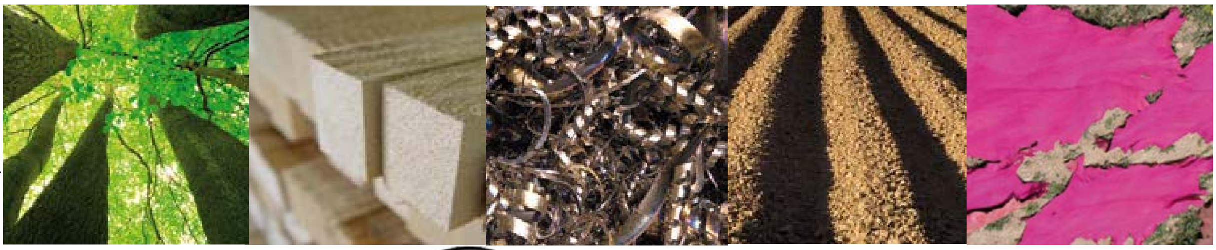

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Deliverables Report

RubWPC

Contract ECO/12/333083

Rubber Fusion of Wood Plastic Composite to Make Functional Composites for Building Applications

Project coordinator: Professor Mizi Fan

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Name of the Author	M Aitken / S Castilho
Partner	CRL
Telephone	+44(0)7800 921653
e-mail	mike.aitken@crumb-rubberuk.co.uk
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1. Abstract

The aim of this report is to present a complete assessment of recycled wood, rubber and recycled thermoplastics together with a review of the additives and other functional agents suitable for the production of RubWPC.

After discussions at the second meeting of the RubWPC group it was agreed that this Work Package would concentrate on the types of materials known to be suitable for manufacturing wood / thermoplastic / rubber composites. The assessment was made taking into account only the thermoplastic materials that were thought to be suitable to be used in the RubWPC project.

The compilation of information was done using internet investigations, consultation of European legislative and standard documents and also existing knowledge of the partners involved.

The outcome of this assessment has been an extensive compilation of information regarding the state of the art of process technologies, legislations in place, quality control and sources of the three raw materials to be used in the RubWPC project. Also databases of EU companies capable of supplying the three components of the planned composite were produced, introducing where possible details of the product specification they can supply.

2. Introduction

Composite materials are composed of two or more constituent materials with usually different physical or chemical properties. In a composite material there are two main constituents, the matrix and the reinforcement. The matrix surrounds and supports the reinforcement materials and the reinforcements are added to the matrix in order to enhance or improve a particular mechanical and/or physical property. A matrix material can be reinforced with a variety of materials from fibres and ceramics to metals or polymers. Reinforcement of the matrix material may be achieved in a variety of ways. Fibres may be either continuous or discontinuous. Reinforcement may also be in the form of particles. The matrix material is usually one of the many available engineering plastics/polymers. Selection of the optimal reinforcement form and material is dependent on the property requirements of the finished part.

One of the most often used thermoplastic groups for obtaining composites are the poly(olefins) such as poly(ethylene) and poly(propylene), but the adhesion of these matrices with natural fibres is rather low due to its different chemical structure. Poly(olefins) are very apolar materials due to their hydrophobic long aliphatic primary chain without any polar group. On the other hand, the natural fibres based on cellulose have hydroxyl groups in their structure which promote the polarity of the materials having a high hydrophilic character. The combination of these two hydrophobic and hydrophilic components in the fabrication of composites involves negative interfacial effects related with the bad adhesion between both surfaces.

There are different ways to improve the adhesion at the interface of the composites. The modification of the fibre surface to change its surface polarity is one of them. In the case of cellulose fibres, the use of this way leads to the modification of the hydroxyl groups on the surface by reaction with different reagents to decrease the polarity of the surface or to increase the affinity of the surface of the fibre towards the polymer matrix. Another way to improve the interaction between the reinforcement and the polymer is the addition of a coupling agent to bond chemically the surface of the fibre and the plastic matrix. This is the case of the maleated poly(propylene) (MAH-PP) which is able to react with materials containing hydroxyl groups on the surface. This is a polymer modified with a polar group (maleic anhydride) grafted in the chain by a radical reaction in the presence of peroxides. The coupling agent has functional groups able to react with other polar functional groups such as amines and alcohols. In the case of cellulose fibres, the hydroxyl groups on the surface of the fibre can react with the anhydride to form ester bonds. This bond induces the chemical linkage and the transference of efforts from the polymer to the fibre, promoting better mechanical properties to the material.

The internet research and experience of staff at Crumb Rubber Ltd, Ecodeck Ltd and University of Girona (previously Modifibres) was used to identify companies involved in the recycling of polyolefins, PET, producers of wood flour suitable for use in the planned composite and producers of suitable fine rubber powder based on end of life vehicle tyres.

A similar approach was taken with regards to additives for WPC with the addition of discussions with a range of suppliers of these materials to gain their views on the “state of the art”.

The information on plastics, rubber and wood was compiled by product group into Excel spreadsheets detailing the company, EU member state, if they belonged to a recognised trade association, their website address and the type of product they produce. For wood flour and rubber where possible the available product size distribution was listed. The European recycling industry is not as sophisticated as the virgin material industries so the detail on products and specification was often limited. The thermoplastics and rubber components for this project are sourced from recycled feedstock. The wood flour component is produced from virgin timber.

3. State of the art of recycled thermoplastics, rubber and wood.

The recycling industry has developed rapidly since the earlier 2000's driven by the oil price rising to over $100 per barrel increasing the feedstock prices for many plastics and rubbers and the pressure on reducing landfill in the EU which has applied considerable pressure to recycle thermoplastics, rubber and wood.

The current "state of the art" is described below for each of the three materials. Attached to this report is the database of potential producers of raw materials to be used on the RubWPC project in an Excel spreadsheet.

3.1. Thermoplastics

From the three main components of the planned composite the thermoplastics recycling industry is the largest, the most diverse and sophisticated in terms of process technologies.

A decision was taken at the second meeting of the partners of RubWPC to focus the research on companies that produce polyolefins and PET as potential feedstocks. This was because nylon, ABS, PS, PVC and PC are known to be unsuitable to use in this project.

3.1.1. Feedstock /Sources of material

Recycled thermoplastics can be obtained by three main supply chains:

- Recycling of end of life industrial waste
- Recycling of in process waste
- Recycling of post consumer waste

The first supply chain produces a good quality recyclate that often allows the polymer to be reused at a controlled percentage back into the same or different product in house.

The second supply chain includes both process waste and rejected components which did not met production standards or specifications required for a determined product. As a result, the "pedigree" of the waste stream is known, as are any contaminants so they can be successfully managed to produce a clean feedstock for the same or other products.

The last category is the largest, the most complex and also the most cross contaminated. Within the post consumer plastic waste that is suitable for recycling, there are a large variety of plastics that have different compositions, colours and properties. This type of waste source is generally grouped in five categories [1].

Plastic bottles, pots, tubs and trays – that are generated mainly by household waste.

Plastic film (includes plastic shopping bags, rubbish bags, bubble wrap, and plastic or stretch wrap) - Main source of this films are companies responsible to wholesale and distribution activities.

Rigid plastics (includes crates, pipes, containers and mouldings) – These plastics can be originated from a variety of sources from industry to agriculture.

Plastic foams - the most common plastic foam used is expanded polystyrene used in packaging.

Flexible plastics (includes strapping and cable sheathing).

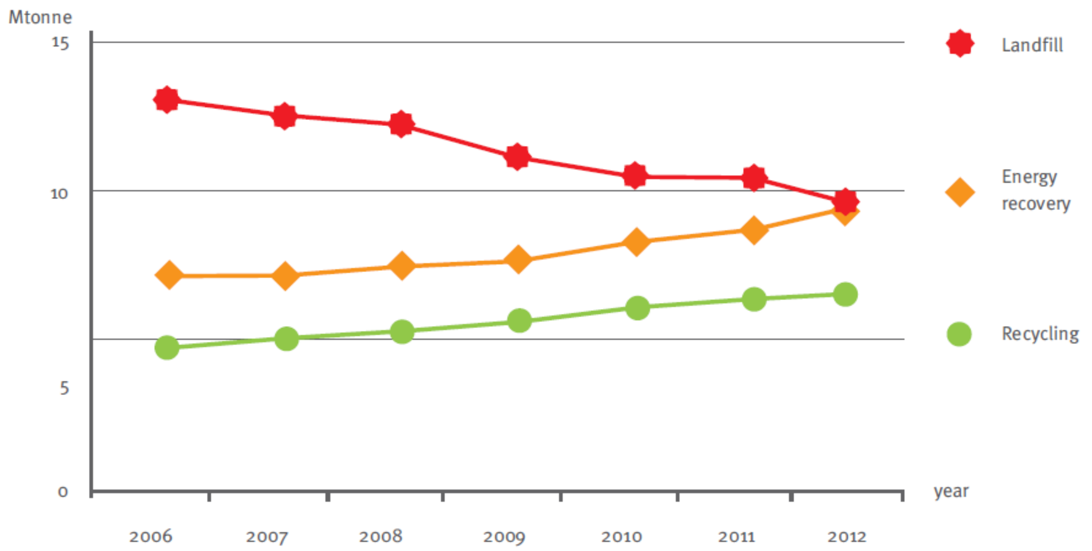


Figure 1 Destination of post consumer plastic waste 2006-2012 [2].

The total amount of post consumer plastic waste generated has been increasing throughout the years in Europe (Figure 1). In 2012, the quantity of post consumer plastic waste generated was 25.2 Mtonne, from which 26.3% was diverted to recycling facilities, corresponding to 6.6Mtonne of waste plastic recycled in that year. Intimately related to this increase is the growth in recovery operations, these increased about 4.7% for the collection of post consumer plastic waste for mechanical recycling.

From all the post consumer plastic waste around 77% was generated by the following European countries: Germany, UK, France, Italy, Spain, Poland, and the Netherlands. Packaging plastic waste was the dominant waste within this category covering 62.2% of the total generated post consumer plastic waste [2].

3.1.2. Process

The European recycling market is rapidly evolving, in particular with the latest technologies that are able to separate co mingled post consumer scrap into discreet clean/decontaminated polymer streams, making their reuse viable.

3.1.3. Collection

The recycling process starts with the waste collection and determines the composition of the waste stream, influencing all the recovery operations ahead. Nowadays, collection schemes of dry recyclables as household plastic goods and others such as metals, glass, card and paper have been done throughout Europe and it is a valuable solution to maximize the amount of waste that can be recovered into a quality resource instead of going to landfill.

3.1.4. Pre-treatment

The pre-treatment necessary to each waste differs from recycler to recycler but can include plastic separation, washing, de-contamination and sorting. There is a wide range of technologies used in the industries to pre-treat the waste that arrives at the recycling plants. They go from manual sorting and picking to automated processes such as, shredding, sieving, air and liquid density separation processes, magnetic separations and highly sophisticated spectrophotometer sorting technologies such as UV/VIS, NIR and laser techniques.

Some of these recycling units are highly complex and efficient being able to produce around 100,000tonnes/year and obtain purity higher than 95%.

3.1.5. Mechanical Recycling

The mechanical recycling of plastic products consists in different mechanical processes, such as, grinding, separation, drying, re-granulation in order to recover plastic waste into plastic recyclates that can be used in new applications without modifying the polymers molecular structure.

The ideal input for mechanical recycling are streams of homogeneous thermoplastic type materials (because they can be re-melted and re-processed) that are clean and preferably free of contaminates.

The output from the process is either flakes or granulates. Depending on the efficiency of the pre-treatment and recycling process these flakes/granulates may still have contaminants in it such as ink, metal, non plastic material or other polymers. In some cases, recyclers have another stage on the recycling process that includes an extrusion process to further clean the material. The extruder is equipped with a melt filter which helps to remove many of the contaminants present on the material. When the material is subjected to an extrusion usually the final product obtained is a granule/ pellet which are physically similar to the virgin material [3].

3.1.6. Feedstock Recycling

Feedstock recycling is a valuable option when low quality mixed plastics, plastics contaminated with food or composite plastics are involved because these are very difficult to recycle by the mechanical recycling process. These type of materials are not suitable to recycling but can be used in gasification or pyrolysis processes.

3.1.7. Legislation

Currently the European directives in term related to the regulation of recycling processes of plastic wastes are the Waste Framework Directive 2008/98/EC and the Packaging Directive 94/62/EC. The Packaging directive is applicable in recycling of post consumer plastic waste because most of this waste comes from packaging products.

Waste Framework Directive – 2008/98/EC

This directive establishes the legislative framework for the handling of waste, providing clarification on basic waste management principles and definitions such as, waste, by-product, recycling and recovery. The directive also presents the necessary requirements for an establishment to carry out waste management operations taking in to account human health and the environment.

Two new recycling and recovery targets are established, a minimum recycling target of 50% for household waste and 70% for building and construction waste to be achieved by 2020 by all EU Member States [4].

Packaging Directive – 94/62/EC

This Directive aims to standardize processes in order to prevent or reduce the impact of packaging and packaging waste on the environment and to ensure the well functioning of the Internal Market. It contains provisions on the prevention of packaging waste, on the re-use of packaging and on the recovery and recycling of packaging waste.

In 2004, the Directive was reviewed to provide clarification on some terms and definitions and also new recovery and recycling targets of packaging waste were imposed. In 2005, the Directive was revised again to allow new Member States to reach the recovery and recycling targets presented on the directive [5].

3.1.8. Quality /Specifications

Throughout the world the quality control of recycled plastics varies greatly. In some cases recycling industries don't follow any specific standards and generally the recycled material has low specification. In these cases the quality of the recycled material is usually linked to the quality of the feedstock and to the effectiveness of the recycling process.

Whilst there are exceptions, e.g. HDPE and PET from post consumer waste being recycled into bottles the specification of recycled plastic usually only covers melt flow index (MFI) and density.

One of the problems when dealing with plastic recycling is the identification of the material being treated. In order to facilitate the recycling process some institutions/associations in different countries recommend the use of a coding system to indentify larger plastic parts and plastic packaging.

For plastic packaging products, many countries are adopting the identification code developed by the American Society of the Plastics Industry – SPI (Figure 2). There is currently no mandatory need to identify the different plastics produced but it is considered of good practise to use an international recognised recycling code [6].

Figure 2 Polymer identification code from SPI [7].

When is not possible to identify the plastic by their codes, it is common in the industry to realise some simple and easy tests in order to have an idea of the material being recycled. Some of these tests are straightforward and there is no need of any special equipment. An example of these are the float test where some of the waste is put in water and oil in order to distinguish materials by their characteristic densities. The flame test is another commonly used test to distinguish different plastics. When the plastic enters in contact with the flame it can present different colours depending on the type of plastic being tested. Also by bending the sample it can be known if the plastic is rigid or flexible [1].

For some of the industries, quality control can be as simple as a visual inspection and matching some of the materials characteristics with a list of non acceptable features or by performing the simples tests described above. Others can have a better defined quality control system where detailed laboratory tests are included in order to have a more accurate composition of the waste being treated.

Other measures of quality control that can be used are related to the handling and storage of the waste materials. They should be handled and stored in a way that the plastics are protected from moisture, dirt and sunlight.

Within the challenges of plastic recycling quality control of plastic waste is regularly one of the topics arising. The big challenges for the recycling of this type of waste are the elimination of contamination and also the high variability of the recycled batches of recycled material that greatly contributes to the quality of the recyclate. For this reason, quality control implementation in the recycling industry is of extreme importance to minimize contamination and generate more consistent batches of recycled materials.

Recently in order to standardize post consumer plastic waste recycling and try to obtain a more consistent and good quality recyclate among the plastic industries, the European Commission co-funded a project, EuCertPlast, which aimed the creation of a certification for post cycle recyclers.

The certification works according the European standards EN 15343:2007 for assessment of conformity and recycled content as well as traceability. Its objective is to encourage plastic recyclers to work according to the standards presented in Table 1 in an environmentally friendly way. This certification also brings standardization for the characterisation of specific recycled outputs [8].

Table 1 – European Standards for plastic recycled outputs [8].

Document Number	Title
EN 15343:2007	Plastics - Recycled Plastics - Plastics recycling traceability and assessment of conformity and recycled content.
EN 15347:2007	Plastics – Recycled Plastics – Characterisation of plastics wastes.
EN 15342:2007	Plastics – Recycled Plastics – Characterisation of polystyrene (PS) recyclates.
EN 15344:2007	Plastics – Recycled Plastics – Characterisation of Polyethylene (PE) recyclates.
EN 15345:2007	Plastics – Recycled Plastics – Characterisation of Polypropylene (PP) recyclates.
EN 15346:2007	Plastics – Recycled Plastics – Characterisation of poly(vinyl chloride) (PVC) recyclates.
EN 15348:2007	Plastics – Recycled Plastics – Characterisation of poly(ethylene terephthalate) (PET) recyclates.
CEN/TR 15353	Plastics – Recycled Plastics – Guidelines for the development of standards for recycled plastics.
EN ISO 472:2001	Plastics, vocabulary.

In terms of quality control, all the recyclers that want to be certified by EUCertPlast have to a have a strict quality control system. For each type of polymer the standards have a defined tolerance for the required and optional characteristics of a specific recyclate.

For example for required assessment of quality of PP recyclates following EuCertPlast, recyclates have to be visual inspected to analyse colour and shape. It is also required an analysis of density, melt flow rate and impact strength test. As optional, parameters like the ash content, bulk density, extraneous polymers, flexural properties, filtration level, recycled content, tensile stress at yield, tensile strain at break and volatile content can be tested [9].

The specifications and the standard deviations to the values obtained in each specification shall then be agreed between the supplier and the purchaser.

The recyclers should have also a quality management system certified to EN ISO 9001 in order to guarantee a consistent recyclate quality.

A number of trade organisations have evolved within the plastic recycling industry, some are national organisations, and others are pan European e.g. European Association of Plastic Recycling (EPRO) [10].

3.2. Rubber

The successful recycling of end of life vehicle tyres (EOLVT) is a global challenge. There are currently stock piles of tyres around the world. The EU has banned the landfill of EOLVT but there is insufficient demand /applications for reprocessed rubber within the EU and therefore there are exports to certain other regions of either whole tyre or downsized material, often as tyre derived fuel (TDF) to be used in power stations to produce electricity.

3.2.1. Feedstock /Sources of material

The rubber that is intended to be used in the RubWPC project is recycled rubber powder from end of life vehicle tyres.

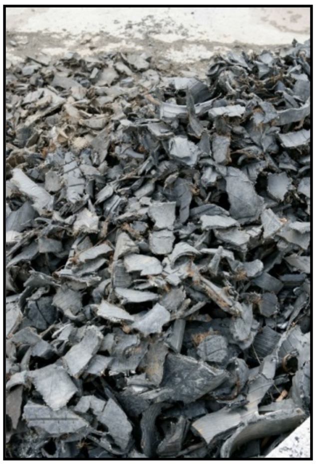
Tyres are highly complex items consisting of steel, fabrics (made from nylon or polyester) and up to 16 different rubber compounds. The compounds are designed to meet the technical requirements of different parts of the tyre (such as the bead, side wall and tread compounds) and also different performance requirements that different vehicles have. Due to this the formulations of tyres are highly complex. Their components include natural rubber (NR) synthetic rubbers (SBR), carbon black, process oils, silica, sulphur and other additives. Further complexity occurs because each tyre manufacturer has their own proprietary formulations.

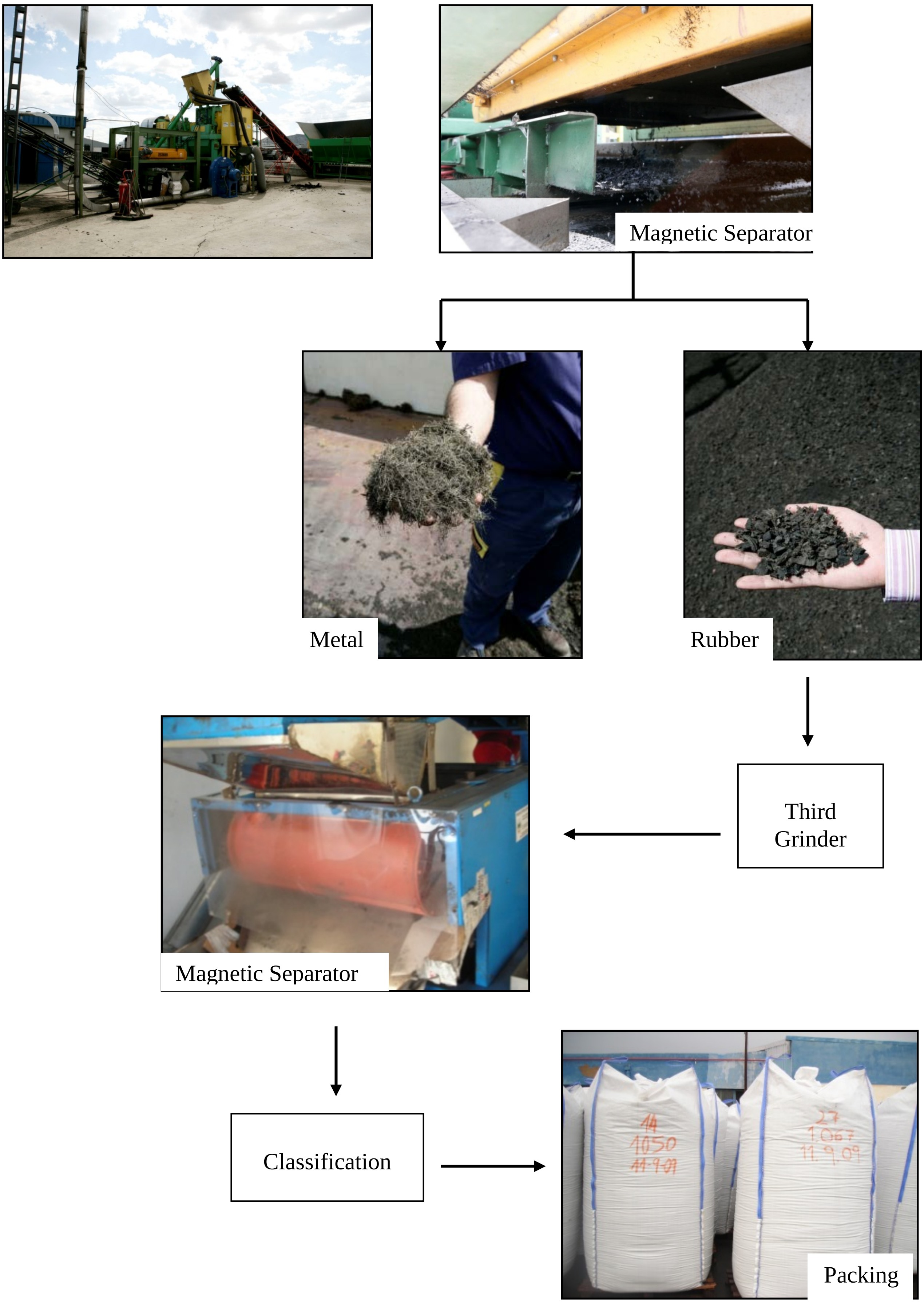
The feedstock for the tyre recycling industry includes tyres from passenger cars, trucks, large machines (e.g. tractors and earth movers) and aircraft. Within all of these categories the largest volumes are from car and truck tyres. Similar to the feedstock for thermoplastic recycling the feedstock for rubber recycling can have great variability.

3.2.2. Process

The tyre recycling process is generally "low technology" and basically consists of a multi step size reduction of the tyre. The majority of tyre recyclers take whole tyres and put them through a mechanical shredding, rasping and granulation process to downsize the material. The segregation of car and truck tyre is not common and there is no segregation by manufacturer. The most common output from this process is a product in the 20mm to 3mm size range. All tyre recyclers will have some stage where a percentage of the metals, fibres and stones are removed. Like any grinding process a fine fraction, i.e. sub 1mm is produced but this is viewed as a by product by the recycler and is not produced to a specification.

Diagram 1 Stages of a tyre recycling process.




Magnetic Separator
Metal
Rubber
Third Grinder
Magnetic Separator
Classification
Packing

In order to produce fine powder below 1mm in size either a cryogenic milling process is required or a specialised ambient grinding process (such as a cracker mill). The feed material for these processes will vary but would generally be sub 5mm material from the process described above. This further grinding process “liberates” more of the metal and fibre contaminates therefore capable of producing a rubber powder that is over 99% free of metal and fibre. Tyre rubber is vulcanised and therefore the only way to remove metals and textiles is by a physical process, unlike thermoplastics the tyres cannot be melted and melt filtered. A small volume of truck and car buffings from the tyre retreading industry is available and is considered a premium feedstock as it has low levels of metal and fibre contamination.

This project has identified only a small number of companies capable of producing EOLVT fine rubber powder below 400 micron in size which is currently understood to be the most cost effective material to incorporate in thermoplastics. Finer materials are available via the cryogenic process but the additional cost of liquid nitrogen make these grades unattractive.

3.2.3. Quality /Specifications

In the UK, the Tyre Recovery Organization and WRAP have produced a standard PAS 107:2012 which sets out to define the type of rubber, size specification and levels of wire and textile contamination. It has not been widely adopted [11].

The industry generally classifies products by mesh size but there are differences between mesh sizes quoted for the heavy duty meshes used in production sieving machines and those used in laboratory equipment. Particle size analysis for any given grade is of greater relevance in terms of its suitability in a thermoplastic composite than a quoted mesh size.

In technical applications such as RubWPC a particle size specification is generally agreed between the fine rubber producer and customer. A product specification should also include the moisture, fibre and metal content.

3.2.4. Trade organisations

There is the European Tyre Recycling Organisation (ETRA) and a number of national tyre recycling organisations which provides a forum for developing the tyre recycling industry. None of these organisations have set mandatory quality standards [13].

3.3. Wood

Wood flour consists of a very fine particle size form of wood. It is manufactured by milling /grinding and sieving material derived from “virgin material” i.e. the wood has not been used for any other purpose. As such it is not a recycled material. One obvious reason for this is that a lot of timber products have chemical treatments to protect the wood from insect and microbial attack. These chemicals would potentially be dangerous if present during the heat processes used when manufacturing composites with plastics and rubber.

A number of the manufacturers of the grades used for compounding in thermoplastics supply similar materials to other manufacturing processes. They supply coarser grades for various types of animal bedding including grades for both domestic pets and farmed livestock.

The project could only identify a small number of wood flour manufacturers within the EU. The larger timber producing regions of the USA and Russia had a larger number of manufacturers.

3.3.1. Feedstock /Sources of material

The feedstock for fine wood flour is virgin timber, either softwood or hardwood varieties.

The species of trees that are commonly used to produce wood flour are white pines, aspen, spruce, maple, oak and cedar trees [14].

3.3.2. Process

In this respect the wood flour industry is similar to the rubber reprocessing industry where a large input material is downsized by mechanical grinding / granulation and sieving. In order to obtain very fine wood flour before the particle size reduction, the industry can have a pre stage where the wood is dried in order to facilitate the grinding process. After the grinding process, particles with different sizes can be obtained and also variation in particle shape and structure is common. The next stage of the wood flour processing is the sieving and screening process where the processor obtains the desired particle size distribution for the material. This stage can be done either by mechanical means or by air screening methods in order to have a narrow range of particle size distribution.

3.3.3. Quality /specifications

Wood by its very nature is variable in the properties that it has and therefore makes its use in products that have to meet a certain specification more challenging than other materials that are made from synthetic feedstock where the manufacturing process can be controlled.

The classification of the wood flour products available comes under the following headings:

Softwood

Hardwood

Moisture level

Particle size distribution and shape

That it is form a sustainable source of timber.

Wood flour is not a standardized product and generally the quality of the wood flour is affected mainly by the raw material used. High quality wood flour comes from hardwoods due to high strength and durability of this type of wood. Low grades of wood flour usually come from softwoods. This can be attributed to the different composition of hard and softwoods. Softwoods usually have more sap content.

Review of the particle size distributions available indicates that manufacturers make specific grades for customers rather than there being an industry generic product offering.

In order to compound wood flour into thermoplastics, processors like Ecodeck have to incorporate drying equipment in their lines to ensure the moisture level is low enough not to cause manufacturing problems and issues such as voids in the final product.

3.3.4. Trade organisations

We could not identify a trade organisation for wood flour. A number of national bodies like the UK Forest Products Association (UKFPA) and the International Programme for the Endorsement of Forest Certification (PEFC) promote the use of timber from sustainable sources.

4. Surface treatments

Due to their polar nature, natural filaments are incompatible with apolar polymers. The compatibility between both materials can be improved by means of the modification of the fibres surface or by means of a chemical modification of the polymer matrix. In most of the cases the chemical modification is made by means of the application of a third component, such as a coupling agent. There are several different ways for chemical treatments, for example the alkaline treatment of fibres, the pre-impregnation of fibres with the matrix, the treatment of filaments with silane and the treatment of the matrix with polypropylene or Polyethylene copolymers (MAPP or MAPE).

4.1. Alkaline treatment

The alkaline treatment increases the amount of amorphous cellulose while decreasing the crystalline cellulose. The important modification is the elimination of the hydrogen union in the structure of the system. Reaction (1) is the result of the treatment with alkaline solution:

$$Fibre - OH + NaOH \rightarrow Fibre - O^{-}Na^{+} + H_2O \tag{1}$$

The alkaline cellulose is formed as a result of the penetration of the sodium hydroxyl within the crystalline regions of the cellulose matrix. The extension of the treatment with NaOH depends on the concentration of alkaline solution, the temperature, pH of the solution and the duration of the treatment. Optimal conditions of the treatment increase the adhesion between the matrix and the interface of the filament and induce an improvement on the breaking stress of the cellulose.

4.2. Silane treatment

The silanisation of the surface of natural filaments increases the fibre-matrix interaction. Several authors [16] have noted that the silanisation of natural fibres modifies the surface properties promoting stronger interaction at fibre-matrix interface. The silane condensation mechanisms use to be catalysed under a base or acid medium.

Additionally, the formation of the structures of "polysiloxanes" can also occur. The reaction between silanes and natural filaments (2) can be written as follow:

$$Filament - OH + CH_2 = CH - Si(OH)_3 \rightarrow Filament - O - \underset{OH}{\overset{OH}{Si}} - CH = CH_2 \qquad (2)$$

4.3. Treatment of pre-impregnation of filaments with the matrix

The impregnating treatment consists of dissolving the polymer matrix in an organic solvent and putting it in contact with the filament, before the extrusion process. This process needs the use of adequate heating to melt the polymer. The purpose of this treatment is to manage to form a film of the polymer matrix, which covers the filament defects, changing its morphology.

A schematic diagram of the untreated surface filaments and treated filaments is shown in Fig.. It can be observed that for the pre impregnating treatment (Fig.b), the matrix penetrates the filaments; whereas, for the treatment with silane coupling agent (Fig.c), the silano groups are grouped chemically in the surface of the filament by one side and connected with some chains from the matrix to the other side.

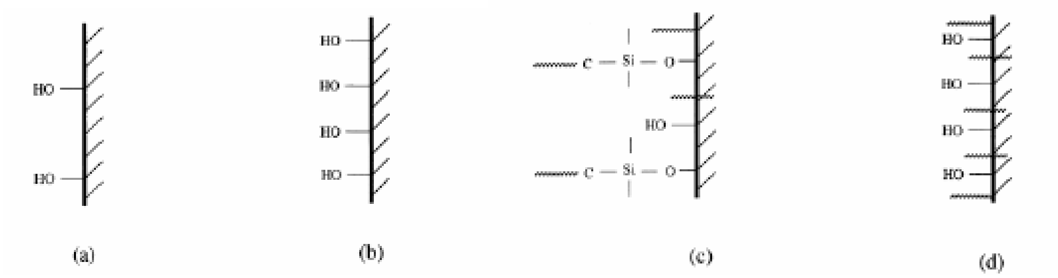


Figure 3 Schematic representation of the interfaces for: (a) untreated fibre; (b) NaOH treated fibre; (c) silane treated fibre; and (d) fibre after a impregnating treatment.

4.4. Additives for property modification

It is estimated that the global market for wood-plastic composites, is growing at 20% annually. Therefore additives manufacturers have become more aware of the particular needs of WPC in applications such as residential decks, railings, fencing, doors, window frames, outdoor spas, and gazebos. Work is also under way on side panels and roofing. Suppliers are identifying optimum choices of existing additives and developing new ones to give WPCs better physical properties, surface appearance, and long-term durability.

Proper additive choices for WPCs are critical to both performance and processing. Decking products have not proven to be as "maintenance-free" as originally promoted. Warpage, splitting, staining, and discoloration have all been problems. As WPCs attempt to move into more structural load-bearing uses, additives that improve mechanical strength are an immediate goal. In the extrusion process, processing additives are essential to achieving both economical line speeds and smooth surfaces without edge tearing.

The most primary areas of additive selection for WPCs are coupling agents, lubricants, and colourants. Also of increasing interest are chemical foaming agents and biocides. Polyethylene-based wood composites—mainly recycled HDPE—account for 80% of the market. Wood-PVC is 10% to 13% and wood-polypropylene, 8%. Wood-polystyrene accounts for only 1% to 2%.

4.5. Introduction: Coupling agents

Coupling agents bond the wood fibre to the resin matrix. They boost the flexural strength and stiffness—usually referred to as modulus of rupture (MOR) and modulus of elasticity (MOE), respectively, which are terms used in the lumber industry. Coupling agents also improve dimensional stability, impact resistance, and fibre dispersion, while reducing creep. Added strength is important in railings, stair treads, fencing and in structural applications. In decking, coupling agents are used mainly to reduce water absorption, which swells the wood fibres near the surface of the board, causing stresses that can lead to cracking.

Coupling agents are especially valuable in polyolefin WPCs because they overcome the incompatibility between the polar wood chemistry and non-polar resin matrix. The most common coupling agents are chemically modified (usually maleated) polyolefins made by grafting maleic anhydride onto the polymer backbone through reactive extrusion. They generally sell for around €4.40 /kg and are used at levels of 1% to 2%.

4.5.1. Modification of the matrix with maleated polypropylene or polyethylene

Another way to improve the interaction between the reinforcement and the polymer is the addition of a coupling agent to bond chemically the surface of the fibre and the plastic matrix. This is the case of the maleated polypropylene or polyethylene, (MAPP or MAPE) which is able to react with hydroxyl groups on the surface. This is a polymer modified with a polar group (maleic anhydride) grafted in the chain by a radical reaction in the presence of peroxides.

The mechanism of reaction between fibres and maleated polypropylene (MAPP) or maleated polyethylene (MAPE) is shown in. After the treatment, the superficial energy of the fibres is approximately equal to the superficial energy of the matrix. The MAPP has effectively “wetted out” the fibre and consequently produced a higher interface adhesion.

In the case of cellulose fibres, the hydroxyl groups on the surface of the fibre can react with the anhydride to form ester bonds. This bond induces the compatibilisation and the transference of efforts from the polymer to the fibre, promoting better mechanical properties to the composite. In the Fig., a scheme of the reaction between a cellulose fibre and MAH-PP is shown.

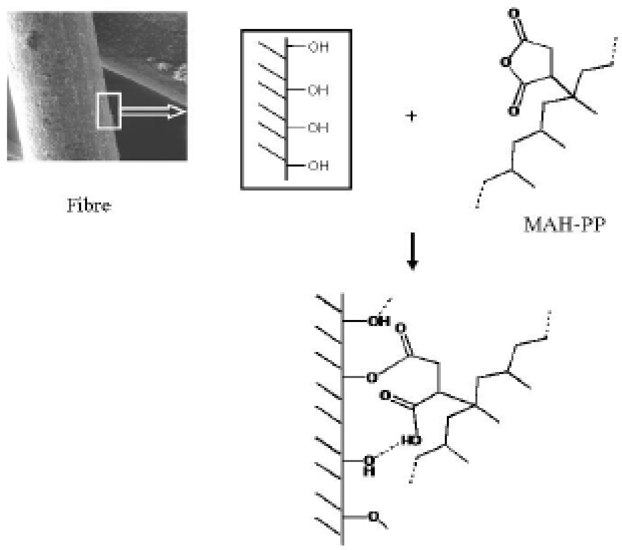


Figure 4 Illustration of the reaction between a cellulose fibre and MAH-PP.

4.5.2. Discussion

Newer developments include chemically modified polyolefins that are not made by grafting, long-chain chlorinated paraffin, and reactive coupling agents for wood-PVC.

Crompton Corp. recently launched Polybond 3029MP, a maleated HDPE in a new smaller particle size —20-mesh micropellet— that’s said to improve dispersion. At 2%, it reportedly can double the flexural and tensile properties of 60% wood in HDPE.

Crompton also has a proprietary maleated PP that reportedly outperforms coupling agents made by reactive extrusion, partly owing to the ability to incorporate higher maleic anhydride (MA) levels. Trials are said to show significantly higher tensile, flexural, and impact strengths with this additive, less susceptibility to lubricant interference, and 40% lower water absorption.

Equistar Chemical offers the Integrate series of maleated PE coupling agents for PE-based composites, plus new maleated PPs for wood-PP. Jim Krohn, business development manager, claims that wood-PE lumber typically shows at least 50% higher MOR and 20% higher MOE with these additives.

DuPont offers MA-grafted Fusabond MB-226D for wood-PE and MD-353D for wood-PP. Tensile strength in wood-HDPE is said to be 200% to 300% higher than uncoupled formulations. DuPont has also developed a new chemistry that replaces grafting with proprietary copolymers made from anhydride-functional monomers that are said to work well in wood-PE.

Eastman Chemical offers Epolene MA-grafted coupling agents such as PE-based Epolene G-2608 and newer PP-based E-43, G-3003, and G-3015 grades. "We have seen a 70% increase in overall tensile properties, 30% to 35% increase in MOR, over 200% in unnotched Izod impact, about 20% improvement in HDT, and dramatic increases in moisture resistance," says business development manager Damon Hollis.

Dover Chemical is offering a long-chain chlorinated paraffin (LCCP) as a non-reactive coupling agent that appears to improve strength retention of HDPE and PP WPCs during moisture cycling. Unlike maleated olefins, which tend to detract from lubrication properties, LCCP reportedly increases lubrication, as well as uv and moisture resistance. According to Dover’s data, the LCCP yields higher flex modulus and tensile strength than a standard zinc stearate/EBS formulation of 60% wood in HDPE; however, the extruder torque was higher with LCCP. But when combined with a proprietary lubricant in a one-pack system (Doverbond DB 4300), both lower torque and higher physicals were achieved. In fact, the lubricated system has higher stiffness and strength than the unlubricated control, unlike the stearate/EBS sample. MOR of PP and HDPE with 60% wood is 40% higher with DB 4300 than with stearate/EBS, adds business manager Tom Kelley. Listing at $1.50/lb, the one-pack can be used at 3% to 5% in place of 1% to 2% of a typical coupling agent plus 3% to 5% of traditional lubricants.

Clariant Additive Masterbatches offers two compatibilizer concentrates. Cesa-mix 8611 is a functionalized copolymer for use in PE and PP, and Cesa-mix 8468 is a highly functionalized system that's said to improve surface quality of wood-PP. New developments for compatibilizing wood-PVC are in the works at Crompton. The issues are different than with polyolefins because both wood and PVC are polar. "But wood has a lot of acid on the surface that degrades PVC, while PVC generates hydrochloric acid that degrades wood," explains Dr. Peter Frenkel, R&D director for vinyl additives. One solution is to treat the wood fibres with a sizing stabilizer before compounding. Mark W15 is a new, proprietary wood sizing agent that acts both as a compatibilizer and heat stabilizer and significantly improves tensile and flexural strength.Crompton is also developing a new reactive compatibilizer for wood-PVC. It is designed to be mixed into the PVC matrix to make it compatible with wood fiber and improve properties.

4.6. Lubricants

Lubricants increase throughput and improve WPC surface appearance. WPCs can use standard lubricants for polyolefins and PVC, such as ethylene bis-stearamide (EBS), zinc stearate, paraffin waxes, and oxidized PE.

EBS with zinc stearate is widely used in wood-HDPE. However, there are new alternatives because metal stearates are known to decouple the maleic anhydride of maleated coupling agents, cancelling the effectiveness of both lubricant and coupling agent. These new lubricants sell for around $1/lb vs. 70¢ to 90¢/lb for EBS and zinc stearate.

WPCs use about twice as much lubricant as standard plastics. For HDPE with a typical 50% to 60% wood content, lubricant level can be 4% to 5%, while a similar wood-PP composite typically uses 1% to 2%. Total lubricant level in wood-PVC is 5 to 10 phr.

4.6.1. Discussion

Struktol has a new proprietary lubricant package, TPW 104, for wood-polyolefin composites. It contains zinc stearate and therefore is not recommended for use with maleic anhydride coupling agents. Also new is TPW-113, a package with non-metallic lubricant for wood-polyolefins. For wood-PVC, Struktol offers TPW-012 and TR-251 lubricant packages, which combine standard rigid PVC lubricants with some "unique chemistry," says product manager Mike Fulmer.

Lonza Group has developed a more advanced alternative to its standard EBS (Acrawax C) plus zinc stearate. Glycolube WP-2200 is a new proprietary amide lubricant that contains no metallic stearates. It reportedly performed well in wood-HDPE field tests and has potential for wood-PP and wood-PVC composites. Recent trials showed a reduction of overall lubricant use from 4.5% to 3% while delivering over twice the extruder throughput.

Crompton offers fatty-acid-based lubricants for wood-polyolefins. These include metallic stearates, amides, and esters. Lubricants for wood/PVC composites include both internal and external Marklube lubricants.

Clariant Additive Masterbatches offers Cesa-process 9102, a fluoroelastomer for extrusion of wood-polyolefins. Cesa-process 8593 and 8633 are proprietary lubricant systems for wood-polyolefin extrusion. Cesa-process 8477 is a highly loaded fatty-ester system for wood-polyolefin extrusion and injection molding.

Ferro Corp.’s Polymer Additives Div. has developed two new series of lubricants for WPCs. The SXT 2000 series blends metallic stearates with non-metallic lubricants for wood-polyolefins. The SXT 3000 series is totally free of metallic stearates. Although SXT 3000 costs more per pound, it is so effective that it is possible to reduce lubricant loading while still achieving improved throughput and product quality, according to lubricants technical manager Louis Brandewiede. Both lubricant families have shown significant increases in output—up to 50% more than traditional rates.

Reedy International, supplier of Safoam endothermic chemical foaming agents, is offering three new lubricants for foamed WPC composites. Safoam WSD is a lubricant and antioxidant that is applied to the wood flour. It is designed for PP and PVC containing up to 70% wood.

Safoam WLB is a reportedly unique HDPE wax external lubricant for PVC, PP, and HDPE composites. It reportedly allows very low use levels. The third product is a highly branched, ester wax internal lubricant designed to allow the wood fibers to wet out better than with EBS/metal stearate combinations.

4.7. Colourants

Colourants are used to provide both a wood-like appearance and UV resistance. Masterbatch suppliers are using colourfast, highly reflective, and weatherable pigments to satisfy demand for better colour-fade resistance at the lowest possible cost. Pigment levels must be 1% to 3% or higher to overcome colour staining from the wood. Colour concentrates tailored for WPCs typically include lubricant and often are customized multifunctional packages that may include coupling agents, antimicrobials, and UV stabilizers.

4.7.1. Discussion

Accel Corp., which has been active in WPCs for over 10 years, offers customized colour and additive masterbatches for wood-PE and wood-PVC composites.

Ferro’s Plastics Colorants Div. has introduced standard wood-polyolefin colours such as teak brown, cedar, weathered gray, and redwood, as well as custom colour matching in concentrates, liquids, and non-dusting granules.

Clariant Masterbatches offers tan, dark red, gray, and oak standard masterbatches, as well as custom colours, for PE, PP, PVC, and PS composites. Colourants are tailored for wood contents from 30% up to 70%.

Techmer PM has introduced redwood, cedar, brown, white, and black- colorants for polyolefin and PVC wood composites.

4.8. Chemical foaming

There is keen interest in chemical foaming of WPCs to reduce weight and materials cost and to improve surface appearance, processing speed, and ease of sawing, nailing, screwing, and painting finished products. About 20% of all WPC products—mostly wood-PVC—are currently foamed.

Both endothermic and exothermic chemical foaming agents (CFAs) are used. Foaming is tougher for crystalline polymers like PE and PP than for amorphous polymers like PVC and PS, as the latter generally have better melt strength. When higher wood content is added to the mix, as in polyolefin decking products, the challenge is particularly daunting.

4.8.1. Discussion

Bill Crostic, president of wood-polyolefin compounder Onaga Composites states, "We see CFAs finding a niche in fence and exterior trim boards and less in decking, where wood content can be as high as 70%." He points out that the more wood is present, the less resin there is to be foamed.

While there are issues, Mike Reedy from Reedy International says foaming of higher wood-content WPCs can be done with the right materials, additives, and processing conditions. He cites the example of a new 65%-wood PP composite decking product produced with Safoam CFAs and lubricants on a conical counter-rotating twin-screw extruder. The result is 0.788 g/cc density—30% to 35% lower than unfoamed wood-polyolefins.

Clariant’s Additives Masterbatches Business unit offers the Hydrocerol PLC series of CFAs, which include endothermic, exothermic, and endo-exothermic blends for polyolefin, PVC, and PS wood composites. Says new business development manager Dennis Haff, "People who are using our foaming agents typically have below 50% wood content, which allows for meaningful foaming potential."

Bergen International has seen its Foamasol CFAs used in PVC, polyolefin, and PS wood composites, primarily for decorative moldings such as siding trim boards, railings, and spa panels, where loss of physical properties from foaming is not an issue. "Most of our customers are using wood content in the 20% to 30% range. We aim at weight reduction of 5% to 10%, says president Dennis Keane.

Crompton offers its Celogen family of exothermic CFAs, which can be used to foam wood-polyolefin and PVC composites. Techmer PM has three new standard CFA masterbatches for wood-polyolefins. These are typically custom formulations including colour and other additives. The products include exothermic types and endo-exothermic blends with different loadings and decomposition temperatures.

Accel Corp. offers both endothermic and exothermic CFAs, typically in a multifunctional additive and colour masterbatch for wood-PE, wood-PVC, and more recently wood-PP decking and fencing.

4.9. Mould & mildew reduction

Mould, mildew, and stains on some WPC decking are driving manufacturers to consider antifungal biocides that protect either the plastic component and maintain its surface appearance or that preserve the wood component from decay and also reduce moisture absorption. Many products purport to do both.

4.9.1. Discussion

Weathering and UV radiation have been shown to degrade the surface of WPCs within a few weeks of exposure. "They tend to get lighter after initial installation as the coloured extractives and lignin from wood fibres is removed by rain. With continued exposure, loosening of the wood fibers and breakdown of the plastic component follow color change. Also, moisture can lead to a loss in mechanical properties and provide a more favorable environment for fungal growth," explains Gerry Capocci, market manager at Ciba Specialty Chemicals.

Ciba offers Irgaguard F3000, a thiazolyl benzimidazole said to be a broadly effective fungicide for wood-polyolefin and wood-PVC composites. Developmental EB 43-25 combines Irgaguard F3000 with a proprietary additive. It is both a broad-spectrum fungicide and can eliminate or reduce stains due to interactions of iron, tannin, and moisture.

U.S. Borax offers Borogard ZB zinc borate as a preservative for wood-polyolefin and wood-PVC composites. It has broad-spectrum activity against wood-destroying organisms plus heat and uv stability and resistance to leaching and weathering, according to technical manager Mark Manning.

"Laboratory evaluations of commercial WPC products against wood- destroying organisms such as decay fungi and termites have shown weight losses of 10% to 20% in as little as four months, which equates to 20% to 40% weight loss in 50/50 wood-plastic WPCs," says Manning. But when Borogard ZB was added to HDPE decking with 50% to 70% wood, weight loss was less than 1.1%, he reports.

Rohm and Haas sells Vinyzene biocides, which are based on dichloro-octyl-isothiazolone (DCOIT) for wood-PVC composites. Newly commercial Vinyzene SB27 is a concentrate of DCOIT in a vinyl carrier. The company is also field testing new SB27-ELV, which is 10% DCOIT in a polyolefin terpolymer, aimed at wood-polyolefin composites.

This leaching-resistant and uv-stable product is said to be effective at 0.04% to 0.1%. New developments for treating natural lumber planks also have potential for treating the wood flour used in WPCs to prevent colour change. Lonza introduced an alternative to chromium copper arsenic (CCA), a carcinogenic wood preservative banned by the EPA in Dec. 2003. Lonza's Carboquat is a quaternary ammonium compound that could be used to treat wood flour for WPCs. Ciba also has a new proprietary wood treatment that is ready for sampling. Struktol is working on anti-staining wood lubricants that will neutralize tannins.

4.10. Other fillers: Talc, SBR, etc.

Replacing some of the wood flour and resin content of wood-HDPE and wood-PP products is a major R&D focus at talc supplier Luzenac America. Trials of HDPE with a 60% filler loading (33% wood/27% talc) reportedly show significant improvement in MOE and MOR, HDT, and creep performance. Throughput increases 15% when 10% of the wood in a formulation is exchanged for talc, Luzenac says. Throughput gains of up to 37% result with a 50% talc-for-wood substitution. Moisture absorption is also much lower.

5. Conclusions

The European plastics recycling industry is effective in producing quality feedstocks from post industrial waste streams. The post consumer /packing waste streams are the largest and more challenging in terms of recycling.

The tyre recycling industry is very challenging primarily because tyres are complex cross contaminated items where it is difficult to separate the components. There are a limited number of producers of fine powders suitable for use in polymer composites.

The wood flour industry is based on virgin timber, there are a limited number of producers and the material is challenging simply because it comes from a natural feedstock that is inherently variable.

Regarding the quality of the recycled materials in all the industries the quality of the recyclates varies greatly. In the rubber and wood flour industries, these materials are not standardized and generally have low specifications. In these cases the quality is intimately related to the quality of the feedstock and to the effectiveness of the recycling process. For the plastics industry in the past few years there has been legislation created with the aim of standardizing recycled plastics in order to obtain a more consistent and better quality material.

6. Proposed development formulations

Taking into account the research done in the previous chapter it can be concluded that any proposed specification /material formulations for the new rubber: wood: plastic composite should meet the following general criteria:

The formulation will provide a practical composite material.

The project leader needs to decide whether any proposed formulation / composite should meet EN 15534-1:2014. This particular standard refers to wood: plastic composites, not rubber.

Any formulations should be processable on existing /industry standard plant and equipment in a cost effective way i.e. meet required output rates and energy costs.

Materials should be readily available from suppliers within the EU.

Materials should not have significant health and safety / handling issues.

In addition to the general considerations above, the proposed formulations have to take into account the technical and practical knowledge of rubber, wood and plastic composites of the partners in the project. In the development of a new product such as the RubWPC composite, a commercial evaluation should be included in order to ensure that the chosen formulations are cost effective. This does not necessarily mean cheaper than current practise but if a formulation is going to be more expensive it needs to deliver improved performance for the customer.

In terms of cost the current hierarchy is:

Additives and processing aids	Highest
Polymer	↓
Rubber	
Wood	Lowest

Regarding the formulations currently used in commercial wood/ plastic composites, they range from:

55-60 %(wt %) wood flour

35-40 % (wt %) thermoplastic

1-5% (wt %) additives /coupling agents

6.1. Proposed material specifications

Additives

Additives or/and coupling agents will be required in order to improve the mechanical performance of the final composite material. The type and amount of additives necessary to include in this formulation will be shown in Table 2.

Wood flour

The wood flour used in RubWPC formulation should be hardwood from virgin timber from PEFC certified sources. WPC composites can be either composed by hard or soft wood. Each type of wood will compound differently and will also give different appearance to the final composite material. .Current experience indicates that hardwood provides the best performance in current applications.

The wood flour should have a maximum moisture content of 8% (wt%) and a density of < 0.3g/cm3.

Regarding particle size distribution, it should have a maximum of 2.5% retained on a 900 micron sieve and 16% retained on a 500 micron sieve.

End of life vehicle tyre rubber powder (EOLVT)

The crumb rubber powder should be derived from car tyre rubber, i.e. predominately SBR. If this is not available then a mixture of car and truck tyre should be considered. Ambient ground material is preferred to cryogenic material on the basis of cost and improved performance in composites.

The rubber powder moisture content should be less than 0.3% (wt%) and a density of 1.1-1.2g/cm3. Regarding particle size distribution, the smaller the particle size of the rubber better is the performance of the final material but we consider that “40 mesh powder” with a maximum of 5% retained on a 425micron sieve is acceptable for the formulation of the RubWPC composite.

Thermoplastic

The thermoplastic used in the formulation should be either a recycled high density polyethylene (HDPE) or a polypropylene (PP) co-polymer from a blow moulding grade.

The material will need to be reprocessed in an extruder with a melt filter to remove contaminants.

HDPE	Density: 0.95-0.96g/cm^3
	MFI: 0.5-1.0 g/10min
PP	Density: 0.9-0.91g/cm^3
	MFI 1-2 g /10mins

6.2. Proposed RubWPC formulation

The proposed formulation for the RubWPC composite is presented on Table 2 and the materials should have the specifications presented above.

Table 2 Proposed formulations for RubWPC composite.

Material	Composition (wt %)		
Recycled HDPE or PP	35-39	35-39	35-39
Virgin hardwood flour	50	40	30
Recycled EOLVT powder	10	20	30
MAPP or MAPE	4-6	4-6	4-6
Struktol TWP 113	1-2	1-2	1-2

Experience of the project partners suggests that a minimum of 40% thermoplastic and additives is required to form a matrix with the wood flour and rubber.

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