.

3.4. Treatment of old newsprint

ONP was soaked in warm water treated by 2% NaOH to remove resins or adhesives, which weaken the formation of bonds between the interfaces of polymer and ONP (Schneider et al., 1995).

3.5. Effect of grinding paper and polymer percentage on the composite properties

Ground ONP and ground wood pulp (50%: 50% w/w) were impregnated into polymer solution (0%, 20% and 30% based on dry weight) and mixed thoroughly, then left for 24 h at room temperature until the solvent (benzene) evaporated. The composite mixture was pressed under 50 KN for 5 min. at 150 °C (melting point of polystyrene). Grinding of mechanical and chemical pulp was performed, before the dispersion into the polystyrene solution to improve fiber dispersion in the polystyrene/paper blends. The expected strength decrease of the paper fibers due to their length decrease after the grinding process, was balanced by the efficient dispersion of fibers in the polymer solution which will eventually

lead to a more homogeneous polymer/paper blend. As shown in Table 1, the strength properties increase with the increase in polymer percentage from 0% to 30%. At the same time the percentage of water absorption decreases with the increase in polymer percentage when pressed at 50 KN. The Highest thickness swelling is at 0 adhesive level. The effect of polymer level on the properties of the composite can be explained as: the increase in strength properties of composites as the polymer level increased can be attributed to the flow and film formation of polystyrene in the composite structure. Also, it may be attributed to the thermoplastic polymer, which may serve as a binder to ONP and wood pulp fibers. When the level of the polymer increased, the binder became much stronger due to the formation of additional hydrogen bonding and consequent increasing of the internal bond (OKarakasi et al., 2006). The solvent technique for the preparation of polyolefin/paper fibers composites is a simple method which leads to final composites with good homogeneity. The tensile properties of the prepared composites did not show essential improvement, except for the modulus of elasticity. In order to improve the interfacial adhesion between the non-polar polyolefin matrices and the paper fibers grafting of polystyrene with acrylonitrile, ethyl methacrylate and butyl methacrylate was carried out. The best results were achieved with polystyrene grafted with ethyl methacrylate and butyl methacrylate.

The decrease in thickness swelling as the polymer level increased revealed that the void content of the composite decreased by increasing the polymer level. Normally, a higher void content means greater susceptibility to water penetration.

3.6. Scanning electron microscopy

Fig. 6 represents SEM micrographs of composites produced from (a) blend of ONP and wood pulp (50%:50% wt) (b) 30% polystyrene and blend of ONP and wood pulp (50%:50% wt) (c) 30% polystyrene grafted with ethylmethacrylate and blend of ONP and wood pulp (50%:50% wt) and (d) 30% polystyrene grafted with butylmethacrylate and blend of ONP and wood pulp (50%:50% wt). It was observed that the composites with grafted polystyrene showed more homogeneity than the composite with polystyrene

Table 1
Effect of waste and grafted waste polystyrene on properties of composite.

Percentage of polystyrene	MOR (N/m ²)	MOE (N/m ²)	Water absorption (%)			
			After immersion in water for 24 h		After immersion in water for 7 days	
			W	T	W	T
0	–	–	625.68	–	–	–
20%	2.6	789	45.11	19.823	51.2	22.68
30%	3.9	998	34.88	13	40.46	17
30% grafted	4.1	1000	94.3	30.2	99.1	34.2
with acrylonitrile						
30% grafted with	6.2	1261	85.4	28.9	95.6	31.9
ethyl methacrylate						
30% grafted with	7.78	1330	54.5	10	60.1	13
butyl methacrylate						

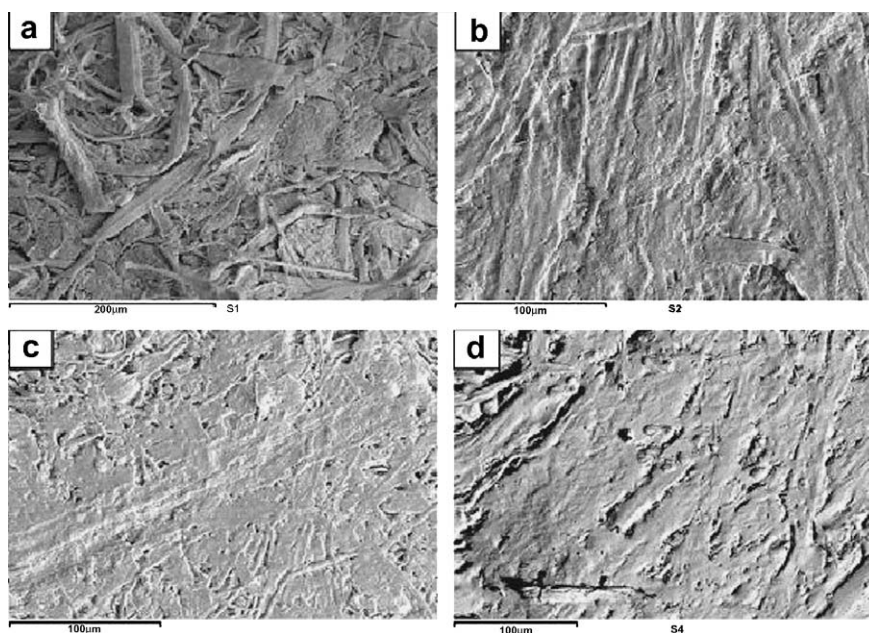


Fig. 6. SEM micrographs of (a) ONP/wood pulp blend (b) polystyrene/ONP/wood pulp blend (c) polystyrene grafted with ethylmethacrylate/ONP/wood pulp blend (d) polystyrene grafted with butylmethacrylate/ONP/wood pulp blend.

and also than blank, so the grafted copolymer is distributed very well improving the mechanical properties of the composites. Strong adhesion between the fiber and grafted polymer found (Fig. 6c and d).

References

- Alexander, W. E., Daniel, G., & Ulrich, R. (2000). Surface modification of polystyrene-microtitre plates via grafting of glycidylmethacrylate and coating of polyglycidylmethacrylate. *Biomaterials*, 21, 441–447.
- American Society for testing and materials. (1990). Standard Test Method for water absorption for plastics, Philadelphia, PA: ASTM D570–81.
- American Plastics Council. Available from: <<http://www.polystyrene.org/>>, 1998, last updated 2001.
- Bikales, M., & Overberger, M. G. (1985). *Encyclopedia of polymer science and engineering* (Vol. 16). (2nd ed.), Wiley.
- Brown, W. E. (1992). *Plastics in food packaging*. Marcel Dekker.
- Byeong, D. P., & Yoon, S. L. (2000). The effect of PEG groups on swelling properties of PEG-grafted polystyrene resins in various solvents. *Reactive & Functional Polymers*, 44, 41–46.
- Chuan, L. F., Anika, E. G., Julius, V., & Holger, S. (2006). Reactive μ CP on ultrathin block copolymer films: Localized chemistry for micro- and nano-scale biomolecular patterning. *European Polymer Journal*, 42, 1954–1965.
- Dan, P., Xiaohuan, Z., & Xiao, Y. H. (2006). Synthesis of amphiphilic graft copolymer with hydrophilic poly(acrylic acid) backbone and hydrophobic polystyrene side chains. *Polymer*, 47, 6072–6080.
- Fuente, J. L., Fernandez, G. M., Cerrada, M. L., Spiess, H. W., & Wilhelm, M. (2006). Small-angle X-ray scattering and linear melt rheology of poly(*tert*-butylacrylate-*g*-styrene) graft copolymers. *Polymer*, 47, 1487–1495.
- Hayal, B. S., & Niyazi, B. (2004). An alternative approach for grafting of acrylate esters from crosslinked polystyrene beads by ATRP and their modification for selective mercury extraction. *Reactive & Functional Polymers*, 61, 33–41.
- Hon, D. N. S., & Sean, Sy. T. (1991). Polystyrene newspaper composites. Part1: Degradation of polymer during processing. *Journal of Thermoplastic Composite Materials*, 4(4), 300–310.
- Huda, M. S., Drzal, L. T., & Misra, M. (2005). A study on biocomposites from recycled newspaper fiber and poly(lactic) acid. *Industrial and Engineering Chemistry Research*, 44(15), 5593–5601.
- Jenkins, W. A., & Harrington, J. P. (1991). Packaging foods with plastics. Technomic.
- MacGuire, F. (1997). *Paper recycling: exposing the myths, briefing sheet*. London: Friends of the Earth.
- Madani, M., Basta, A., Abdo, A. E., & El-Saied, H. (2004). Utilization of waste paper in the manufacture of natural rubber composite for radiation shielding. *Progress in Rubber Plastics Recycling Technology*, 20(4), 287–310.
- Maldas, D., & Kokta, B. V. (1994). An investigation of the interfacial adhesion between reclaimed newspaper and recycled polypropylene composites through the investigation of their mechanical properties. *Journal of Adhesion Science and Technology*, 8(12), 1439–1451.
- Mathlouthi, M. (1998). *Food packaging and preservation*. Chapman & Hall.
- OKarakasi, I. B., Pappa, G., Tarantili, P. A., Economides, D., & Magoulas, K. (2006). Preparation and study of plastic compounds containing polyolefins and post used newspaper fibers. *Composites: Part A*, 37, 1613–1625.
- Olfate, Y. M., Samir, K., & Mona, A. N. (1998). Lignocellulosic Polymer Composite IV. *Journal of Applied Polymer Science*, 69, 845–855.
- Pehanich, J. I. (2004). Wood fiber surface treatment level effects on selected mechanical properties of wood fiber cement composite. *Cement and Concrete Research*, 34(1), 59–65.
- Ren, S., & Hon, D. N. S. (1993). Newspaper fibre-reinforced polypropylene composite. *Journal of Reinforced Plastics and Composites*, 12(12), 1311–1322.
- Rowell, M., Young, A., & Rowell, K. (1997). *Paper and Composites from Agro-Based Resources*. New York, London, Tokyo: Lewis Publisher. p. 251.
- Sanadi, A. R., Young, R. A., & Rowell, R. M. (1994). Recycled newspaper fibers as reinforcing fillers in thermoplastics. *Journal of Reinforced Plastics and Composites*, 13(1), 54–67.
- Schneider, J. P., Myers, G. E., & Clemons, C. M. (1995). Biofibres as reinforcing fillers in thermoplastic composites. *Engineering Plastics*, 8(3), 207–222.
- Virtanen, Y., & Nilsson, S. (1983). Environmental impacts of waste paper recycling. London.