

Comparative Effects of Chemical Pretreatments on Mechanical Properties of Sustainable Rubberized Concrete

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Abstract. Chemical pretreatments are known to have significant influence over mechanical properties of concrete and being able to quantify the effect of chemical pretreatments will be of great help in trying to anticipate the rubberized concrete's possible mechanical properties. This paper presents an experimental study that was conducted on cylindrical concrete samples prepared by using different proportions of natural coarse aggregates (NCAs) replaced by pretreated; with different concentrations of chemicals, rubber coarse aggregates (RCAs). The aim was to ameliorate the mechanical properties of concrete using sustainable alternative; rubber coarse aggregate. After chemical treatment, washing and air drying, RCAs were first coated with cement paste and then dried and cured for 28 days to enhance their bonding behavior in concrete. The results confirmed the efficiency of pretreated RCAs, in improving the mechanical properties of rubberizes concrete especially the compressive strength.

1. Introduction

Rapidly growing urbanization and industrialization has resulted in generating huge amount of non-degradable wastes which has intensified the need for sustainable development (Fleming et al. 2017). Sustainable concrete (Struble & Godfrey, 2004) is an innovative research practice towards minimizing the climate change, Global warming and making concrete an economical source for construction purpose using economical and non-degradable wastes (Pepe, 2015). Rapid consumption of aggregates, which are 70% of the total mass of concrete (de Brito & Saikia, 2013), have ought to find an economic alternative without compromising its strength.

Approximately 1 billion scrap tires are being discarded globally per annum (Mohammed et al. 2017; Dobrot and Dobrot 2016) and billions of scrap tires had already pile up in illegal stocks according to US Environmental Protection Agency (EPA). Scrap tires are being utilizing for; fuel in kiln (Siddique & Naik, 2004), used as an additive to mortar/concrete (Corinaldesi et al. 2011), as a light weight filler (Rashad, 2016). For effective utilization of the rubber tire wastes (Li et al. 2004) and for considering the environmental benefits, extensive research has been undertaken (Etrma, 2011) to incorporate them in concrete; by changing percentages and applying different pretreatments on rubber aggregates (Mavroulidou & Figueiredo, 2010).

Varying the rubber content in concrete results in significant variation in its mechanical properties; decrease in compressive, tensile and flexural strength as well as increase in water permeability (Ganjian et al. 2009; Snelson et al. 2009), increase in toughness (Liu et al. 2013), decrease in workability (Wang et al. 2013), increase in setting time (Al-Akhras & Smadi, 2004), increase in the cumulative bleeding (Wang et al. 2013), increase in shrinkage (Bravo & de Brito, 2012), increase in impact energy (M.M et al. 2008) and superior damping behavior (Nadal Gisbert et al. 2014).

Researches have been undertaken to compensate these abnormalities using different pretreatment techniques; sodium hydroxide (NaOH) pretreatment resulted increase in compressive strength (Ling et al. 2011) as well as improved other mechanical properties (Segre & Joekes, 2000) due to improvement in bond between cement paste and residue (Marques et al. 2008), silane pretreatment

increased compressive strength and thermal conductivity (Rana and Dina, 2011), pre-treatment of both NaOH and silane improved flexural strength and splitting tensile strength (Albano et al. 2005). Replacing rubber aggregates and adding silica fumes resulted in; improved compressive as well as tensile strength (Gesoğlu et al. 2010), pore structure modification (Sohrabi & Karbalaie, 2011), reduced chloride penetration (Elchalakani, 2018). Adding silica fumes and applying FRP (Fiber reinforced polymer) confinement to the rubberized concrete increased its ductility, volumetric strain and energy dissipation (Dattatreya & E, 2015). Pretreatment with carbon tetra chloride (CCl_4) and water increased compressive strength (June et al. 2010). When treated with sulphuric acid (H_2SO_4) increase in stiffness and tensile strength was found (Colom et al. 2007).

Pre-coating with cement mortar have a significant effect on interfacial bonding and stress transformation which enhance compressive/splitting tensile strength, flexural toughness behavior as well as pre-micro crack strain capacity (Najim & Hall, 2013). Increased compressive strength as well as flexural strength was found when rubber aggregates were pre-coated with cement paste (Yazdi et al. 2015).

In this research, rubber coarse aggregates (RCAs) were obtained from truck tires and converted into the sizes of natural coarse aggregates (NCAs). All the rubber aggregates were first washed with water and dry in air then they were pretreated; using different concentrations of Carbon tetra chloride (CCl_4), sulphuric acid (H_2SO_4), sodium hydroxide (NaOH) and ethanoic acid (CH_3COOH) to increase their surface reactivity. After chemical treatment, washing and air drying, all the RCAs were first coated by cement paste and then dried and cured for 28 days to enhance their bonding behavior in resultant concrete.

The aim of this study is to strengthen such structural materials; rubber coarse aggregates (RCAs), having low-cost non-biodegradable wastes and to find all possible ways that could help in introducing and practicing such materials in actual structures and construction practices.

2. Experimental Program

To the best of our knowledge such work has been conducted for the first time in which all the effective and suggested methods of rubber pretreatments i.e. CCl_4 , H_2SO_4 , NaOH, CH_3COOH have been applied in parallel with different percentage of RCAs i.e. 0%, 10%, 20%, 25%, 30% and compared with each other to investigate their effects on slump, dry density, water absorption and compressive strength of 17 samples of rubberized concrete. Experimental program starts with material properties and pretreatment of rubber, followed by concrete mix variables and specimens' preparation, and concluded with results and discussion.

2.1 Materials

Ordinary portland cement (OPC), with initial setting time 137 minutes, final setting time 211 minutes, normal consistency 33%, as dictated by manufacturer, was used in this research that confirmed to ASTM C150/C150M (2017).

NCAs were crushed lime stones with maximum size around 0.75 inch (19.05mm) and specific gravity of 2.64 measured as per ASTM C127 (2007) specifications. The flakiness index of these was 25% as per ASTM D 4791-10 (2011) and water absorption was 1.7 % as per ASTM C12 (2007). Fine aggregates (Siliceous) with a fineness modulus of 2.54 as per ASTM C136-01 (2015) and water absorption 1%, were used ASTM C128-97 (2011). RCAs with a specific gravity 1.08 and relative density 1.3, were obtained by shredding scrap rubber tire with an average size limit of 19 mm and of the same grading as NCAs, all properties of RCAs were determined by ASTM (C127) (C128) (C136) as shown in Fig. 1.



Fig. 1. Rubber aggregates obtained from scrap rubber tires

To ensure dense packing and good bonding strength between cement paste and aggregates, 5% silica fume by weight of cement was also used in all the samples (Onuaguluchi & Panesar, 2014). A commercially available, economical super-plasticizer nepthaplast F707 was used to enhance the workability and to control water cement ratio of concrete mixes containing RCAs (Sancak et al. 2008). The super-plasticizer dosage was 0.7% by weight of cement based freshly prepared concrete mixes.

2.2 Pretreatment of rubber

Pretreatment of RCAs was done to enhance the surface reactivity and to mitigate the strength losses (Pacheco et al. 2012). Stearic acid zinc salt ($C_{36}H_{70}O_4Zn$) present on the tire surface during manufacturing reduce the bonding behavior of RCAs (Ling, 2012) while pretreatment remove this salt layer as well as makes the rubber surface rough and activate for bonding with cement paste (Siddique & Naik, 2004).

In current study, all RCAs were washed with distilled water and dried at normal temperature before pretreatment. Then these RCAs were divided into 4 groups and immersed in 4 solutions separately having different concentration of chemicals; [Group.1 in carbon tetra chloride- CCl_4 (5400 ppm), Group.2 in sulphuric acid- H_2SO_4 (30% solution), Group.3 in sodium hydroxide- $NaOH$ (10% solution), Group.4 in ethanoic acid- CH_3COOH (50% solution)] for one hour at room temperature while special care was taken during handling of the chemicals to avoid any mishap.

After chemical pretreatment, RCAs were washed well with distilled water to remove any residue of chemicals left on aggregate surface which can negatively affect the bonding behavior of RCAs. Once dried, all 4 groups of RCAs were treated with cement paste so that the surface of each aggregate gets coated with cement paste (Najim & Hall, 2013).

2.3 Variables

Each pretreated RCAs group was further divided into 4 sub-groups depending upon the percentage by volume replacement of NCAs in concrete mix design and specified by symbols; NC (for control mix), C (for CCl_4), H (for H_2SO_4), N (for $NaOH$) and E (for CH_3COOH) as given in Table 1. Other variables were NCAs, cement and silica fumes.

2.4 Concrete Mix and Sample Preparation

Total 17 batches of concrete mix were prepared; there were four sets of RCAs based on pretreatment, out of which 16 batches of concrete were prepared (4 from each batch) while one was control batch with no rubber aggregates. The concrete mixture was designed for a compressive strength of 38 MPa as per ACI 211.1 (2002). The detail of these batches and proportions is given in Table 1.

A power-driven tilting concrete mixer was used to prepare the standard concrete mixes. Cylindrical samples of 150mm diameter and 300mm length (Khaloo et al. 2008) were prepared from each of the

17 batches at room temperature as per ASTM-C192 (2002) and all these samples were compacted using vibrator in order to ensure uniform and proper compaction. Freshly prepared samples covered with plastic membrane sheets to prevent moisture loss and were kept at room temperature. After 24 hours, samples were de-molded and subjected to curing for 90 days keeping relative humidity $95\pm5\%$ and room temperature 25°C . Mixing of materials and curing were all done using drinking water.

Table 1. Details of mix proportions and fresh concrete properties.

Chemical Pretreatment	Rubber Aggregates (%)	Symbols	Rubber aggregates Kg/m^3	Coarse aggregates kg/m^3	Fine aggregates Kg/m^3	Cement+5 % Silica Fume Kg/m^3	Water liters	Slump mm
None	0	NC	0	1087	840	389	155	64
CCl_4	c	C_1	109	978	840	386	155	58
	20	C_2	217	870				53
	25	$\text{C}_{2.5}$	272	815				53
	30	C_3	326	761				40
H_2SO_4	10	H_1	109	978	840	386	155	58
	20	H_2	217	870				53
	25	$\text{H}_{2.5}$	272	815				53
	30	H_3	326	761				40
NaOH	10	N_1	109	978	840	386	155	58
	20	N_2	217	870				53
	25	$\text{N}_{2.5}$	272	815				53
	30	N_3	326	761				42
CH_3COOH	10	E_1	109	978	840	386	155	58
	20	E_2	217	870				53
	25	$\text{E}_{2.5}$	272	815				53
	30	E_3	326	761				40

Note. C_1 for samples with 10% RCAs and pretreated with carbon tetra chloride, similarly C_2 for 20%, $\text{C}_{2.5}$ for 25%, C_3 for 30% and respectively for other pretreated samples.

2.5 Testing Plan

Testing on different specimens were conducted according to the appropriate ASTM and ACI specifications. Slump values were measured for each batch of fresh concrete according to ASTM-C143 (2015). Dry density for all the batches was measured after 90 days of curing according to ASTM C642 (2006). Water absorption tests were conducted as per ASTM C642 (2006) after 90 days of curing on oven dried samples after 48 hours immersion in water at room temperature and the 5 hours immersion in boiling water. Compressive strength tests were conducted on each batch after 7, 14, 56, and 90 days of curing according to ASTM-C39 (2014).

Results of all these tests were compared with each other as well as with normal concrete to evaluate the effective pretreatment technique and optimum percentage replacement of RCAs that could be adopted to enhance the mechanical behavior of rubberized concrete.

3. Results and Discussion

This section includes the results and optimum solution; the effect of RCAs on slump, dry density, water absorption and compressive strength, by varying the percentage of rubber content as well as the appropriate pretreatment technique for RCAs to get the best alternative of NCAs.

3.1 Slump test

Workability of rubberized concrete was decreasing with the addition of rubber content (Raj et al. 2011). Up to 20% replacement the observed value of slump was reduced by 21% (Batayneh, Marie, & Asi, 2008; Ganjian et al. 2009; K. & M, 1999). In current research work, replacement of RCAs up to 10% reduce the slump value by 9% and up to 25% replacement, slump was reduced by 17% as compared to normal concrete (NC).

This effect is due to the addition of super-plasticizer Nepthaplast F707 which helped in improving the workability of rubberized concrete. Fig.2 shows the details of slump values for all the batches measured in mm.

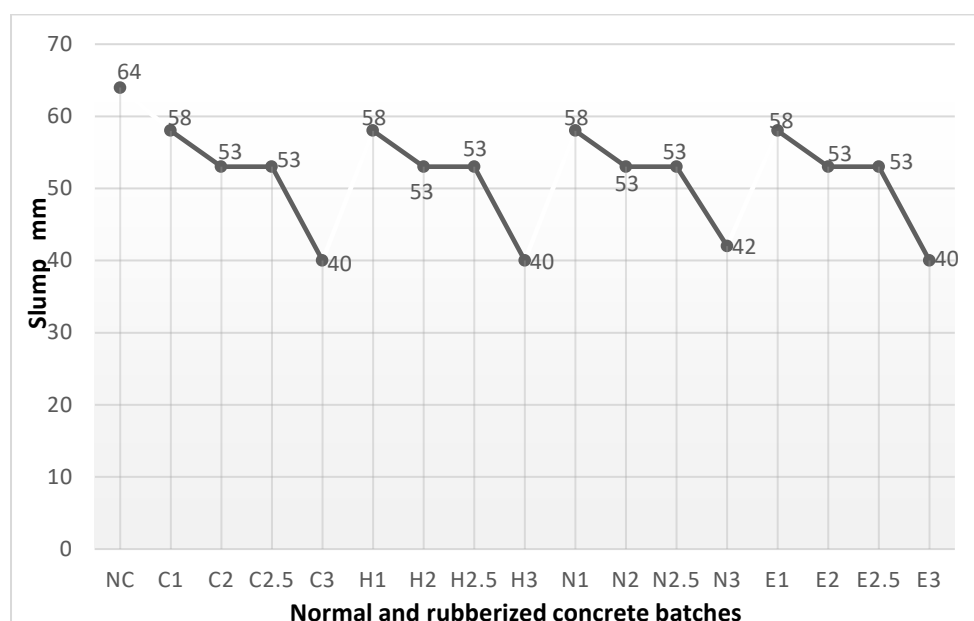


Fig.2. Slump values for all the batches measured in mm.

3.2 Dry Density

Addition of RCAs cause reduction in unit weight of rubberized concrete (Albano et al. (2005); Gesog˘lu et al. (2014); Taha et al. (2008); Khaloo et al. (2008); Batayneh et al. (2008)). Comparing the dry density of rubberized concrete to normal concrete (NC), after 90 days of curing for all methods of pretreatment, it has been observed that increasing the rubber content had inverse effect on the dry density of rubberized concrete. Fig.3 shows details of dry density for different percentage replacements of rubber aggregates.

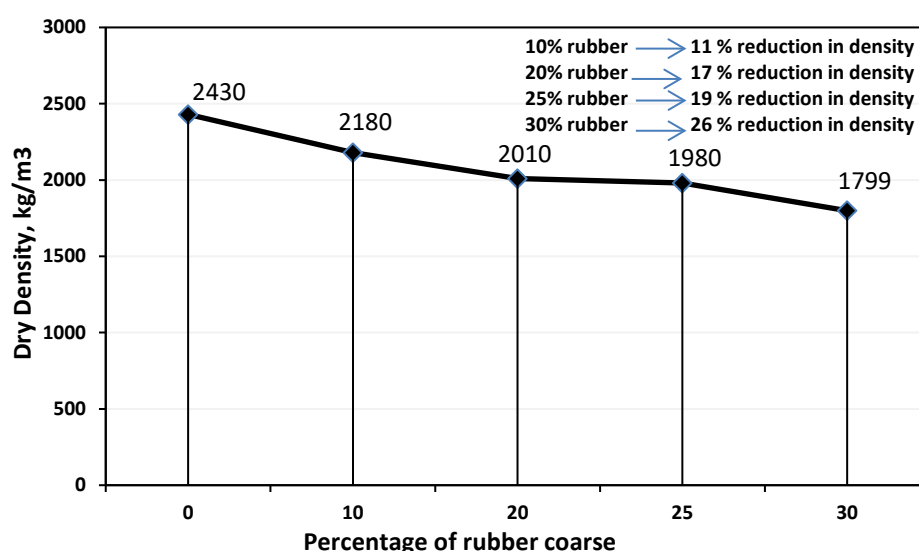


Fig.3. Dry density for different percentage replacements of rubber aggregates

3.3 Water Absorption

By replacing rubber content in concrete mixtures, water permeability was increased (Ganjian et al. 2009; Snelson et al. 2009). An increase in water absorption was observed in all samples containing RCAs. Maximum values of water absorption were observed in samples containing 30% RCAs and pretreated by sulphuric acid as well as those samples pretreated by sodium hydroxide. Water absorption in case of sodium hydroxide 11% while in case of sulphuric acid 17% was observed as compared to 4.5% of normal concrete. Fig.4 shows details of water absorption for different percentage replacements of rubber aggregates.

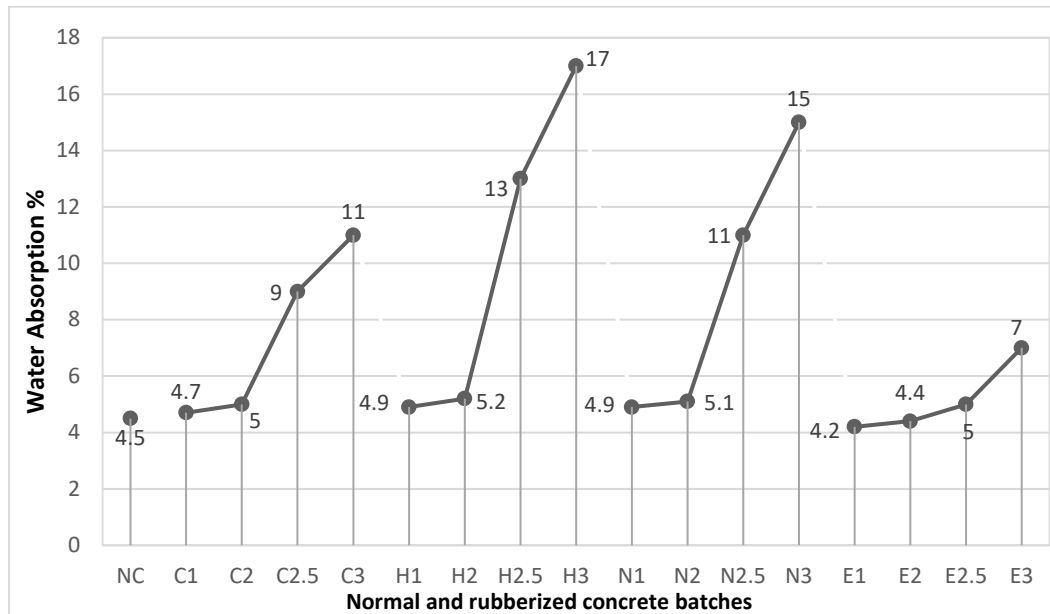


Fig.4. Water absorption in percentage for normal and rubberized concrete

3.4 Compressive strength

Being a fundamental property of concrete, generally compressive strength had an inverse relation with the incorporation of RCAs in concrete (Ling, 2012; Youssf, Hassanli, & Mills, 2017; Ganjian et al., 2009; Segre & Joekes, 2000; Raghavan et al, 1988). The compressive strength test was performed on samples that has undergone 7, 14, 56 and 90 days of curing by universal testing machine (UTM) having load capacity of 200 KN.

In samples pretreated by CCL_4 , an appreciable increase in Compressive strength was observed as compared to NC after 90 days of curing for batches C_1 and C_2 but for $\text{C}_{2.5}$ and C_3 , the strength values remained almost unchanged and were too less as compared to the NC as shown in fig. 5. In samples pretreated by H_2SO_4 , H_1 shows more compressive strength as compared to NC while an appreciable compressive strength was also observed for H_2 and $\text{H}_{2.5}$ except H_3 as compared to NC as shown in fig. 6.

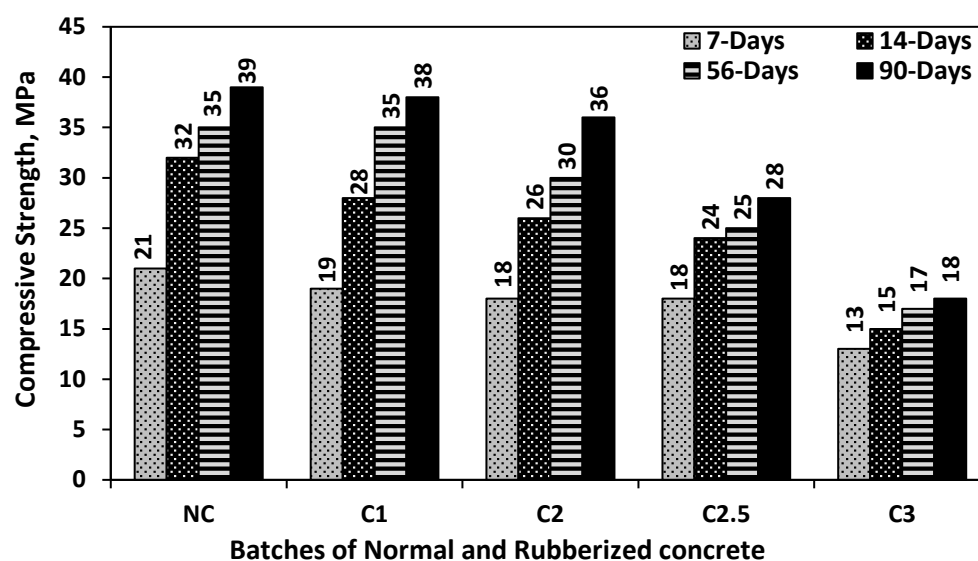


Fig. 5. Compressive strength of normal concrete and all the batches pretreated by using CCl_4 , at various stages of curing

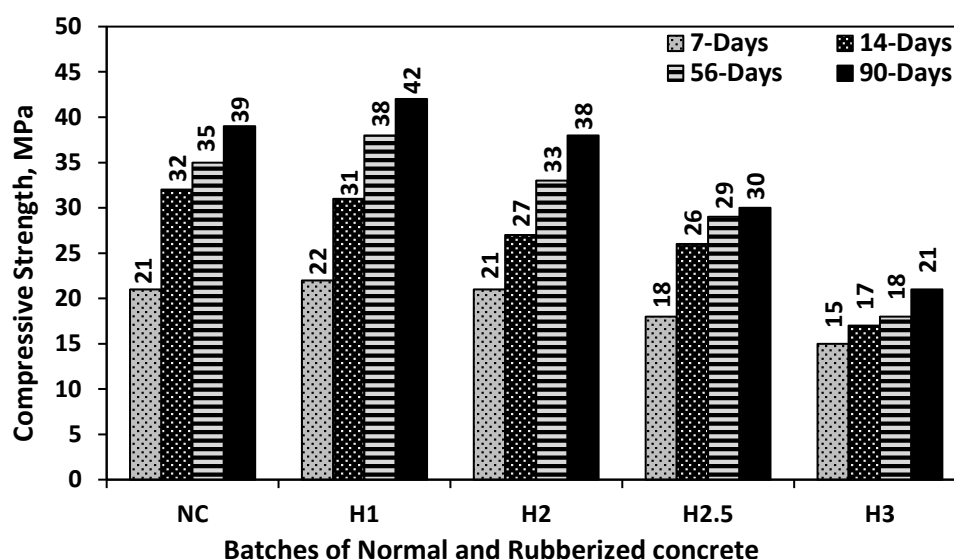


Fig. 6. Compressive strength of normal concrete and all the batches pretreated by using H_2SO_4 , at various stages of curing

For samples containing RCAs pretreated by NaOH , N_1 shows even more compressive strength as compared to the normal concrete while the strength values for the remaining batches; N_2 , $\text{N}_{2.5}$ and N_3 , were not much appreciable even after 90 days of curing as shown in fig. 7. The compressive strength values, for samples containing RCAs pretreated by ethanoic acid, did not rise to an effective value over the period of 90 days of curing as shown in fig. 8.

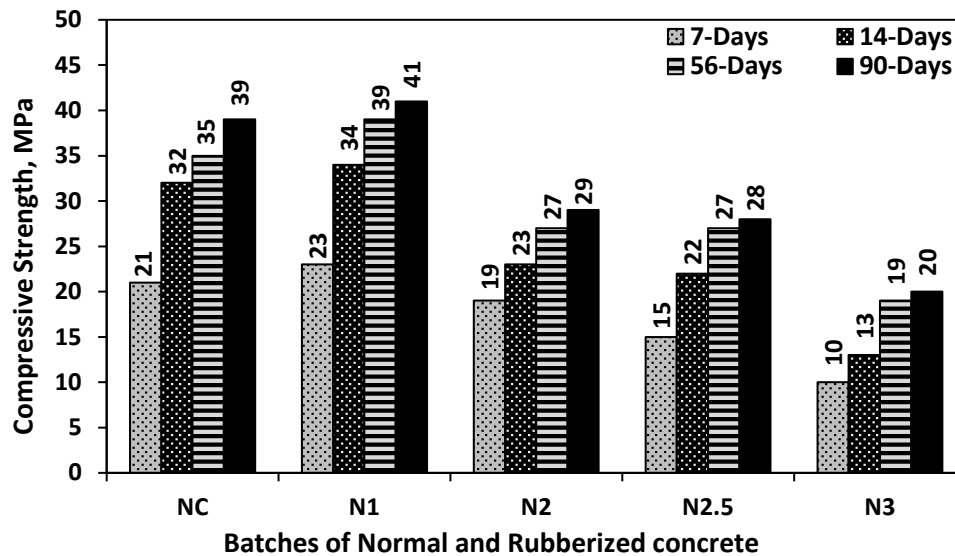


Fig. 7. Compressive strength of normal concrete and all the batches pretreated by using NaOH at various stages of curing

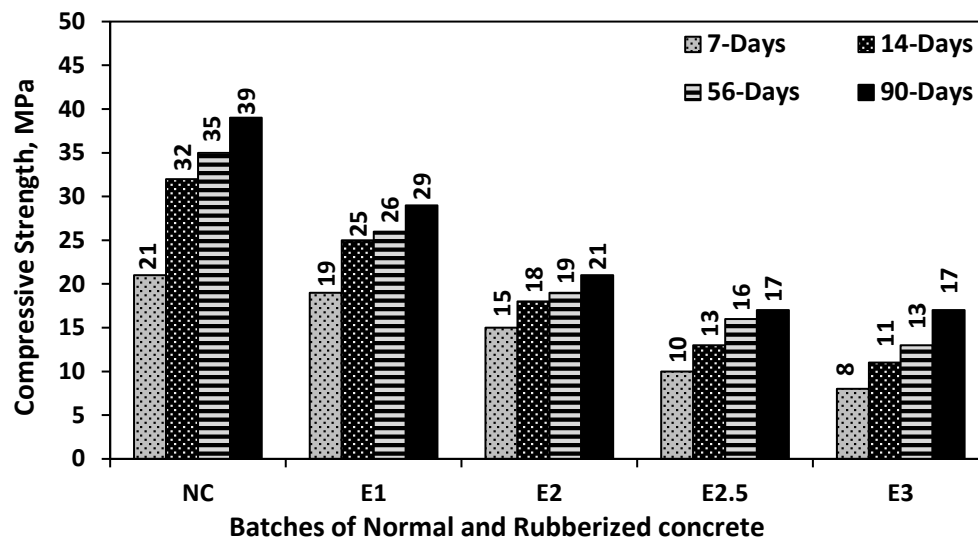


Fig. 8. Compressive strength of normal concrete and all the batches pretreated by using CH_3COOH at various stages of curing

It was observed that after 7 days of curing, samples containing up to 25% RCAs of all categories of pretreatment, developed an appreciable compressive strength except $\text{E}_{2.5}$. Least strength gain was observed in all samples with 30% replacement of RCAs as shown in Fig.9. A similar trend of strength gain was observed after 14 days of curing.

After 14 days of curing the strength gain was slow for all samples but they gained maximum compressive strength at the age of 56 days. An appreciable strength gain was observed for samples containing RCAs up to 25% and pretreated by NaOH, H_2SO_4 and CCl_4 , while for samples pretreated by ethanoic acid, the strength values were less, as compared to NC as shown in fig.9. Similar trend was seen after 90 days of curing as observed for all samples after 56 days of curing as shown in fig.9.

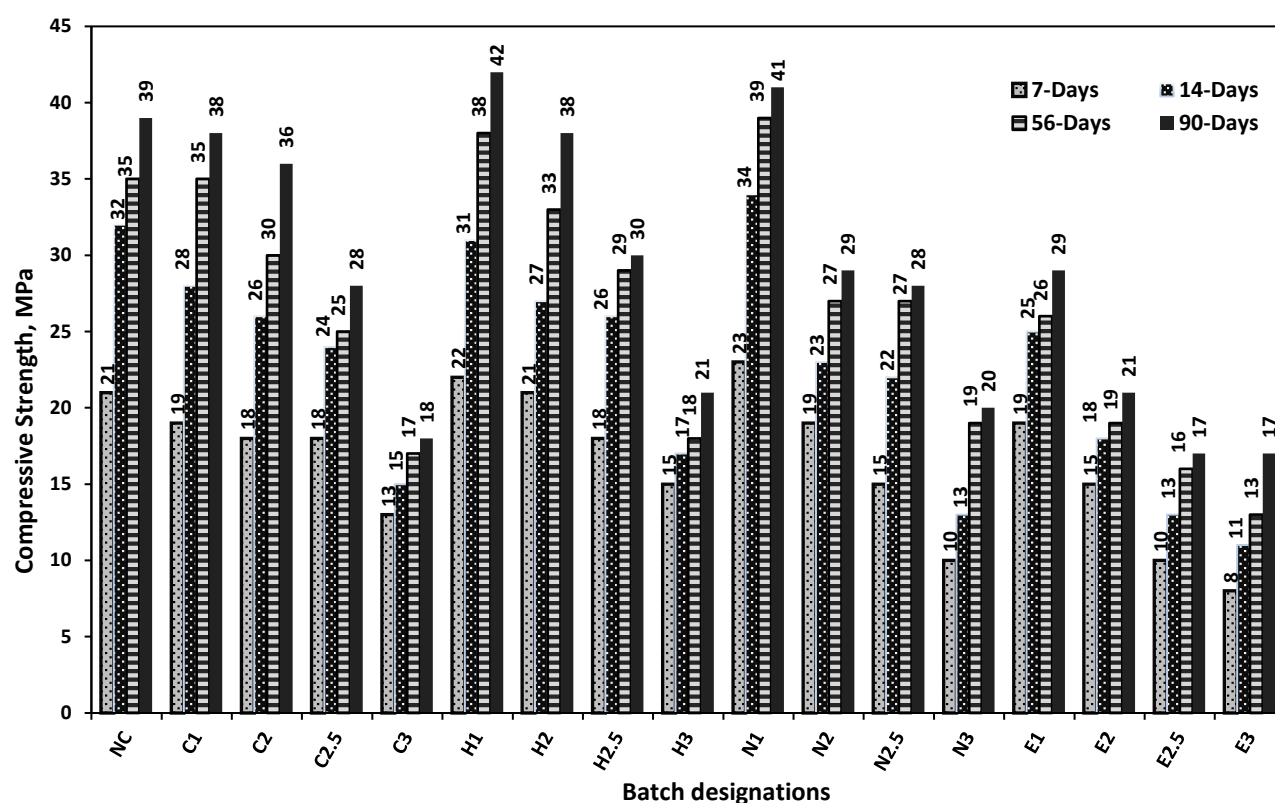


Fig.9. Compressive strength of all the batches at all stages of curing

3.5. Cost Analysis

Cost analysis was also conducted for these batches of concrete per cubic meter. The cost of total coarse aggregates was reduced approximately by 36% when replaced by rubberized aggregates in different percentage. Since rubber aggregates were obtained from scrap tyres that are available at negligible cost, so the only cost involved is for the shredding process. Whereas the treatment process is very less costly for NaOH and H₂SO₄ which are available at the cost of Rs. 20/Kg and Rs. 35/kg (available in local market) while the solution can be reused many times. The tax expense on the disposal of waste tyres, saved by reusing the waste tyres, can almost offset the additional costs introduced by surface treatment, which makes this application economically viable. Therefore, replacing coarse aggregates with rubber aggregates not only saves the overall construction cost and improves certain properties but it also aids to development of sustainable construction by reducing threats to environment caused by burning and uncontrolled disposal of rubber tires. (Su, Yang, Ghataora, & Dirar, 2015).

4. Conclusions and Recommendations

This research was conducted to compare the effect of different pretreatments techniques on mechanical properties of rubberized concrete with up to 30% RCAs, including the slump, dry density, water absorption, and compressive strength. From the above results, it can be concluded;

- Samples with 20% RCAs, pretreated with sulphuric acid shows significantly improved mechanical properties, especially more compressive strength than normal concrete.
- The workability of RCAs, even with the incorporation of super-plasticizer, shows gradual decline upto 25% replacement. There was a steep decline in workability of RCAs with 30% replacement.
- The dry density has an inverse relation with the increase in content of RCAs in rubberized concrete; a gradual decline was observed.

- An appreciable water absorption was observed in almost all type of pretreated samples. Maximum water absorption was observed for samples with 30% RCAs pretreated by H_2SO_4 and NaOH.
- Samples holding 10% RCAs pretreated with sulphuric acid and sodium hydroxide gave even more compressive strength as compared to normal concrete after 90 days of curing. For samples containing up to 25% RCAs, and pretreated with carbon tetra chloride, sulphuric acid and sodium hydroxide, the compressive strength values were appreciable as compared to NC.
- Coating of rubber aggregates by cement and addition of silica fume could also be the key factors in enhancing the mechanical behavior but their exact role is needed to be studied through microscopic analytical techniques like scanning electron microscopy (SEM).

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