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Composites with recycled rubber aggregates: properties and opportunities in construction

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Abstract

Vulcanised rubber is extensively used in many industrial sectors due to its good physical, mechanical and dynamic properties, as well as excellent durability, outstanding abrasive resistance and relatively low cost. Unfortunately, most post-consumer rubber-derived products are still discarded as waste, buried in landfills or incinerated. Such materials require many years to degrade naturally due to i) their complex cross-linked composition, and ii) the additives used during manufacturing to extend the lifespan of rubber. Extensive research has investigated the use of end-of-life rubber as binder (e.g. elastomers, bitumen), or as conglomerates (cement, gypsums) to produce innovative composites in construction. To improve the properties of composites made with recycled rubber, the surface of rubber has been treated with different costly processes to improve the Interfacial Transition Zone (ITZ). However, the results available in the literature are inconsistent and many technical and practical aspects remain unsolved, thus preventing the cost-effective use of rubber in the construction industry. This study provides a comprehensive review on rubber properties and surface treatments of rubber recycled from post-consumer components so as to identify potential applications in composites for construction. It is concluded that an understanding of the chemical, physical and mechanical properties of rubber, as well as a proper characterisation, are necessary to take full advantage of this high quality material. Future research needs in the field are also suggested.

Keywords: *recycled rubber, recovered tyres, composites, construction, concrete*

1   Introduction

Rubber (cured rubber compound or vulcanised rubber) has been used in various industrial applications since the Industrial Revolution. In particular, the development of the vulcanisation process [Goodyear, 1844] allowed the cost-effective production of large volumes of high-quality rubber. Current global rubber production is approximately 26.7M tons, of which 12.31M are natural and 14.46M synthetic rubber to produce tyres and other industrial and consumer products [Rubber Statistical Bulletin 2017]. Global tyre production is estimated at 1.5Bn units/year, and approximately the same number of tyres reach their service life every year [ETRA 2016]. End-of-life tyres contain up to 90% of vulcanised rubber which cannot be easily recycled due to the complex cross-linked structure achieved through vulcanisation [Adhikari 2000]. The inappropriate disposal of rubber from these tyres is hazardous to the environment [Zheng 2005] and, consequently, stringent EU directives prioritise the reuse and recycling of rubber and ban tyre landfilling (Directive 2008/98/EC and Landfill Directive 1991/31/EC, respectively). This has increased the efforts towards generating novel applications for all end-of-life tyre components in various industrial sectors.

Vulcanised rubber is extremely durable, strong, flexible and can maintain its volume under loading, thus making it suitable to be used as aggregate for composites. However, to date most of the rubber recovered from tyres is burnt as fuel, a process which produces hazardous gases and only recovers 25% of the energy used to produce rubber [ETRMA 2010a]. More environmentally friendly processes have been developed to recover rubber, such as tribo-electric separation, froth flotation method or laser-induced breakdown spectroscopy [Adhikari 2000, Yi 2001, Singh 2016]. However, these are still expensive, and the recovered rubber varies considerably in cleanliness, size, shape and quality of surface finish. Recovery methods affect the suitability of recycled rubber for use in the manufacture of new composite products. For instance, small rubber granulates have more contact surface than large rubber chips, and therefore the former adhere better to a matrix [Herrero 2013, Su 2015, Flores 2016]. However, the associated costs of obtaining small rubber sizes also increase [Guoqiang Li 2004].

Over the last decades, extensive research has investigated the use of recovered rubber in composites [Adhikari 2000] and particularly in the construction industry, which is the main consumer of raw materials worldwide. The use of tyre rubber in concrete as a replacement of portions of the concrete mineral

aggregates has also been considered [Najim 2010, Thomas and Gupta 2016]. However, the addition of rubber reduces the workability and strength of concrete, and increases its micros-cracking and lateral expansion under compressive load. Consequently, the use of rubberised concrete in high-value structural concrete applications is very limited to date. Recent research by Raffoul (2016) identified a lack of consensus on how to quantify the influence of rubber on the physical and mechanical properties of fresh and hardened concrete. The insufficient understanding of the chemical and mechanical behaviour of rubber, combined with its adverse effect on some concrete properties has limited its widespread use in the construction industry. Moreover, the composition and fundamental behaviour of the different types of rubbers need to be understood to fully exploit their properties in high-value applications in construction.

This article examines critically the current challenges and future potential applications of rubber in composites for construction, including composites with different binders and conglomerates. Based on a comprehensive literature review, Section 2 reviews the properties of different types of rubbers, their manufacturing and recycling processes, and discusses the feasibility of rubber characterisation before recovering/recycling. As the mechanical properties of rubberised composite depend heavily on the bond between aggregates and matrix at the Interfacial Transition Zone (ITZ), the different techniques used to treat the surface of rubbers (and other polymers) are critically revised in Section 3. Section 4 summarises the typical properties of composites used in the construction industry, with emphasis on the amount of reclaimed rubber and mix designs investigated in the literature. Finally, Section 5 gives new directions on potential high-value applications of rubber in construction, as well as recommendations for future research.

2   Composition and properties of rubber

The properties of rubber compounds depend directly on its microstructure, which is generally formed by elastomeric chains (also named as natural rubber, polymer or resin) and fillers/additions that in turn form a continuous and homogeneous polymeric composite. There are two main types of plastic products: thermoplastics and thermosettings [Greensmith 1963, Nakajima 1993]. Thermoplastics are polymers composed by monomers organised in independent large chains that change their properties with an increase in temperature without an associated phase change. The degree of polymerization DP (or molecular weight) of a rubber is determined by the number of monomeric units in a macromolecule. Higher density and

mechanical strength of a thermoplastic correspond to higher values of DP. Whilst chemical covalent forces bond strongly a single chain, different chains are bonded with secondary (weak) 'Van der Walls' forces. The 3D zigzag molecular architecture of these chains has freely rotating bonds, which enable the rubber molecule to stretch and shorten without any change in its internal energy [Ponnamma 2014]. This gives thermoplastics a high deformability but low strength due to Van der Walls forces.

To enhance rubber strength, sulphur (or other vulcanizing agents) is added to unsaturated rubbers to link the chains using primary (strong) bonds that create thermoset polymers. Unlike thermoplastics, the properties of thermosets do not change with temperature, and therefore, they are widely used to manufacture tyres that can resist harsh mechanical/environmental conditions. The vulcanisation process, curing time, temperature and type of filler can affect the chemical and physical properties of thermoset rubbers [González 2005; Heinrich 1993]. Nonetheless, the overall stress-strain behaviour and microstructural changes of thermosets subjected to tensile stress follow common patterns, as shown schematically in Figure 1. Initially, strains develop quickly due to the weak Van der Waals bonding between the polymer and the filler (see stage 1 in Figure 1). After the Van der Waals bond is overcome, the response stiffens in the second stage due to i) the work of the covalent bonds of some aligned chains, and ii) the friction between the polymer chains and the fillers during the chains' realignment in the direction of the applied tensile load. In the third (and final) stage, the response stiffens further as the majority of the polymer chains have been stretched and aligned with the direction of the applied force [Thomas 2013].
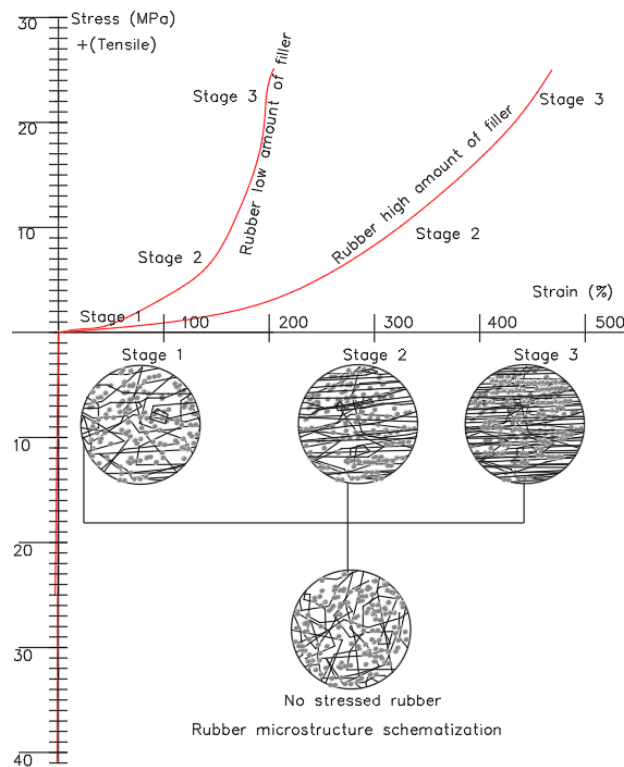
Figure 1. Schematic representation of the microstructure and stress-strain behaviour of two thermoset rubbers with different amounts of filler subjected to tensile stress.

The chemical composition of tyre rubber influences its mechanical behaviour, grip and lifespan. Whilst such composition varies from manufacturer to manufacturer, the raw materials used for tyre production in the EU are similar, as summarised in Table 1. In general, the properties of rubber are defined by the a) type/amount of elastomer used as binder, b) cross-linking process, and c) type, size and amount of filler. Table 2 summarises the available information in literature on rubber properties, including the type of elastomers, type and amount of fillers, tensile strength, elongation at rupture, Poisson's ratio, as well as the elastic modulus of rubber at different tensile strains (shown as percentages of the elastic modulus $M_{50\%}$, $M_{100\%}$ and $M_{300\%}$ at 50%, 100% and 300% strain respectively). The following sections discuss the effect of the type of elastomers and fillers on the mechanical properties of rubber.

Table 1. Summary of raw materials used in tyre production according to the European Tyre and Rubber Manufacture´s Association [ETRMA 2011b]).

Material	Car (%Wt.)	Trucks (%Wt.)	RDV*
Elastomer: Rubber/Elastomers	40-45	42	Yes
Carbon black and Silica (fillers)	28	24	Yes
Metal reinforcement	13	25	No
Textile reinforcement	5	-	No
Zinc oxide	2	2	Yes
Sulphur (crosslinker)	1	1	Yes
Accelerators/Antidegradants	2.5	n.a.	Yes/No
Stearic acid	1	n.a.	Yes
Oils	7	n.a.	No

* Reacting during vulcanization (**RDV)**

Table 2. Summary of composition of different types of rubber and their main mechanical properties

Author (year)	Elastomer	Filler	Amount of Filler (phr)	Tensile strength (MPa)	Elongation at break (%)	M 50%(MPa)	M 100%(MPa)	M 300%(MPa)	M 500%(MPa)	Poisson´s ratio
M.Cadambi (2011)	HNBR	Carbon Nanotube	0	26,6	204	3,4	9,1			
			2.5	26,9	206	5,8	13,7			
			3.5	28,6	209	6,9	15,0			
			5	28,5	210	6,8	15,2			
			7.5	29,5	190	5,4	15,9			
			10	29,2	163	8,3	21,1			
J. Leopoldès (2003)	NR	CB	40 (Not treated)	26,7	460	*	2,9	3,6		
			40 (Surface treated)	26,6	390	*	14,9	18,9		
B. Omnès (2008)	NR	CB (N330)	0	1,5		1,8				0,499
			2.4	1,8		1,9				0,499
			6.8	2,3		2,4				0,498
			12.8	3,7		4,3				0,498
			18.0	5,3		6,5				0,497
		CB (N650)	0	1,5		1,8				0,499
			2.4	1,6		1,9				0,499
			6.8	2,2		1,9				0,498
			12.8	3,2		3,6				0,498
			18.0	4,4		4,8				0,497
Teh (2004)	NR+ENR	no filler	0	16,0	1120		0,6	1,3		
		Organoclay	2	28,0	1220		0,9	2,1		
		CB	50	23,0	750		1,9	6,5		
		Silica	30	21,5	700		1,3	5,4		
WEI-GWO HWANG (2004)	NBR	Organosilicates	0	2,1	600		0,9	1,24	1,7	
			1	6,2	521		1,1	1,51	2,0	
			3	7,9	816		1,1	1,64	2,3	
			5	9,5	826		1,2	1,81	2,5	
			7.5	12,0	784		1,4	2,42	3,6	
			10	13,4	833		1,7	2,7	3,9	
Rattanasom (2007)	NR	Silica/Carbon Black	0/50	30,0	430		3,7			
			1/4	31,0	440		4,3			
			20/30	28,0	440		3,8			
			30/20	31,0	510		3,2			
			40/10	29,0	520		2,8			
			50/0	28,0	550		2,7			
Rattanasom (2009)	NR	no filler	0	27,0				2,6		
		Clay	6	30,0				5,3		
		CB	6	28,0				3,4		
			14	27,0				5,9		
		Precipitated silica	6	26,0				3,2		
			35	27,0				5,9		
Bulent Ozbas (2012)	NR	no filler	0	6,2	700					
		FGS	4	11,5	250					
		CB	16	7,1	500					
Liqun Zhang (2000)	SBR	Clay	0	2,0	*					
			20	12,0	450					
			40	15,5	420					
	SBR HAF CB	Clay	0	2,0	*					
			20	16,0	350					
			40	22,0	340					
	SBR Silica	Clay	0	2,0	*					
			20	12,0	460					
			40	14,0	720					
Rajasekar (2009)	NBR	ENR-nanoclay	0	2	380		0,9	1,8		
			5	3,2	340		1,3	2,8		
			10	4,1	320		1,7	3,5		
Yong-Lai Lu (2007)	SBR	RCNs	0	1,9	290					
			10	5,1	500					
			40	12,8	680					
			100	15	610					
			150	13,2	440					
Karger (2004)	EPDM rubber	Organoclay open mill	10 (20 T°C)	3,9	380		1,5	2,3	3,0	
	EPDM + 50wt%MA		10 (20 T°C)	6,6	395		2,0	3,3	4,9	
	EPDM rubber		10 (20°C)	5,2	495		1,6	2,3	2,9	
	EPDM + 50wt%MA		10 (20°C)	8,1	360		2,7	4,6	6,9	
	EPDM rubber	Organoclay internal mixer	10 (20 T°C)	4,9	520		1,5	2	2,6	
	EPDM + 50wt%MA		10 (20 T°C)	10,5	321		3,9	7,3	9,9	
	EPDM rubber		10 (100°C)	7,1	645		1,6	2,3	3,0	
	EPDM + 50wt%MA		10 (100°C)	14,9	403		5,4	9,3	12,1	
Arroyo (2003)	Natural Rubber	no filler	0	4,2	>700		0,6	1,33	2,6	
		Clay	10	3,6	555		0,5	1,38	2,9	
		Organoclay	10	15	>700		1,7	4,31	9,7	
		CB	10	4,9	464		0,8	2,53	**	
			40	10,3	434		1,6	5,52	**	
Quinfu Liu (2008)	SBR	PS	50	17,6	740			4,23	8,5	
		NK	50	16,3	767			2,63	3,8	
	NR	PS	45	16,8	561			6,31	13,7	
		NK	45	26,8	622			7,07	17,7	
	BR	PS	60	5,8	261			**	**	
		NK	60	7,5	796			1,45	2,0	
	EPDM	PS	60	13,3	446			8,8	**	
		NK	60	17,2	566			4,87	11,3	

***Acronyms:** *Amount of filler is in parts per one hundred parts rubber (phr), HBNR (Hydrogenated Nitrile-Butadiene Rubber), NR (Natural Rubber), BR (Butadiene Rubber), SBR (Styrene-Butadiene Rubber), NBR (Nitrile Butadiene rubber), ENR (Epoxidised Natural Rubber), EPDM (ethylene/propylene/diene), MA (maleic Anhydride), RCN (Rubber/Clay Nanocomposites), CB (Carbon Black), FGS (Functionalized Graphene Sheets), NK (Nanokaolin), PS (Precipitated silica), HAF (high-abrasion furnace black).*

2.1   Microstructural composition

2.1.1   Elastomers

Natural Rubber (NR) is the most widely used elastomer in rubber production [ETRMA, 2010a] due to its

high tensile strength and tear growth resistance (see Table 2). This behaviour is mainly attributed to its

ability to crystallize rapidly during stretching, as well as to its high molecular weight and long branched chains [Gonzalez 2003, Nakajima 2000]. To improve further its properties in tyre manufacturing, NR is typically blended with other synthetic elastomers such as Butadiene Rubber (BR), Hydrogenated Nitrile-Butadiene Rubber (HNBR), Nitrile Butadiene Rubber (NBR), Styrene Butadiene Rubber (SBR), and Ethylene Propylene Diene Monomer (EPDM).

2.1.2 Fillers

Rubber is often produced using fillers such as carbon black (CB), precipitated silica (PS), clay, calcium and/or carbonate [Liu 2008]. Fillers enhance the strength of polymers by forming a flexible filler network and a strong polymer-filler coupling [Thomas 2013]. Stiffening fillers (mainly CB and silica) increase entanglement and shear strength between polymer chains [Heinrich 1993], which in turn enhances rubber stiffness, as well as tensile and tear strength, abrasion resistance, hardness, thermal stability and rupture modulus [Rattanasom 2007, Liu 2008]. Whilst CB is the most commonly used strengthening filler in rubber production, alternative clay-based fillers (such as montmorillonite, synthetic mica, hectorite and saponite) have also been used. For instance, Okada (1995) showed that NBR containing 10% volume fraction of organoclay achieves similar tensile strengths as rubber with 40% CB. However, larger amounts of filler (>20% depending on filler type) result in higher rubber viscosity, which can complicate the rubber manufacturing process [Nakajima 2000].

Fillers used in the manufacturing process also differ in size. For instance, Teh (2004) used organoclay, silica and Carbon Black 330 (CB330), with mean particle sizes of 4.43, 7.17 and 9.14 nm respectively. Nanofillers have also been used as fillers, e.g. Liu (2008) added nanokaolin of 300nm average diameter and 20-50nm average thickness. In general, the size of fillers used in rubber production has reduced in the last decades (from micrometres to nanometres) to increase the mechanical resistance and storage modulus (E´) of rubber. However, this is accompanied by higher production costs [Hu 2001]. To reduce polymer consumption, researchers have sought to increase the bulk volume of rubber. Likewise, production costs were reduced by adding fillers [Dai and Huang, 1999, Okel 1955, Nie 2004].

The size, shape and molecular structure of fillers can modify the behaviour of rubber microstructure when stressed. For example, layered silicate fillers can interact in the polymer structure as separated phases

(microcomposite), in the same way as an intercalated or exfoliated structure does [Alexandre 2000]. The use of nanoclay can also enhance rubber properties due to its better distribution in the rubber matrix compared to the common clay fillers [Rajaselar 2009]. To improve the rubber–filler interaction in a rubber composite, the filler's surface can also be pre-treated [Leopoldes 2004]. Fillers have also been treated to improve the manufacturing process and the mechanical properties of the rubber composite. Leopoldes (2002) used oxidative gas at 40% relative humidity during several days on CB330. Arroyo (2003) obtained organoclay through the activation of montmorillonite with Na+ and dispersing it in hot water (80ºC) with continuous stirring and later with acids to yield after filtering the solution. Alexander (2000) used thermal treatments, methylaluminoxane or cations (Na+) when layered fillers were used as layered silicates so as to increase layer spacing. However, much of the existing literature do not provide the size of fillers or corresponding treatments, which hinders a proper characterisation of rubber.

2.1.3   Other additives

A variety of additives and solvents are often used to increase rubber durability and speed up sulphur interlinking reaction [ETRMA 2010a]. Zinc oxides are widely used as activators during vulcanization for tyre manufacturing (see Table 1). Mild extract solvate (MES), naphthenic oil, treated distillate aromatic extract (TDAE), and paraffinic oils are also used to improve the processability of compounds and to enhance mechanical endurance.

2.2   Mechanical Properties of Rubber

Previous studies have examined experimentally rubber properties used in tyre manufacturing, such as static/dynamic service life, traction, wear resistance and rolling resistance [Kohls 2002]. However, the test results depend heavily on the rubber free surface energy, distance between filler aggregates, and the effect of filler–rubber interactions on the rubber dynamic mechanical properties [Wang 1998 and 1999, Wolff 1992].

The curing process also influences the mechanical properties of rubber. Karger (2004) studied EPDM rubber blended in an open mill, or in an internal mixer at either room temperature or at 100ºC. It was found that the tensile strength of rubber increased by up to 50 % when an internal mixer is used at 100ºC instead of open mill blending. Gonzalez (2005) reported that a curing process which generates over-crosslinked

domains in the network topology of rubber also increases its tensile strength, although the level of the increase depends on the curing temperature.

2.2.1 Influence of elastomers on the rubber mechanical properties

Liu (2008) studied the differences in SBR, NR, BR and EPDM elastomers with precipitated silica and nanokaolin (NK) as fillers. It was found that NR has the highest tensile strength among these elastomers when nanokaolin was used as filler, whereas BR had the lowest tensile strength (see column 5 in Table 2). Liu (2008) also reported that the highest tensile strength was obtained by using Styrene-Butadiene with precipitated silica. It should be noted that natural rubber has a higher strain capacity compared to other elastomers such as BR, SBR or EPDM. Blends of elastomers are used to improve the rubber mechanical characteristics, reduce cost and increase elongation capacity [Gil-Negrete N. 2013]. Teh (2004) reported the mechanical behaviour of NR blended with epoxidised Natural Rubber with different fillers, showing that blends can obtain better results. The data in Table 2 indicate that fillers enhanced the strength of rubber in all elastomers investigated in previous studies.

2.2.2 Influence of fillers on the rubber mechanical properties

The properties of rubber blends also depend on the type of filler and on their compatibility with the type of elastomer used. CB is by far the most used filler in rubber. The data by Rattanasom (2007) in Table 2 show that, for the same type of elastomer, the use of silica and CB fillers (e.g. 30% and 20%, respectively) led to a tensile strength up to 5% higher than in composites with CB fillers only. Arroyo (2003) also showed that organoclay fillers in NR enhanced the tensile strength by more than 300% when compared to NR with clay (15 MPa vs 3.6 MPa, respectively). This may be due to the free surface energy of the filler, which enhances its compatibility with the rubber. For instance, highly polar silica does not interact well with a non-polar elastomer [Kohls 2002]. The results of Liu (2008) also indicate that the use of precipitated silica (PS) increased the rubber tensile strength by 7.3% over the use of similar amounts of nanokaolin (NK) in SBR. Rattanasom. (2007) reported that NR with silica and carbon black as fillers combined in proportions of 10% to 40% was more resistant, thus concluding that filler blends generally lead to stronger rubber composites. However, the use of fillers can only increase the rubber tensile strength up to a point. For example, the tensile strength of NR reduced from 28 to 27 MPa when the proportion of CB filler increased from 6% to 14% (see results by Liu (2008) in Table 2).

Fillers also increase the hardness and abrasion resistance of rubber composites, which is fundamental in tyre manufacturing. Hwang (2004) reported that, compared to a plain elastomer, NBR nanocomposites with organosilicates increased the hardness (obtained with a Shore durometer) by up to 24% when 10 phr of such filler was used. Zhang (2000) and Rajesar (2009) reported similar results from SBR with clay fillers and NBR with nanoclay fillers, respectively.

2.2.3 Strain of rubber aggregates.

Previous studies showed that the elongation capacity of NR reduces with the addition of fillers (see column 6 in Table 2). Whilst NR without fillers had a rupture elongation of 700%, the addition of CB or functionalised graphene sheets (FGS) reduced this value to 500% and 250%, respectively [Bulent Ozbas 2012]. The results of Rattanasom (2009) show that the elongation at rupture of NR reduced by 22% when CB was added to NR. Zhang (2000) also reported low rupture elongations when clay fillers were added to SBR. Rajaselar (2009) examined the mechanical performance of NBR with epoxidized natural rubber and nanoclay fillers. The addition of nanoclay (up to 10 phr) reduced the elasticity from 380% to 320%. Conversely, the use of organically modified clay (OMC) fillers in SBR enhanced the rupture elongation from 290% to 440% [Yong-Lai Lu 2007]. These results confirm that the increase of elongation and strength values are usually inversely proportional, and that the elastomer-filler interaction is of paramount importance to understand the final properties of rubber.

Columns 7-10 in Table 2 summarise the elastic modulus of rubber at different tensile strains. The results indicate that the elastic modulus and tensile strains increase proportionally (see also Figure 1). The increase of filler additions can also increase the elastic modulus [e.g. Hwan 2004, Rattanasom 2009, Rajaselar 2009, Arroyo 2003]. These observations (and Figure 1) confirm that the stiffness of rubber varies considerably depending on the applied level of stress.

Due to their incompressibility (i.e. Poisson's ratio close to 0.5) and high damping coefficient, rubber composites have been widely used in vibration control and seismic isolation [Kelly 1997, Amin 2006, Bergström and Boyce 1998]. The results shown by Omnès (2008) indicate that the compressive strength of NR increases from 1.8 to 6.5 MPa with 0.18 volume fraction of CB with 29nm size and from 1.8 to 4.8 MPa for a CB with 50nm size. However, the Poisson's ratio reduced marginally from 0.499 to 0.497, which

can be attributed to the lower mobility of the rubber microstructure [Omnès 2008]. Recent research [Raffoul 2017] showed that, under axial strain (ε_l), the high Poisson's ratio of rubber leads to large lateral strains, which reduces the compressive strength of composites with a high stiffness matrix such as cement or gypsum.

2.3   Thermal properties of rubber

Thermal conductivity in polymers depends mainly on the lattice vibration/phonon (energy quanta of atomic lattice vibrations) mean free path, which is very small due to the scattering with other phonons, defects and grain boundaries in their microstructure [Chen 2016]. The thermal conductivity of most polymers is 0.1-0.5 W/(m.K). However, the addition of fillers can change the thermal conductivity of a blended polymer. For example, the thermal resistance of a composite increases if the coupling at filler-polymer and filler-filler interfaces is poor [Sadasivuni 2014, Seol 2010]. As mentioned in section 2.2, small (micro or nano) filler particles have large interfacial area, which can cause phonon scattering and hinders phonon transport, thus reducing the thermal conductivity of composites [Tsutsumi 1991]. Moreover, fillers such as CB (with a low thermal conductivity) can reduce further the conductivity of composites [Chen 2016, Samaca-Martinez 2013].

To date, information about the thermal behaviour of thermosetting rubber composites is limited as they are mainly used in mechanical applications. Conversely, the low thermal conductivity of other plastic composites such as polyethylene (PE), polystyrene PS and polyurethane (PUR) polymers with foamed microstructure (0.041, 0.032 and 0.025 W/m K, respectively) make them very suitable for thermal insulation [Al-Homoud 2005, Antunes and Valesco 2014].

Overall, the results in the literature indicate that the mechanical properties of rubber vary widely and depend heavily on its rubber chemical composition. However, the physical characteristics of rubber can also influence the properties of the composite. Consequently, and as discussed in the following section, a careful characterisation of the properties of recycled rubber is necessary before it can be used in practise.

3 Understanding rubber as aggregate in composites

3.1 Reclaiming rubber from tyres

Numerous reclaiming procedures exist to extract rubber from end of life tyres. Most tyre rubber is reclaimed by mechanical, cryo-mechanical or thermo-mechanical processes. Mechanical recovery is usually carried out in facilities such as grinding mills, rolling mills, or rotary crushing mills [Fang 2001]. The geometry, surface, and texture of the rubber aggregate depend heavily on the reclaiming process. These properties, in turn, determine the bonding of rubber aggregate to the matrix of the composite, which can also affect the mechanical properties of the composite. However, whilst several techniques exist for sorting out plastics [Singh 2016], only a few techniques for sorting out the rubber aggregates are found in the existing literature [Liang et al. 2015, Onyshchenko 2016].

The full recovery of virgin rubber is also possible, although expensive. Thermoplastic rubbers can be recycled two or three times to obtain virgin rubber, but their mechanical properties degrade during the recycling process. Conversely, the recycling of thermosetting rubbers requires breaking the crosslinks of the microstructure, which involves a costly process known as 'devulcanisation'. Rubber can be decomposed through chemical/thermal processes or microwaves to devulcanise the rubber or to produce crosslink scission [Rajalingam 1993]. Through this recycling process, the devulcanised rubber can be used again as raw material (blended with raw polymers) to vulcanise the composite again. Nevertheless, the new material will have lower mechanical properties as old chains of the recycled rubber cannot be restored to achieve continuity (or bond) with the matrix. Other methods of devulcanisation include pyrolysis, cracking, chemolysis and gasification [Singh 2016].

3.2 Rubber aggregate geometry

The geometry, size and shape of rubber aggregates determine the possibilities of reusing granulated rubber as aggregate in composites. The aspect ratio (ratio of the largest to the smallest orthogonal dimension) of the aggregate is important for the manufacture of composites that need a specific rheology, such as concrete or asphalts [Banfill 1993]. Tyre treads have thicknesses of around 10-20 mm [ETRA 2016], and therefore, the aggregates with sizes smaller than 20 mm will be more spherical with an aspect ratio closer to one. Rubber can be also sliced to form fibres that can be used as internal reinforcement [Li 2011]. Small size

powders can be blended with polymers to obtain regenerated rubber or blended with bitumen to produce asphalts [Rebala 1995].

Overall, previous research has shown that concrete with rubber granulates have better mechanical properties than those made of shred or chips [Siddique 2004, Papakonstantinou 2006, Hall 2014]. Therefore, the applications of shreds and chips have been limited mainly to ground refilling and overlays in covers of buildings instead of composite manufacturing [Rincon et al. 2014].

3.3   Bond at Interfacial Transition Zone (ITZ)

Bond between recycled rubber and its composite matrix at the Interfacial Transition Zone (ITZ) depends on the chemical and physical properties of both components. Bonding can be achieved through mechanical coupling, molecular bonding, or thermodynamic adhesion. In these processes, physical, mechanical and chemical interactions between aggregate and matrix take place. The physical and mechanical interactions depend mainly on the roughness of the aggregate surface and on the refilling of voids by adsorption. Conversely, chemical bonding depends on molecular inter-forces, such as dipole-dipole interactions, Van der Waals forces and chemical interactions between the rubber and the composite matrix [Awaja 2009].

Achieving a good bond in composites with rubber is challenging. The adhesion between rubber and binder depends on the surface properties of the rubber aggregate including: roughness, polarity, chemical composition and surface free energy [Poisson 2006]. Contaminants at the ITZ interface can also reduce adhesion [Comyn 2005]. Rubber is a cross-linked polymer with very low permeability and smooth surfaces at the microstructural scale [Awaja 2009]. For instance, the surface and interfacial region ranges are very small, typically over one polymer chain, and with a radius of gyration of the order of 3–30 nm as the polymer and the filler fill the microstructure. The low surface free energy and lack of polar functional groups on the surface of the recycled rubber may lead to poor adhesion [Awaja 2009]. Even after recycling, the chains of the rubber surface continue to be part of the cross-linked structure. The old chains of the recycled rubber cannot be reactivated to achieve continuity or bond with the matrix. Hence, weak interfacial adhesion develops between binder and rubber aggregate even if polymers of the same composition are vulcanised [Creton 2002]. In many cases, very finely ground rubber is melted with thermoplastics to increase the interaction with the matrix [Fang 2001]. Figure 2a shows schematically the adhesion of a

rubber grain to a polymeric matrix. Bond at the ITZ changes when rubber aggregates are subjected to high temperature (around 100ºC). As shown in Figure 2b, an interphase region (mixture of rubber and matrix) appears when polymers are melted at high temperatures, causing a migration of CB from the recycled rubber to the matrix, thus improving bonding [Yildirim 2007]. In asphalts, the most volatile components of bitumen can be transferred to the rubber, leading to a more viscous composite [López-Moro 2013].
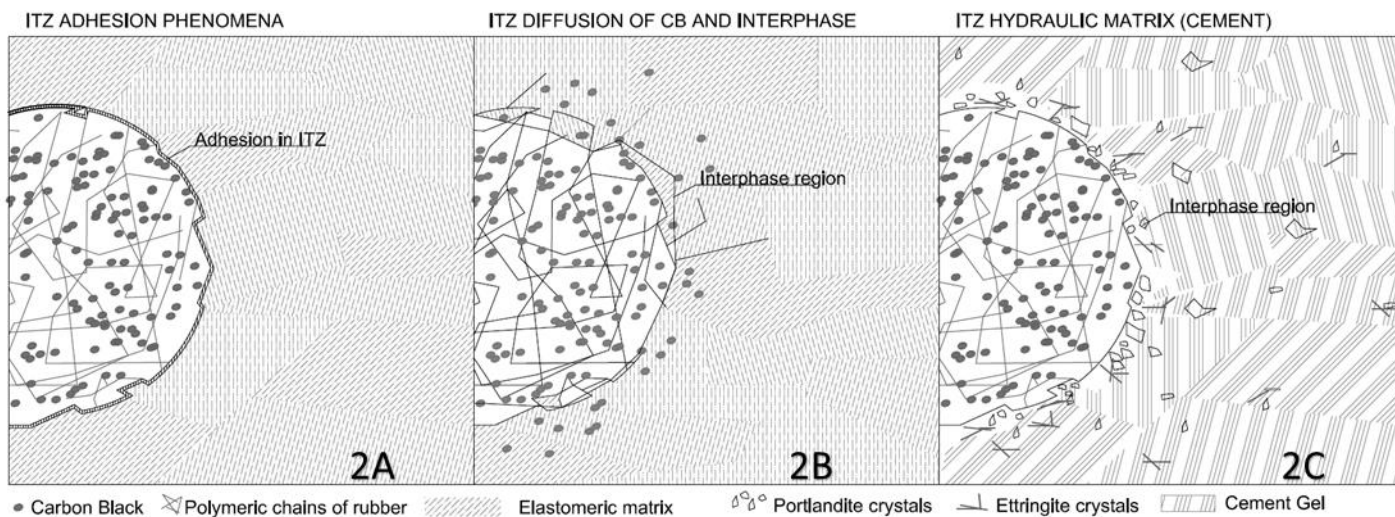

Figure 2. Schematic representation of different types of bond in the ITZ.

Unlike asphalts, the bonding of rubber to hydraulic binders (e.g. cements or gypsums) is less effective (Figure 2c). This is attributed to the hydrophobic nature of rubber, which causes a migration of hydraulic phases away from rubber and produces a less dense matrix at the ITZ [Naaman 1996]. Research on concrete with rubber aggregates show that calcium oxide crystals concentrate at the rubber-cement phase ITZ, while the amount of silicon and aluminium oxides is small [Hernández-Olivares 2002, Raffoul et al. 2016]. Furthermore, the intrinsic surface characteristics of the rubber aggregate (e.g. friction coefficient, adhesion and adsorption) can lead to a poor bond with the hydraulic binder [Myers 1999]. In this case, only physical and mechanical interactions form between the rubber aggregate and cement (i.e. chemical bonds do not exist) [Hernández-Olivares 2002, Hall 2014].

Overall, the roughness of the rubber depends heavily on the utilised recovery/recycling technique [Adhikari 2000]. Consequently, the tyre recycling industry should direct more effort towards specifying the recovery process for rubbers available in the market. However, even if good contact between the matrix and the

rubber aggregate can be achieved, the very different stiffness between recycled rubber and hydraulic binders [Naaman 1996] can hinder the development of strong bond.

3.3.1   Methods to improve rubber aggregate bond

Bond between rubber and binder can be improved by modifying the rubber surface, using activators for re-vulcanisation, or using adhesives and additives [Najim 2013, Lee 1998]. The most common method involves the modification of the rubber surface by either increasing surface roughness and/or by chain scission within rubber particles. The increase of roughness produces a larger contact surface area and more friction between the matrix and the rubber aggregates, while the opening of chains and grafting obtained by chain scission facilitate new crosslinking with the matrix [Rajan 2006, Shanmugharaj 2005, Punnarak 2006, Tan 2009]. Benazzouk (2003) compared the behaviour of concrete with expanded rubber aggregates (ERA) and compact rubber. It was found that, compared to concrete with compact rubber, the alveolar surface of ERA aggregates increased the compressive and flexural strength of concrete by up to 85% and 11%, respectively, which was attributed to a better bond between rubber and cement matrix.

Increasing the polarity of particles and adding a cross-linkable polymer can also increase the bond between the matrix and rubber aggregate at the ITZ [Fang 2001]. Available techniques include ionising irradiation [Ismail 2016], ultraviolet radiation (UV) [Ossola 2014, Shanmugharaj 2006], desulfurisation [Fang 2001, Rajan 2006], oxidation through gamma irradiation or potassium permanganate [Sonnier 2006], surface treatment with chemical acids such as H_2SO_4, HNO_3 and $HClO_4$ [Colom 2006, 2007], NaOH [Najim 2013, Segre 2002, Chou 2007, Li 2004], chlorination [Fang 2001, Tan 2009], as well as the use of solvents such as ethanol, acetone, and methanol [Rivas-Vázquez 2015]. A bath with saturated NaOH solution can increase rubber roughness and surface composition (rich in zinc stearate), thus resulting in low bond. However, this can be solved by a potentiometric titration of the suspension of powdered rubber in 0.1 M NaCl [Segre 2002]. Surface coating with a silane coupling agent and a subsequent layer of cement was also proven effective at enhancing bond [Huang 2013]. Polymer degradation with acids can improve the compressive strength of concrete composites by up to 60% when rubber aggregates were used [Najim 2010]. The use of activators after the above mentioned treatments can also increase the success of re-vulcanisation. Regenerated rubber can be obtained using waste rubber or new rubber as elastomeric matrix, through

reactivating the polymeric surfactants for interface modification and inter-penetrating polymer networks [Fang 2001].

Previous studies also indicate that the use of latex adhesive enhances bonding of rubber. Lee (1998) achieved a 16% compressive improvement in rubberised concrete when latex was added. Additives like silica fume or fly ash have been also used to enhance the bond between cement and rubber aggregates [Rafoul et al. 2017, Najim 2013]. Both silica fume and fly ash were proven effective at mitigating the loss of strength in rubberised concrete by replacing cementitious material, which in turn increased the concrete density [Onuaguluchi 2014]. Though it has been shown that the mechanical properties of composites with modified/treated rubber can be relatively improved, the cost-effectiveness of any of the above-mentioned treatments has not been proven yet.

4 Composites with recycled rubber aggregates

4.1 Composites based on polymeric binders

4.1.1 Rubberised bitumen composites

Bitumen is a thermoplastic polymer widely used to produce asphalt and waterproofing materials. In recent decades, asphalt rubber (AR) has been produced by blending plain bitumen, additives and recycled ground rubber (vulcanised or not). AR is an environmentally friendly and cost-effective material that outperforms traditional asphalt concrete and stone mastic asphalt (SMA) [Pasquini 2011, Yildirim 2007]. Rubber powder can be added to asphalt to partially replace bitumen (wet process) or mineral aggregates (dry process). Previous studies [Adhikari 2000] suggest that, compared to the dry process, the wet process is more effective as powder rubber melts for 2-3 hours at high temperatures in the hot bitumen, which transfers CB from the rubber to the bitumen. Moreover, the CB absorbs paraffin and maltenes from rubber, which are later transferred or diffused into the bitumen [López-Moro 2013]. The transfer of CB from the rubber increases the thickness of the ITZ, thus improving the bond between rubber and bitumen. In addition, depolymerisation/devulcanisation of rubber occurs at high temperatures (usually >75º C), which blends the polymers from rubber and bitumen [Karakurt 2015]. Wet-processed AR is less susceptible to temperature changes compared to traditional asphalt, and its fatigue and rutting behaviour is similar to SMA [Pasquini 2011]. The addition of crumb rubber increases pavement service life and stiffness, as well as rutting and

cracking resistance [Fontes 2010, López-Moro 2013]. Moreover, compared to plain asphalt concrete, tyre-rubberised asphalt generates less noise in service conditions [Paje 2008]. Blends of tyre rubber and recycled polyethylene have been used in bitumen blends to obtain better rheological behaviour [Zaman 1995]. The compatibility of rubber-bitumen and the rheology of the blend can be improved by using transpolyoctenamer rubber additives in the bitumen [Liu 2014].

4.1.2 Other rubberised polymeric composites

The composition and mechanical properties of different composites with polymeric matrix and recycled rubber aggregates have been studied in the past. Several techniques have been used to increase the compatibility of rubber with the matrix. For instance, peroxide and free radicals have been added to the blend to increase the elongation at rupture and impact energy absorption of rubber [Sonnier 2006]. Styrene-ethylene-buthylene-styrene (SEBS) has also been used to enhance the compatibility of Polypropylene (PP)/waste rubber composites, which in turn increases the elongation at rupture of the composite [Lee 1998]. Moreover, bitumen can be used to improve the bond of waste rubber in PP blends by increasing the devulcanising and plasticising effects [Zhang 2012].

Table 3 summarises the composition and mechanical properties of different composites with polymeric matrices and recycled rubber aggregates. The results in columns 5-6 of Table 3 indicate that the addition of rubber reduces the tensile strength and elongation at rupture of the composite, even if rubber is devulcanised or if another polymer (bitumen or SBS) is used as compatibiliser. For instance, the addition of rubber aggregates reduces the tensile strength and elongation at rupture of PP blends by 33% and 75%, respectively, as opposed to using PP only [Costa 2010]. Further reductions were observed in PP/EPDM blends when rubber aggregates were added [Costa 2010]. The data in Table 3 also indicate that the use of compatibilisers (such as SEBS) improved further the behaviour of rubberised polymeric composites. Zhang (2009) obtained higher elongations at break by improving the adhesion of rubber with bitumen and SEBS (+260% and +370% respectively), but with similar tensile strengths. The use of the pressure and temperature in the manufacturing process of composites with rubber can improve their final properties. For example, Scaffaro (2005) examined different properties of recycled PE blends with ground rubber from tyres, obtaining better results when the composite was manufactured through compression than through injection moulding. High temperature also promotes the destructuring of the 3D network of crosslinked

rubber, as well as its carbonization with a filler-like effect. Such effect can increase the composites' viscosity, elastic modulus and tensile strength, thus reducing its elongation at rupture, as discussed in section 2.2.2.

Table 3. Composition and mechanical properties of different composites with polymeric matrix and recycled rubber aggregates.

Author	Elastomer	Rubber aggregate type	Recycled rubber (%)	Tensile strength (MPa)	Elongation at break (%)
H.M. da Costa (2010)	PP	Scrap Tyre	0-25	30 - 20	300 - <75
	PP+EPDM (2:1)	Scrap Tyre	0-25	20 - <5	375 - 75
H. Ismail (2002)	NR	Powder	0-10-50	20-22-17	1080-980
P. Phinyocheep (2002)	Compatibilized PP	Scrap Tyre (midsole)	0-25	33.8-21.9	581-19
	Compatibilized PP	Scrap Tyre (outsole)	0-25	33.8-19.4	581-10
N. Rattanasom (2005)	NR	conventional vulcanizati	0-50	28-18	460-240
	NR	P. efficient vulcanization	0-50	26-17	500-320
R. Scaffaro (2005)	Recycled PE	wder (compresion mould	25-75	6.2-3.2	70-52
	Recycled PE	owder (injection moulde	25-75	7.1-2.0	94-51
Shu Ling Zhang (2009)	PP	Powder	60	9,8	51,6
	PP	Powder + Bitumen	60	9,5	134,6
	PP	Powder + SEBS	40	9	190,6
X. Colom (2007)	HDPE	Powder	0-40	18-6.5	999-18
		Powder + H_2SO_4	0-40	18-16	999-6
		Powder + HNO_3	0-40	18-8.7	999-12
		Powder + $HClO_4$	0-40	18-6.8	999-8
Aliabdo et al. (2015)	Epoxy resin	(0.42-2 mm)CR	**	3.62 (compression)	**
	Epoxy resin	8-2.36 mm)Fibrous rub	**	5.66 (compression)	**
	Epoxy resin	8-4.75 mm)Fibrous rub	**	6.11 (compression)	**

Although recycled rubber reduces the strength of polymeric blends, it can be used as a toughening agent in stiff polymers such as PP [Tantayanon 2004]. Therefore, rubber aggregate can increase the energy absorption capacity of the composite during loading.

Aliabdo (2015) investigated the compressive strength of rubber composites with an epoxy resin matrix. Overall, composites with fibrous-shaped rubber had higher strength than those with crumb rubber. This was attributed to the rubber acting as internal reinforcement, which in turn restrained crack development. An increase in fibre rubber length (from 2.36 to 4.75) also resulted in higher compressive strengths.

Recycled rubber aggregates have been also added in PUR foams to manufacture floating water-cleaning trays, shock-absorbing marine buoys [Cachaço 2013], sound-proof polyurethane foamed panels [Zhang 2012] and polyurethane resin-based sound absorbent foams [Maderuelo-Sanz 2013].

The studies summarised in this section confirm that bond in composites with rubber aggregates can be improved using several techniques. However, the chemical characteristics of the rubber and matrix need to be taken into account during the manufacturing process. Overall, recycled rubber aggregates can improve

the behaviour of composites when their manufacturing processes involve high temperatures and pressures, although this does not necessarily enhance the mechanical properties of the composites.

4.2 Composites based on conglomerates.

4.2.1 Gypsum-based composites.

Limited research exists on the use of rubber aggregates in plaster or gypsum. Serna (2012) reported reductions in both compressive strength (-18%) and bending strength (-16%) when rubber (1%-5% of the composite by volume) was added to gypsum. Herrero (2013) studied the influence of the size of rubber aggregate in gypsum-based composites. For the same volume fraction, it was found that the thermal conductivity dropped by up to 15% when finer rubber particles were used. However, the addition of 60% of fine rubber aggregate (0.0-0.6 mm diameter) in plaster enhanced the acoustic insulation of boards by up to 13% [Herrero 2013].

4.2.2 Cement-based composites.

4.2.2.1 Fresh state

Rubber has influences the fresh behaviour the cement-based composites [Najim 2010, Younis 2018]. The addition of rubber in concrete, especially in Self Compacting Concrete (SCC), worsens the fresh characteristics of the mix and reduces the compressive strength. Indeed, rubber modifies the rheology of concrete, thus limiting the amount of rubber that can be used in SCC to low volumes (unless plasticizers or superplasticizers are used) [Flores-Medina 2013]. Bignozzi (2006) showed that a SCC with up to 21% of rubber volume fraction (VF) maintained its rheology, while its viscosity increased. Meddah (2014) found that the consistency of RCC pavements improved by replacing 30% of gravel with rubber, which in turn reduced 30% the compaction time.

Previous studies [Hall 2014, Siddique 2004] demonstrated that the air content in fresh rubberised concrete mixes is higher than in plain concrete. This can be attributed to the hydrophibicity and non-polar nature of rubber aggregates, which entraps air on the rubber surface [Siddique 2004]. However, silane coupling agents can be used to increase the water affinity at the rubber's ITZ [Huang 2013].

Compared to plain mortars, mortars with rubber shreds have lower plastic shrinkage cracking as the shreds limit crack propagation [Raghavan 1998]. A similar behaviour was observed in rigid pavements made of crumb rubberised concrete [Mohammadi 2015]. Conversely, other authors reported a higher free shrinkage in conventional concrete, self-compacting concrete and mortar specimens when rubber aggregates were used [e.g. Hall 2014, Turatsinze 2006]. Overall, rubberised concrete is expected to be more permeable (due to air entrapment) and experience a higher shrinkage (due to less resistance to strain), which can affect durability (see section 4.2.2.3) [Demir 2015, Sgobba 2015].

4.2.2.2 *Mechanical behaviour*

Table 4 summarises the composition and compressive strength of different rubberised cement based composites. The results in Table 4 include the type of concrete, rubber aggregate type (fine or coarse) and size, treatment method (surface treatment or addition as pre-treatment), volume of replaced aggregate and drop in compressive strength. To allow for direct comparisons, Table 4 reports the total volume of rubber replacement considering both fine and coarse aggregates.

Table 4. Summary of composition and compressive strength of different rubberised cement based composites.

Author	Concrete Type	Rubber aggregate type	Size(mm)	Process/Method	Recycled rubber Volume (%)*	Max. Strength Variation (%)
Hee Suk Lee (1998)	Conventional	CR	0.5	None	2.8	-55
				Latex	2.8	-46
F. Hernández-Olivares (2002)	Self compacting	CR from truck tire	02-08	None (PP fiber addition)	0-7.4	-27
M.C. Bignozzi	Self compacting	Scrap and CR	(0.5-2) - (0.05-0.7)	None	0-21	-39
Papakonstantinou CG (2006)	Conventional	Steel Beads	20-60	None	0-8	-26.5
Liang Hsing Chou (2007)	Conventional	**	**	None	**	-32
				Na(OH) pre-treatment	**	-24
Zheng et al. (2008)	Conventional	Powder	<2.6	None	0-20	-45
		CR	42095	None	0-37.5	-53
Eshmaiel Ganjian (2009)	Conventional	Scrap	1.5-11.5	None	0-13	-26
		CR	0.2-0.85	None	0-5	-40
K.B. Najim	Self compacting	CR	2-10	None	0-15	-52
K.B. Najim (2013)	Self compacting	CR	2-6	Na(OH) pre-treatment	15	*5
				cement paste precoating	15	*15
				mortar precoating	15	*29
				waterwashing	15	*6
Flores-Medina et al. (2014)	Conventional	CR	4-8	None	0-60	-85
		CR	4-8	None	0-60	-92
Chen Bing (2014)	Conventional	CR	2.4-11.6	None	0-65	-72
				Emulsified asphalt	0-65	-69
Obinna Onuaguluchi (2014)	Conventional	CR	0.8-1.5	None	0-7	-40
				limestone precoated	0-7	-37
				precoated + Silica Fume	0-7	-14
L. P. Rivas-Vázquez (2015)	Conventional	CR	1.5-11.8	None	0-10 (fine agg.)	-11
				Acetone	0-10 (fine agg.)	16
				Methanol	0-10 (fine agg.)	5
				Ethanol	0-10 (fine agg.)	-5
Aliabdo et al. (2015)	Conventional	CR	0.42-2	Polivinil Acetate	0-40	-93.3
	Paste cement	Fibrous rubber	1.18-2.36	Polivinil Acetate	**	*-5.5
	Paste cement	Fibrous rubber	1.18-4.75	Polivinil Acetate	**	*+58
Sara Sgobba (2015)	Conventional	CR + Chip	(3-10)+(25-30)	None	0-37	-71
				Latex	0-37	-89
				NaOH	0-37	-77
				None (fly ash)	0-35	-76
				None (slag)	0-35	-66
Haolin Su (2015)	Conventional	CR	3	None	0-10	-10.6
		CR	0.5	None	0-6.5	-9.6
		CR	0.3	None	0-6.5	-9.5
Raffoul S. (2016)	Conventional	Fine Rubber	0-5	None	0-45	-85
		CR	5-10	None	0-55	-86
		Fine Rubber+CR	(>0.5)+(5-10)	None	0-60	-89
		Fine Rubber	0-5	Silica Fume+Fly Ash	0-45	-88
		CR	5-10	Silica Fume+Fly Ash	0-55	-86
		Fine Rubber+CR	(<0.5) + (5-10)	Silica Fume+Fly Ash	0-60	-84

Acronyms used in the table: CR Crumb Rubber, FCR (fiber coated with Rubber). "Recycled rubber volume*"

Volume is a percent of the total aggregate volume.
*variation between the reference rubberized concrete and rubberized concrete after the method or treatment.
**not provided.

Previous studies by Raffoul (2017) showed that the compressive strength of rubberised concrete is not affected by the specific physical characteristics of the rubber, the size of the rubber used or the type of aggregate replacement, but rather influenced by the total volume of aggregate replaced in the mix. Most studies on rubberised concrete do not mention the recovery process of rubber, even though such process affects the finishing of the rubber surface and hence the final bonding at the ITZ [Hernandez-Olivares 2002]. As expected, the replacement of mineral aggregates with rubber resulted in a reduction of strength, but the loss of compression strength depends on the additives or pre-treatments.

Table 4 also indicates that SCC exhibited smaller reductions in strength than conventional concrete for similar replacement fractions, which can be attributed to the lower amounts of water used in SCC, as well

as to the use of higher amounts of fillers and cement paste that can improve the packing of the binder material at the level of the rubber-matrix ITZ [Bignozzi 2006, Olivares 2002].

Only a few studies [Su 2015, Li 2004] have examined the effect of rubber size and shape on concrete behaviour. Rubber aggregates can be round, flaky or fibrous, which can affect their aspect ratio (see section 3.2). Small size ground rubber is typically round (Figure 3a), whereas shredded and scrap rubber (size>20 mm) is generally flaky (Figure 3b) [Aliabdo 2015]. In general, rounder aggregates favour concrete packing and compactness and therefore they have been recommended for use in concrete [Mehta 2013]. Overall, for the same volume fraction of rubber, concrete with large rubber particles tends to be more workable than concrete with fine rubber, although the former has a lower strength and higher permeability [Su 2015].

Figure 3, Crumb rubber and powder (3a) and shredded rubber with flaky shape and steel fibers (3b).

To improve the flexural strength of rubberised concrete, Papakonstantinou (2006) used steel fibres coated with rubber (FCR) from recycled tyres with lengths from 20 to 60 mm. The use of FCR reduced the workability of the mix, while it also reduced the concrete strength by 27%. To limit the detrimental effect of the steel fibres on the compressive strength, Papakonstantinou recommended the use of a maximum amount of 2% of fibres. Flores-Medina (2013) showed that the use of FCR with sizes 4-8 mm led to higher compressive and flexural strength (up to 24% and 60%, respectively) when compared to concrete with similar volumes of crumb rubber. Other studies have proven the effectiveness of using industrial steel fibres [Turatsinze 2006] and polypropylene fibres [Hernandez-Olivares 2002] at controlling cracking and increasing the flexural strength of rubberised concrete components. Recent research has also investigated the combination of tyre steel fibres and rubberised concrete to produce flexible concrete roads [Alsaif et al. 2018].

Numerous studies have investigated the pre-treatment of recycled rubber before its addition to concrete to improve the bond at the ITZ between rubber particles and the cement matrix (see section 3.3.1). The pre-treatment of rubber typically aims at increasing its roughness and reducing its hydrophobicity. Chou (2007) pre-treated rubber aggregates with a NaOH solution that led to lower strength losses (up to 8%) over control specimens with the same rubber content. Najim (2010) compared the effectiveness of several rubber pre-treatment methods such as NaOH, water washing and cement mortar pre-coating (see Table 3). It was reported that mortar pre-coating was the most effective pre-treatment at improving rubberised concrete behaviour (compressive strength improved by 29% over a mix with untreated rubber). Rivas (2015) reported a 16% and 5% increase in rubberised concrete compressive strength when using methanol or acetone rubber pre-treatments, respectively. A double treatment method based on a $KMnO_4$ solution (rubber oxidization) and a $NaHSO_3$ solution can enhance the compressive strength of rubberised concrete by up to 4*% over untreated counterparts [He et al. 2016]. To date, this pre-treatment is the most effective method reported in the literature for rubberised concrete. Unfortunately, the cost of the pre-treatments is not always reported so their cost-effectiveness is difficult to assess.

The use of additives, such as polymeric adhesives (latex or emulsified asphalt) has also been studied for improving concrete strength, but with limited success as the interface was weak [Karakurt 2015, Shen 2013]. Overall, the use of mineral additions such as metakaolin and nanosilica improves the concrete characteristics, and prevents strength reductions [Ismail 2015, 2016, Mohammed 2016].

Compared to normal concrete, rubberised concrete is less brittle [Zheng 2008] and has higher damping coefficient [Hernandez-Olivares 2002] and impact energy absorption capacity [Sukontasukkul 2013, Atahan 2012, Liu 2012]. The concrete brittleness index decreases with increasing the rubber content, and can tend to zero for a concrete composite containing 40% rubber aggregate content [Topcu 2009, Hernandez-Olivares 2002]. Rubberised concrete subjected to flexural loads absorbs more energy, although its flexural strength reduces [Ismail 2016]. Rubber aggregates also increase the concrete toughness up to a certain rubber content, after which the concrete toughness decreases due to the very low compressive strength [Hernandez-Olivares 2002]. The above properties make rubberised concrete attractive for applications such as slabs [Holmes 2014, Najim 2010], columns under seismic loads [Son 2011, Youssf 2014], precast lightweight blocks [Sukontasukkul 2009], pavements [Tian 2011, Ho 2012, Meddah 2014],

and bullet-proof panels [Sukontasukkul 2013]. The toughness and ductility of rubberised concrete with low rubber volume fraction (1-3%) can be further improved by adding steel fibres [Jian-He 2015]. Similarly, rubber can also increase the strain capacity of mortar before macro-cracking occurs [Nguyen 2010].

Recent research has examined the use of external confinement to recover the compressive strength of rubberised concrete and exploit its deformation capacity. The confinement controls the volumetric expansion of rubberised concrete, as its lateral deformations and Poisson's ratios are larger than conventional concrete [Khaloo 2008, Raffoul 2017]. The confinement systems investigated include Glass/Carbon/Aramid Fibre-Reinforced Polymer (FRP) sheets [ElGawady 2010, Youssf 2014, Raffoul 2017], vinylester wetted E-glass [Li 2011], and steel tubes [Duarte 2015,2016]. The test results indicate that while such confined rubberised concrete can be used for structural applications (strength of up to 112.5 MPa for three Carbon FRP layers), the use of low rubber contents prevents developing the full deformability potential that rubberised concrete can offer.

4.2.2.3 Durability

Compared to conventional concrete, rubberised concrete with rubber volume fractions over 40% has been found to have higher water penetration depth (+675%), water absorption coefficient (+61%), and chloride ion penetration depth (+63%) [Hall 2014]. Compared to normal concrete counterparts, water permeability is 2.5 times higher in rubberised concrete with a 10% of chipped rubber, and 2 times higher for rubberised concrete with a 10% of crumb rubber [Ganjian 2009]. The higher permeability and porosity of rubberised concrete is mainly attributed to rubber hydrophobicity [Demir 2015].

Rubber aggregates also tend to swell in an alkaline environment (which can increase cracking and permeability), although the swelling can be reduced by adding latex to the mix [Sgobba 2015]. Experimental evidence indicates an increase in cracking and spalling in rubberised concrete cured in moist conditions [Sgobba 2015]. Such behaviour can reduce the final service life of concrete pavements [Ho 2012, Hernandez-Olivares 2002] and rubberised asphalts [Lei 2016].

Hernandez-Olivares (2004) used a low amount of 2-8 mm rubber (3% aggregate volume fraction) to reduce spalling in concrete under fire, without evident reductions in concrete strength. The reduction in spalling

was attributed to the presence of voids left by burnt rubber particles, which allowed the release of pressure from gas/water vapours.

4.2.2.4 *Thermal and acoustic properties*

The polymeric characteristics, low density and thermal conductivity of rubber aggregates have been shown to reduce the thermal conductivity of rubberised concrete composites [Hall 2012, Flores 2016] and mortars [Corinaldesi 2011]. Aliabdo (2015) studied the thermal conductivity (k) of non-structural concrete with rubber aggregates. He reported a 57% reduction of k when 100% of the concrete sand was replaced with ground rubber. The reduction in thermal conductivity can be partly attributed to the lower thermal conductivity of rubber, as well as to the increase of air entrapped during mixing. The entrapped air also causes a higher moisture-dependent effect on thermal conductivity, which increases in saturated state [Hall 2012].

The damping properties of rubber contribute to an increase in the sound absorption of rubberised concrete. Therefore, rubberised concrete has been used in noise absorbing panels for motorways [Ekopan, Insul-eco, Ruconbar, Pfretzschner 1996], and noise-blocking blocks in buildings [Sukontasukkul 2009, Turgut 2008, Meshgin 2012]. Research suggests that the sound absorbing properties of rubberised concrete depend on the sound frequency, with up to 37% sound absorption observed for concrete with 20% CR volume fraction in the range over 500Hz [Sukontasukkul 2009, Flores-Medina 2016]. Rubberised concrete panels have been used for building facades to absorb (instead of reflecting) traffic noise [Crocker 2007].

5   Conclusions and further research needs

From the comprehensive literature review summarised in this article, the following conclusions are drawn:

Currently a large variety of rubbers are commercially available. Rubbers are made with different elastomers, fillers and manufacturing processes, all of which affect the final properties of a rubber composite. The mechanical behaviour of rubber depends heavily on the matrix and fillers used for its manufacturing. Several methods exist to sort rubbers with different elastomers before recycling, but it is still challenging to sort them according to their fillers or amount of fillers. The nature and amount of filler added to the rubber blend defines its physical and mechanical properties. However, the mechanical

properties of recycled rubber are generally not provided by tyre manufacturers and/or tyre recyclers, which increases the chances of failures of composites made with recycled rubber. Consequently, it is necessary to characterise rubber before it can be used in composite manufacturing. Current trends include some efforts towards the use of advanced chemical, physical and mechanical methods to characterise recycled rubbers, but more work is deemed necessary to develop cost-effective characterisation methods suitable to process large volumes of recycled rubbers as those required by the construction industry.

The manufacturing process of a composite made with reclaimed rubber also modifies its final characteristics. Processes involving high temperatures and pressures provide the best results. Rubber can be also finely ground and added to a melted mass to produce extruded composites. Future research should focus on the inclusion of fine rubber aggregates in products manufactured at melting temperature and high pressure. Under these conditions, the high temperature is expected to "swell" the recycled aggregate, thus allowing the diffusion of fillers into the new composite and improving bond at the ITZ. Thermosetting rubber is hard to decompose or devulcanise and, although the recovered raw material can be reused, the final mechanical properties of the composite are negatively affected. Given the high cost of devulcanisation, the use of this process to produce composites in construction does not seem to be feasible.

A correct understanding of the bond mechanism at the Interfacial Transition Zone (ITZ) between rubber and matrix is of critical importance in composite manufacturing. Major issues to address include the smoothness and hydrophobicity at the rubbers surface, as these reduce the bond with the matrix. Current efforts in research aim at improving the bond between rubber and matrix using mechanical and chemical pre-treatments. However, pre-treatments increase the cost of rubber and, in most cases, the behaviour of the composite is only slightly improved. Accordingly, future research should investigate how to enhance bond at the ITZ using cost-effective techniques suitable for the construction industry where rubber is currently mainly used in low-value applications (e.g. traffic barriers, thin overlays, concrete panels, paving blocks, thermal and acoustic insulators, and elements able to resist vibrations, impact and cyclic loads). Rubber aggregates perform well in bitumen matrix-based composites for roads, as the high temperature used during casting increase the carbon black diffusion from CR to bitumen, thus improving bond at the ITZ.

Small volume fractions (VF) of rubber (10-20%) can increase the toughness and the fire spalling resistance of concrete. Larger VF of rubber reduce the concrete strength, but this can be slightly enhanced with the use of fibres, latex, or fillers. Externally bonded FRP confinement was found to be very effective at restoring the strength of rubberised concretes (112.5 MPa for three CFRP layers) and can reach strains up to 8%. Current research is investigating the use of this innovative concrete in structural applications that require large deformability, such as seismic isolators and plastic hinges of columns. Potential future applications of this concrete include integral bridges and coupling beams of multi-storey buildings.

Promising potential applications of recycled rubber aggregates in concrete also include the construction thermal and acoustical insulators, which are currently manufactured with polymeric binders. To date, however, the use of rubber as a construction material is limited since fire protection measures should be employed to reduce the fire risk. Nevertheless, rubber is a durable material that can be used in external walls and covers with insulation properties. The reduction of thermal conductivity of composites such as non-structural concrete with rubber can be a good way of using a high volume of recycled rubber. Moreover, the increased damping of rubber composites reduces noise in buildings.

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