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Feasibility of Using Foamed Styrene Maleic Anhydride (SMA) Co-polymer in Wood Based Composites

Mogućnosti primjene upjenjenog kopolimera stiren anhidrida maleinske kiseline (SMA) u kompozitima na bazi drva

ABSTRACT • Wood plastic composites (WPCs) have often been used in consumer applications, automotive industry and exterior construction. WPCs consist mostly of wood and thermoplastic polymer. WPCs can have superior outdoor durability and much lower maintenance costs than regular wood. WPCs can be used instead of wood. Styrene maleic anhydride (SMA) is used in plastic composites for the automotive industry and also in engineering applications. SMA wood composites, as one of the WPCs using wood fibers as reinforcing fillers, produces composites with mechanical properties that are stiffer and stronger than the neat polymer. This paper evaluates the feasibility of using foamed SMA copolymer composites in wood applications. Although it is currently used in the automotive industry and construction industry, this copolymer presents interesting opportunities for wood applications.

Key words: Wood Polymer Composite, Foaming, Styrene Maleic Anhydride (SMA), Physical and Mechanical Properties

SAŽETAK • Drvo-plastični kompoziti (WPCs) imaju vrlo široko primjenu, a uglavnom se sastoje od drva i termoplastičnog polimera. Mogu imati vrhunsku trajnost na otvorenome i mnogo niže troškove održavanja od običnog drva te se mogu upotrebljavati svuda gdje se obično upotrebljava drvo. Stiren anhidrid maleinske kislina (SMA) primjenjuje se u plastičnim kompozitima za automobilsku industriju, ali i u tehniki. SMA drvni kompoziti jedan su od WPCs-a u kojima su drvna vlakanka punilo za ojačavanje kompozita i imaju bolja mehanička svojstva od čistog polimera. U ovom se radu procjenjuje isplativost upotrebe upjenjenih SMA kopolimera kao zamjene za drvo. Iako se zasad rabi u automobilskoj industriji i graditeljstvu, taj kopolimer ima višestruke mogućnosti primjene kao zamjena za drvo.

Ključne riječi: drvo-polimerni kompoziti, pjena, stiren anhidrid maleinske kislina (SMA), fizikalna i mehanička svojstva

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Wood plastic composite (WPC) is a general term related to wood-based elements like lumber, veneer and fibers, where they are combined with polymers to produce a composite material. Wood plastic composites are thought of interchangeably and are categorized as different material types when produced from either thermoplastic or thermosetting polymers (Forest Products Laboratory, 2010). Examples of wood plastic composites made from different polymer types and wood elements are listed in Table 1.

Approximately one hundred years ago, a composite material combining phenol-formaldehyde resin with wood flour was used for making automobile gearshift knobs (Gordon, 1988). Around 60 years ago, there are references to combining wood with thermoplastic resin via extrusion processing (Oksman and Sain, 2008; Klyosov, 2007). Extrusion, injection and compression molding are the preferred production processes for WPCs (Figure 1).

WPC has gained the interest of material engineers because of its structural properties (El-Haggar and Kamel, 2011). Some of its main properties are high durability, low maintenance, strength and stiffness, lower prices and decrease in bio-degradation, which makes the composites suitable for outdoor applications. Some of the applications of these composites are: decking, sheathing, roof tiles, window trim and automobile parts. WPCs perform like conventional wood; however they are not stiff and may require special fasteners or design changes. WPCs are still stiffer than plastics (Clemons and Caufield, 2005). A developing class of materials, including WPC has favorable attributes – they are cost effective and have good performance (Marutzky, 2004; Nickle, 2003; Aydemir et al., 2014; Aydemir et al., 2015a; Aydemir et al., 2015b). Figure 1 Wood fiber filled thermoplastic composites (WPCs) and their applications (Anonymous, 2016a)

The esterification reaction between the hydroxyl groups of wood and the anhydride groups of SMA generates water, which is used as a foaming agent. The density of neat SMA is 1.08 g/cm^3 and of the foamed SMA/wood composites 0.60 g/cm^3 (Han and Gardner, 2010). The water by-product of the esterification reaction between SMA and wood is strategically created during the carboxylic acid and alcohol reaction process (Figure 3.). A contaminant from hemicelluloses degradation can be removed after the acids react with alcohols, which produces one mol of ester and another mol of water as a by-product. A hydroxyl group breaks the furan anhydride structure as an electron donator and esterifies with the hydroxyls of wood, which produces water as a by-product (Han and Gardner, 2010) (Figure 4).

Under extrusion processing, a large, soluble amount of a blowing gas into a polymer may be completely dissolved under a high pressure. How-

<table>
<thead>
<tr>
<th>Polymer type</th>
<th>Wood elements</th>
<th>WPC types</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermoplastic polymer</td>
<td>Lumber, veneer, fibers, particles, flour, etc.</td>
<td>Extruded lumber, injection-molded automotive components</td>
</tr>
<tr>
<td>thermoplastični polimer</td>
<td>piljenice, furnir, vlakanca, iverje, drvo brašno i dr.</td>
<td>ekstrudirana grada, inječijski prešani automobilski dijalovi</td>
</tr>
<tr>
<td>Thermosetting polymer</td>
<td>Lumber, veneer</td>
<td>Polymer impregnated wood (impreg, compreg)</td>
</tr>
<tr>
<td>termostabilni polimer</td>
<td>piljenice, furnir</td>
<td>polimerom impregnirano drvo (impreg, compreg)</td>
</tr>
</tbody>
</table>

Table 1. Wood-plastic composites (WPCs) are materials comprising polymers and wood elements (Gardner et al., 2015)

Tablica 1. Drvo-plastični kompozit (WPCs) – materijali koji sadržavaju polimere i drvne elemente (Gardner et al., 2015)
ever, to reach appropriate conditions in the microcellular foaming system, there must be a mechanism for regulating the growth of bubbles and additionally preventing them from coalescing and collapsing (Park et al., 1994; Park and Suh, 1996; Baldwin et al., 1996; Park et al., 1998).

The generation of high cell density for foaming may be possible when thermodynamic instability happens in a polymer gas solution. These newly formed cells should be preserved through a stabilization process that controls the growth of the cells and re-equilates the gas bubbles (Park and Suh, 1996; Park et al., 1994). During initial testing, a batch process was used to create microcellulose foams. Now, these foams are produced in continuous extrusion, injection and compression molding systems (Martini et al., 1982).

Extrusion is one of the most commonly used plastic technologies. In extrusion, there are several ways to transform a plastic resin including heated, melted, compressed and conveyed downstream by rotating screw/screws in a barrel. In terms of cost effectiveness, extrusion based technologies are leading in the commercial production of plastics. As compression molding gently shapes thermoplastic prepregs, it successfully retains different layer orientations (Faruk et al., 2007). Wood fiber reinforced plastic composites are converted by extrusion processes to get structural building profiles including, sheathing, decking, roof tiles, and window trim,
with enhanced thermal and creep performance compared with unfilled plastics (English and Falk, 1996; Verhey and Laks, 2002).

Usually, the production of foamed polymers comes from blowing agents such as a gas, a liquid or solid (Klempner and Frisch, 1991; Tavasoli et al., 2011). There are limitations of using blowing agents because they have a negative impact on the ozone layer. On the other hand, common aliphatic hydrocarbons are highly flammable. The blowing agents have a high price and low gas concentration during their decomposition (Rizvi et al., 2000). The government continues to promulgate regulations aimed at enhancing environmental protection and worker safety. Developing environmentally friendly blowing agents should help in addressing regulations and save on chemicals (Seo et al., 2011). Since water is available, non-toxic and environmentally friendly, it can be used as a blowing agent in the production of foams in the extrusion process when transformed into a gaseous state at temperatures above 100°C.

Several studies have been published on thermal analysis of fillers that can be employed as both nucleating agents and reinforcing components. To enhance performance aesthetics, processability and productivity, many additives in foamed composites are necessary (Klempner and Frisch, 1991). When it comes to the use of natural fillers, such as cellulose particles, it appears to have advantages over inorganic fillers and properties of the fillers that can be changed by either surface treatment or the use of coupling agents (Maldas and Kotka, 1991; Wang et al., 2003; Mishra and Patil, 2003). Fiber properties (orientation of fibers and natural properties of fiber), combined with the use of coupling agents, may enhance the properties of the composite manufactured (Andreopoulos and Tantili, 1988). Natural fibers are much preferred for use in commodity plastics because of their easy processability (Raj et al., 1992). After all, natural fiber-filled polymer composites commonly have high densities. Therefore, the composites can be foamed to lessen their density using chemical or physical blowing agents (Rizvi et al., 2000). Natural filler reinforced composites have shown excellent performance regarding physical, mechanical and thermal properties (Ozen et al., 2013; Kiziltas et al., 2014).

Even though, lignocellulosic and wood fiber reinforced composite are used in automotive and decking application, their use is limited because of lower impact resistance and higher density in comparison to neat plastics (Matuana and Heiden, 2004).

The likely innovative applications of these materials could be increased if these advantages were improved. The reduced weight of foamed plastic makes it stronger than non-foamed analogs, and also makes it achieve outstanding cost to performance ratios, as well as favorable strength to weight ratios. Foamed wood fiber reinforced composites enhance their capability to withstand constant nailing and screwing operations in comparison to un-foamed products of the same composition. In the end, the results are better surface definition and sharper contours and corners. Plasticizing effects of gas and foamed composites reduce the cost of the foaming process (Schut, 2001). The specifics of mechanical properties are significantly improved when microcellular wood fiber reinforced composite generate a finer microcellular structure. Microcellular foamed structures are created to enhance the performance in the composites (Matuana et al., 1996).

3 CHARACTERISTIC PROPERTIES OF FOAMED SMA

3. Karakteristična svojstva upjenjenog SMA kopolimera

Foamed styrene-wood plastic composites (FSW-PC) have been produced at the Advanced Structures and Composites Center at the University of Maine using reactive extrusion (Han et al., 2013). To prevent loss of blowing agents through venting, they are created by chemical reaction during the extrusion process and dissolved into the polymer melt, where the dissolution occurs in the mixing zone of the barrel next to the venting zone. Supercritical water is formed under high pressure and high temperature enabling foaming cells to locally initiate and grow to a certain size level. For the creation and maintenance of supercritical water, the extrusion system should be developed for appropriate pressure levels with a foaming die.

The industrial manufacturing arena has paid significant attention to the use of wood as reinforce-
 filler for thermoplastics (Kishi et al., 1988; Mai das et al., 1988; Woodhams et al., 1984; Yam et al., 1990). The injection molding process and thermforming of interior parts is used along with styrene maleic anhydride (SMA) copolymer in the automotive industry (ARCO Chemical Company, 1990). The main reason for the choice of maleic anhydride is to improve the properties of the copolymer. The importance of using SMA lies in the fact that it shows a similar behavior to maleic anhydride polypropylene (MAPP) (Takase and Shiraishi, 1989). The other advantages of using SMA plastics in automobiles include the fact that SMA can be recycled and combined with other materials in order to improve the strength properties. Filler effect, reinforcement of polymer, and superior mechanical properties can be improved by using glass fillers. These fillers have shortcomings with regard to environmental safety. Natural fillers can improve the environmental effects. Using natural fillers will enhance mechanical and thermal properties; low density, high aspect ratio and no abrasiveness are beneficial properties (Bledzki et al., 2002; Sperber, 2002; Riedel and Nickel, 2003).

Over the past several decades, it has been established that foamed composites provide high cost savings (30–40 %), lower density and rapid manufacturability attributable to its properties (Faruk et al., 2007; Bledzki and Faruk, 2005; Bledzki and Faruk, 2006). Micro-fibrillated cellulose, using water as a foaming for PLA matrix composites, was investigated by Boissard et al., (2011). It was found that density and morphological properties of the foams were related to processing temperatures and to water contents ranging from 3.7 to 98 wt. %. To obtain lower densities, a low processing temperature and MFC water content of 9 wt. % were required.

Polystyrene/wood foamed composites were studied by Rizvi et al., (2000), who used hydrocerol compounds and wood particle water (moisture content of 8 %) at 130 °C and 140 °C. These results have shown that expansion ratio was 9 to 20 %. During the last decade, bigger profiles and density reductions (5-50 %) have been achieved in foamed wood composites including ABS, ASA, SAN, PVC, PP, and monolayer, coextruded and even tri-extruded profiles (Bledzki and Faruk, 2006).

Figure 5 shows the difference in mechanical properties when compared to other wood composites when designing structures. The flexural modulus of elasticity or stiffness is not the only mechanical properties that needs to be considered.

Figure 5 Comparison of flexural modulus of various wooden materials for structural applications (Wood-1 - Red Maple; Wood-2 - White Oak; Wood-3 - Douglas Fir – South; GL - Glued laminated timber; PLY - Plywood; OSB - Oriented Strand Board; PB - Particleboard; MDF - Medium Particleboard (Wood Handbook, 2010); WPC-1 - PP-based 60 % wood (Wechsler et al., 2008); WPC-2 - Recycled PE-based 40 % wood (Najafi and Khademi-Eslam, 2011); WPC-3 - SMA-based wood plastic composite, a pilot product of sheet pile by University of Maine) (Han and Gardner, 2010) (Maximum values are shown)

Slika 5. Usporedba modula elastičnosti različitih drvnenih materijala za građevinske konstrukcije (Wood-1 - javor; Wood-2 - bijeli hrast; Wood-3 - duglazija; GL - lijepljena drvena građa; PLY - furnirska ploča; OSB - OSB ploča (ploča s orijentiranim ijerjem); PB - ploča ivericna; MDF - MDF ploča (ploča vlaknatica srednje gustoće) (Wood Handbook, 2010.); WPC-1 - ploče na bazi PP-a s udjelom drva od 60 % (Wechsler et al., 2008.); WPC-2 - reciklirane ploče na bazi PE-a s udjelom drva od 40 % (Najafi i Khademi-Eslam, 2011.); WPC-3 - drvo-plastični kompoziti na bazi SMA-a, pilot-proizvod Sveučilišta u Maineu) (Han i Gardner, 2010.) (prikazane su maksimalne vrijednosti)
4 ADHESIVE BONDED JOINTS OF WOOD PLASTIC COMPOSITES
4. LIJEPLJENI SPOJEVI DRVO-PLASTIČNIH KOMPOZITA

Many articles have studied the characteristics of WPC bonding (Gramlich et al., 2006; Oporto et al., 2007; Gupta and Laborie, 2007; Laborie and Gupta, 2008; Wolkenhauer et al., 2008; Oporto et al., 2009), specifically polyolefins (Kharitonov and Kharitonova, 2009; Lee et al., 2009; Pandiyaraj et al., 2009; Wang et al., 2009; Farris et al., 2010; Jacobs et al., 2010; Kirk et al., 2010) and wood treatments (Custodio et al., 2008; Wolkenhauer et al., 2009; Custodio et al., 2009). Various methods of surface treatments on wood plastic composites have been reported by Gramlich et al., (2006); Oporto et al., (2007); Gupta and Laborie, (2007); Laborie and Gupta, (2008); Wolkenhauer et al., (2008); Oporto et al., (2009) to improve adhesive bonding. These surface treatments resulted in the increase of joint strength.

More research should be made on load carrying capacity of WPC joints as they are used in structural applications. So, this research will help identify the most effective design and cost considerations (Vinson, 1989). Some research has been conducted on bolted joints of WPC panels; however, further research is required (Thoppul et al., 2009). There is no current evidence of the effect of geometrical configuration of screws, pilot hole diameter and penetration depth on withdrawal resistance of related joints of WPC composites.

WPC is used commercially in automotive interiors, furniture, packaging and housing. There are

![Figure 6](image-url)
some critical factors that affect the application of wood plastic composites (English and Falk, 1996). These are:
Cost
There are many variables affecting costs, including cost of compounding fillers, wood and paper fibers or inorganic fillers. Fillers are often less expensive than the polymer on a price per weight basis.
Hygroscopicity
Wood fiber is hygroscopic and when used in the plastic process at normal processing temperatures, the plastics will foam attributable to steam. Water is occasionally used for a foaming agent in plastic lumber profiles.
Fiber loading limits
A continuous thermoplastic matrix is required to process WPC. Upper fiber loading limit is about 70 wt.%. To maintain ideal melt viscosity, the fiber loading limit is around 50 wt.% (Charrier, 1991).
Water absorption
There is little water absorption when wood component is surrounded by the plastics. Even when immersed for several days, the water absorption values are typically less than 2%. Humidity variation has shown little effect on dimensional changes (Kokta and Danueault, 1986).
Engineering properties
An engineering property is the capability of WPC to safely resist the expected loads. Another property is the short and long term serviceability limits when functioning within the design load.
Creep
Creep is related to the wood’s ability to sustain shape during time dependent mechanical loading. Research shows that WPC has lower resistance to creep deflection, which reduces its structural applications (Felby, 1992).

Figure 6 shows the short term creep response of WPC and polyvinyl chloride (PVC) at three different temperatures (21 °C, 30 °C and 45 °C). According to Tamrakar et al. (2011), creep deformation of WPC was lower and more stable at 21 °C and 30 °C than that of PVC.

5 CONCLUSION

Natural fiber-filled plastic profiles are used as a non-structural wood-replacement in specific applications such as decking. Processors are evaluating foamed composites, which weigh less, accept screws and nails and more closely resemble real wood. Foaming gives better surface definition and sharper contours and corners because of internal pressures created by foaming. Heavier foamed profiles can be joined like conventional wood with no caps or hiding edges. Most wood foamed profiles are combined with un-foamed cap layers to provide color, decoration or UV stability, which provides important structure engineering applications.

In recent years, an increasing number of attempts have been made to combine wood with plastics to create interiors (window or door frames, staircase railings, screens and even decorative items), garden furniture and other outdoor applications (terrace decking, weatherboarding and fencing panels).

Industry and academia are now evaluating foam-like structure in WPCs to decrease their density and cost, improve mechanical properties (impact strength and toughness), nailing and screwing properties.

6 REFERENCES

http://dx.doi.org/10.1002/(SICI)1097-4628(19981024)70:4<747::AID-APP14>3.0.CO;2-U.
http://dx.doi.org/10.1080/03602559.2014.935406.
http://dx.doi.org/10.1007/s10934-014-9856-x.
http://dx.doi.org/10.1080/1023666X.2015.1012792.
http://dx.doi.org/10.1002/pen.10537.
http://dx.doi.org/10.1002/app.21685.
http://dx.doi.org/10.1016/j.composites.2005.08.010.
http://dx.doi.org/10.1080/0336844141407233.
Zor, Tankut, Kiziltas, Gardner, Yazici: Feasibility of Using Foamed Styrene Maleic...


http://dx.doi.org/10.1080/09668421003616329.


http://dx.doi.org/10.1163/092764009X12477463089116.


http://dx.doi.org/10.1002/pc.22463.


http://dx.doi.org/10.1016/j.apsusc.2008.10.090.


http://dx.doi.org/10.1016/j.compositesa.2011.03.011.


http://dx.doi.org/10.1002/pen.10077.


http://dx.doi.org/10.1163/156856108X12477463089116.


http://dx.doi.org/10.1016/j.ijadhadh.2007.11.001.


http://dx.doi.org/10.1002/pen.760241504.


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