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Technology, Properties and Application of NRL Elastomers

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1. Introduction

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1.1. General appraisal

Polymer latexes are being increasingly used in the construction industry as modifiers, especially in hydraulic cement concrete and mortar. Figure 1 presents polymeric latexes used as cement modifiers. Among the different presentations of polymeric latexes, elastomers are the most widely used (Ohama, 1995). In practice, there are two basic elastomers applicable to cement mixes and these are natural rubber latex (NRL) and synthetic latexes. Figure 2 shows some prominent derivatives of these elastomers. Indeed, elastomers are mainly added into hydraulic cement concrete and mortar in order to improve their performance properties.



Figure 1. Polymer latexes for concrete and mortar modifications (Ohama 1995)

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Even though, concrete is the most preferred construction materials on earth, but it has some limitations which inevitably affects its quality and general performance. These limitations include; delayed hardening, inherent brittleness, weak tensile capacity, low flexural strength, small failure strain, large drying shrinkage, susceptibility to frost damage, high moisture absorption and most critically low resistance to chemicals. To improve on these deficiencies, elastomers are added as modifiers (Ohama, 1995; Joao & Marcos, 2004; Rajni, Asthana & Anupam 2006; Bala *et al.*, 2011a).



Figure 2. Elastomeric latexes for concrete and mortar modifications

1.2. Performance of elastomers in cement mixes

Depending on the type of elastomer used, modified concrete (MC) and mortar exhibit excellent performance in both mechanical and durability functions. Normally, addition of appropriate quantity of elastomer in cement-based mix improves; workability, through ball bearing actions; cement hydration, through water retention qualities; compressive, tensile and flexural strengths, through latex-film formation; and water tightness, through effective void and capillary fillings (Ramakrishnan, 1992).

Application of elastomers into cement-based infrastructures has been successful in the last few decades perhaps due to prominent qualities usually exhibited by these substances. The most desired of these qualities include high amorphousness and low particle size which makes it possible for the elastomers to effectively fill cavities and capillaries of hardened cement paste, and ability to coalesce upon withdrawal of the surrounding moisture in the cement-elastomer co-matrix systems (Bala, Yussuf & Mohammad, 2009). Admixing rather than impregnation is mostly applied in both laboratories and on construction sites. Comparatively, admixing entails simple operations and it ensures overall homogeneity between cement and elastomer. Compatibility of elastomer in the voids of hardened cement paste provides protection against ingress of moisture which normally serves as the main transporter to agents of chemical attack. In addition, the ability of an elastomer to coalesce in the co-matrix usually leads to latex-film formation which forms the basis for improvements in mechanical properties.

Although, inclusion of elastomers in hydraulic cement mixes is tremendously becoming popular worldwide, elastomers are basically rubbers, and rubbery substance softens when exposed to high temperatures. Thus, in the event of elevated temperatures, it is feared that the comparatively low softening point temperature of elastomers may cause failure in MC members or promote durability threats much earlier than the recommended design limits. Therefore, as much as elastomers are desired in the construction industry for their excellent performance, a clear margin of performance at elevated temperatures is necessary, so that both mechanical integrity and durability functions are ensured. Indeed, absence of clear margin of performance in cement-elastomer phase could render structures made with cement-elastomer co-matrix unsafe particularly at high temperatures. This creates a major point of concern to professionals in the technology sector since structures are often exposed to temperatures beyond the normal ambient limits (Bala et al., 2011b). This issue has been addressed in the experimentation which follows. In fact, a section which presents experimental findings regarding behavior of elastomeric concrete under elevated temperatures has been included in the analysis and discussion of results.

Considering the general performance of elastomers in the hydraulic cement concrete and mortar particularly their positive and negative roles in the cement-elastomer phase, the following advantages and disadvantages could be enumerated.

Advantages of elastomers as modifiers in cement concrete and mortar

- 1. Improvement of workability which normally provides additional ease to complete mixing, proper placement and adequate compaction.
- 2. Enhancement of cement hydration with consequent increase in strength due to water retention capacities of elastomers.
- 3. Greater mechanical properties especially tensile and flexural strengths. This is mainly the result of reduced brittleness in the modified phase.
- 4. Improvement of water tightness, resistance to chemical aggression and freeze-thaw. Ability of elastomers to fill capillaries and voids of the hardened phase normally contributes to these achievements.

Disadvantages of elastomers as modifiers in cement concrete and mortar

- 1. Some elastomers impair certain qualities of concrete. For example, polyvinyl acetate and chloroprene rubber were observed to increase the drying shrinkage of concrete.
- 2. Inclusion of high dosage of elastomer such as NRL into concrete mix could render hardened phase susceptible to strength weakening especially at elevated temperatures.
- 3. In some cases, allergic reactions from exposure to proteins found in NRL could be experienced. Therefore, the use of deproteinized NRL is most recommended.

1.3. Natural Rubber Latex

NRL is a whitish to off-white milky fluid usually obtained by tapping the bark of Para tree (*Hevea Brasiliensis*). Figure 3 portrays some of the principal operations involved in the production of NRL. In its fresh state, NRL comprises "30%'' - "40%'' rubber hydrocarbon particles (C₅H₈) suspended in a serum together with about "6%'' non-rubber substances (Ong, 1998; Jitladda, 2006). The non-rubber substances include proteins, lipids, carbohydrates, sugars and traces of some metals such as zinc, magnesium, copper and iron. Natural rubber is a high molecular weight polymer of isoprene (cis-1,4-polyisoprene). It has a particle diameter of $0.1 - 4.0 \mu m$ and a chemical structure as shown in Figure 4 (Rattana, 2003; David & Richard, 2002).



Figure 3. Production of natural rubber latex



Figure 4. Chemical structure of cis -1,4-polyisoprene (David & Richard, 2002)

Most of the properties of NRL are determined during the process of natural polymerization rather than controlled as normally is the case with emulsion polymerization. This forms the basis for the presence of non-rubber substances. Bacterial activities and coagulation are known to exist in NRL also. An in-depth analysis on the non-rubber contents (NRC) present in NRL is given in this chapter under properties of NRL. In order to combat bacterial growth as well as coagulation, NRL is usually preserved with ammonia when harvested from the tree and again after concentration (Esah & Paul, 2002). Preservation is generally achieved

through high or low ammonia-tetramethythiuram disulfide/zinc oxide (HA-TZ or LA-TZ). However, LA-TZ ensures good color, chemical stability and low toxicity (Bala, 2009). Medium of dispersion in the NRL is greatly reduced after concentration so that density of the rubber hydrocarbons is increased to about "60%" (David & Richard, 2002).

While both NRL and synthetic latexes are used for the purpose of academic research works, the later is mostly applied in practice. Meanwhile, due to the prevailing increase in global awareness of environmental issues, a high level of interest in NRL and its derivatives has been triggered. The reason for this is that NRL is a renewable resource, whereas its synthetic counterparts are mostly manufactured from non-renewable oil-based resources. Thus, by virtue of its renewable origin in addition to its higher sticky quality, superior building tack, extremely high resilience, and excellent mechanical characteristics (John, 1987; Schneider, 1997; Kondou, 2006), NRL is chosen for the experimentations that follow in this chapter.

2. Aims of the chapter

This chapter aims at expounding properties, application and performance of NRL as a modifier in cement concrete and mortar. Properties of NRL influencing performance in mechanical and durability functions are dealt with in the first part of the discussion section. Furthermore, influence of high temperature on these two important qualities of concrete; strength and durability was investigated in the subsequent sections. Recent trends in research activities and challenges facing applications of elastomers are provided in the concluding parts of the chapter.

Regarding properties of the NRL relevant to concrete and mortar applications, the clonal lattices involved in the experiments were analyzed for sixteen compositional properties each. In addition, scanning electron microscope (SEM) captions of microstructural units were observed. The objective of these rigorous chemical analyses was to evaluate nature and contents of each substance present in the latexes so that factors affecting performance of each of the latexes when added to the cement-mixes are identified. The SEM on the other hand provides additional information on the structure of the individual phases as well as that of the integrated phase. Eventually, the much desired properties for optimum performance of the latexes in cement-based mixes and developments in the physical structure of the co-matrix systems were noted and concisely reported.

In order to address one of the most important problems affecting elastomerically modified cement concrete and mortar, an in-depth study on the mechanical integrity and durability characteristics of cement-elastomer phase due to changes in temperature was conducted and observations were discussed. In particular, loss in compressive strength and crack formations under high temperatures were assessed. While details on the factors surrounding the excellent roles of elastomers in cement-elastomer co-matrix systems was based on performance assessments, intermolecular softening believed to be caused by the presence of elastomers particularly at elevated temperatures was evaluated through a comparative study between compressive strength test and thermogravimetric analysis (TGA).

Finally, critical limit of performance at elevated temperatures for cement-elastomer systems has been proposed. Parameters considered for the critical limit of performance include content of elastomer in the cement-elastomer co-matrix, temperature margin, degree of degradation entertained and loss in the compressive strength of the hardened phase.

3. Experimentation

3.1. Materials

OPC conforming to BS 12: 1989 was used throughout. Chemical composition and physical properties of the cement are shown in Table 1. Naturally occurring river-washed quartz sand passing through ASTM sieve No. 4 and crushed granite stones with nominal maximum sizes 10 mm are used as fine and coarse aggregate respectively. NRL derivatives which include six clonal latexes and concentrated latexes were involved. Stabilization was achieved through the use of LA-TZ. Latexes were supplied by Rubber Research Institute and Sime Darby Research Center, Malaysia.

Chemical Composition	("%")		
Silicon dioxide (SiO2)	20.1		
Aluminum oxide (Al2O3)	4.9		
Ferrous oxide (Fe2O3)	2.4		
Calcium oxide (CaO)	65.0		
Sulphur oxide (SO3)	2.3		
Magnesium oxide (MgO)	3.1		
Insoluble residue	1.9		
Loss of ignition	1.0		
Lime saturated factor	0.85		
Physical Property	Value		
Surface area (Blaine)	3.14 m ² /kg		
Initial setting time	105 min		
Final setting time	190 min		
Soundness	8.7 mm		

 Table 1. Chemical composition and physical properties of cement

3.2. Methods

Principal operations involved in this section are preparation of specimen for various property assessments, mode of curing regimes and performance tests. Relevant standards are employed for each of the operations and these are spelt out accordingly. Details on mix-design, mixing, casting, demoulding and curing are included.

Batching and mixing were conducted in accordance with BS 1881-125: 1986. Mixing involves careful dispersion of latex into the mixing water followed by overall mixing in a pan mixer

conforming to BS 1881-125:1986. Casting was conducted in accordance with BS 1881-108:1983. Standard steel cube moulds; 100 mm were employed for all specimens. However, 75 mm diameter cored specimens are used as water absorption samples. In fact, coring was diligently carried out in order to avoid visible cracks.

In the case of specimens for chemical attack, two curing mediums containing "5%" sulfuric acid (H₂SO₄) and "2.5%" (Na₂SO₄) each are used as aggressive environments. In order to understand what really happens when concrete is 'cast-in-situ'; where concrete is introduced to the service area during its initial age, specimens for H₂SO₄ were placed into the aggressive curing environment immediately after removal from moulds. However, specimens for Na₂SO₄ were given one month treatment in ordinary water at 23 °C and "80 ± 5%" RH before subjection to the aggressive medium. In fact, in the case of specimens for Na₂SO₄, 72 h air drying at 20 ± 3 °C and "80 ± 5%" RH was entertained before immersion into the diluted curing medium.

Although, air-curing in addition to the moist-curing is necessary for latex-film to develop in the modified specimens, these were given similar moist-curing treatment with the NC. Uniform curing treatment was considered important so that MC do not absorb higher content of the simulated aggressive moisture when immersed into the curing medium. This could obviously render results from the two categories of concrete non comparative.

In the case of morphological observations, samples were cured for 6 months under laboratory atmosphere; 20 ± 3 °C and " $80 \pm 5\%$ " RH. Latex-film was obtained by drying few drops of latex in an oven at 85 °C. The latex-film was also stored under similar laboratory atmosphere until day for testing. Conditioning specimen for SEM observations is necessary in order to expel moisture so that a clear realization of microstructural matrix is achieved.

3.3. Testing program

3.3.1. Chemical analysis

The clonal latexes were analyzed for physical properties and chemical compositional contents. The chemical parameters and respective standards employed in each case are shown in Table 2. However, polydispersity index (PDI) is calculated as the weight average molecular weight divided by the number average molecular weight.

3.3.2. Scanning electron microscopy

JEOL Scanning Electron Microscope JSM 6390 LV was used. Morphologies were obtained at a current and working distance of 15 Kv and 9 mm respectively. Specimens were coated with 10 nm platinum in an 'Auto Fine Coater' before positioning against electron gun. Platinum coating was carried out at 20 mA for about 60 sec.

Parameter	Standard		
Total solid content (TSC)	BS ISO 124:2008		
Dry rubber content (DRC)	BS ISO 126:2005		
Volatile fatty acid (VFA)	ISO 506:1992		
Sludge content (SC)	ISO BS 2005:1992		
Protein content	MS 1392:1998		
Zinc	MS 1449: Part 1:1999		
Copper	MS 1449: Part 3:1999		
Manganese	MS 1449: Part 4:1999		
Iron	MS 1449: Part 5:1999		
Magnesium	MS 1449: Part 6:1999		
Molecular weight (M _w)	BS ISO 16564:2004		
Alkalinity (as NH3)	ISO BS 125:2003		
pH	ISO 976:1996		

Table 2. Chemical analysis and standards

3.3.3. Mechanical properties

Compressive and flexural strength tests were conducted. In addition, compressive strength test was also conducted on specimens after chemical attack and firing. While compressive strength test was in conformity with BS EN 12390-3:2002, flexural strength test was conducted in accordance with BS EN 12390-5:2000. At the end of every curing period, an average of three cubes was taken as the strength of each particular batch.

3.3.4. Water absorption test

Measurement of water absorption was conducted in accordance with BS 1881–122: 1983; 'Method for Determination of Water Absorption'. The cores were kept in an oven for 72 h at 105 ± 5 °C followed by subsequent cooling for 24 h in dry airtight vessels. At the end of drying and cooling processes as described in the standard specimens were immersed in water for 30 ± 0.5 min at 20 ± 1 °C and then weighed. Average water absorption of three cored specimens expressed as a percentage of dry samples is considered as the water absorbed in each particular batch.

3.3.5. Fire endurance

Heating was performed in an automatic furnace with an average temperature gradient of 15.6 °C/min, evaluated from the ratio $(T_f - T_o)/M_t$. Where T_o and T_f are the initial and final temperatures respectively, and M_t represents minutes taken to raise the temperature from 27 °C to 800 °C. However, further heating beyond 800 °C was conducted mainly for the purpose of monitoring disintegration at failure. Heating is terminated once the desired temperature is attained. Specimens are cooled to room temperature (27 °C) in the furnace and then taken out for testing.

3.3.6. Thermogravimetric analysis

Thermogravimetry analyzer, Mettler Toledo TGA/STDA 851e was used for the thermal degradation assessments. Observations were made by raising applied temperature from 25 - 900 °C, with heating rate and flow of nitrogen at 10 °C/min and 10 ml/min respectively.

4. Results and discussions

4.1. Properties of NRL

Properties of NRL influencing cement mixes were obtained through chemical analysis. Table 3 presents results of the six clonal latexes. It is important to note that DRC represents the main hydrocarbon substance sought in civil engineering applications for the purpose of void-filling and latex-film formation in the modified matrix.

The main importance of these results is to identify other properties in addition to DRC which influence performance of the NRL in cement concrete and mortar. This issue was appropriately dealt with after compressive strength assessments on the performance of each of the latexes. Thus, observations were fully discussed in section 4.2.

Parameter	Clonal Latexes						
	KT 3935	RRIM 2015	RRIM 937	RRIM 926	PB 350	PB 260	
TSC ("%")	30.34	33.47	35.43	45.54	33.56	27.20	
DRC ("%")	27.75	31.03	32.64	41.66	31.09	25.39	
Mol. Wt. (u)	3390292	3146156	3141284	3230285	3059752	2863935	
PDI	1.7176	1.6397	1.7535	1.6564	1.6009	1.7485	
VFA ("%")	0.045	0.041	0.285	0.029	0.041	0.038	
Protein ("%")	4.94	3.69	4.19	3.25	4.31	3.81	
Zinc (ppm)	170.8	694.3	702	659.8	266.9	273.7	
Magnesium (ppm)	139.9	101	102.1	100	9.53	9.64	
Copper (ppm)	5.48	4.93	4.62	4.30	8.71	8.10	
Iron (ppm)	3.38	1.97	2.29	1.92	0.97	1.14	
Manganese (ppm)	0.82	0.40	0.09	0.25	0.56	0.51	
Sludge ("%")	0.3368	0.3548	0.1048	0.1032	0.1397	0.1223	
NH3("%")	1.77	1.92	0.36	0.35	0.37	0.37	
рН	11.27	11.45	10.01	10.08	10.15	10.24	

 Table 3. Properties of NRL-clonal latexes

4.2. Influence of compositional properties on compressive strength of concrete

Figure 5 presents results of the compressive strength for concretes modified with the six clonal latexes each. The results were obtained through an addition of "2%" latex/water ratio. However, the compressive strength of the control concrete is 34.87 N/mm². Concretes modified with RRIM 2015 and PB 260 exceeded control concrete by "4%" and "2%"

respectively. On the other hand, concretes modified with RRIM 926 and RRIM 937 yielded lowest compressive strengths values. In fact, RRIM 937 depicted strength reduction of up to "12.4%" when compared with that of control concrete. Differences in the amounts of the compositional substances present in the latexes are believed to be responsible for the variations in the compressive strength.



Figure 5. Compressive strength of NRL concrete due to clonal latexes

Even though, RRIM 937, RRIM 926 and PB 350 contain the highest amounts of DRC but these three latexes gave rise to the least three strength values; 30.54 N/mm², 30.83 N/mm² and 32.48 N/mm² respectively. On the other hand, specimens modified with latexes associated with comparatively low DRC yielded the best three compressive strength results; 32.63 N/mm², 35.55 N/mm² and 36.26 N/mm². Therefore, it could be suggested that what really influences strength is not the actual quantity of DRC, rather, it is to do with other compositional substances.

Close observations on the properties of clonal latexes given in Table 3 in relation with the compressive strength assessment revealed that parameters with strong potentialities of positive impact on the strength are sludge and pH. Conversely, those with high negative tendencies of impairing the strength are VFA and zinc. The rest of the parameters appeared to have little or no impact on the strength evaluations. This could be a result of their insignificant quantities in the NRL.

From the results, RRIM 2015 contains highest sludge content and the concrete modified with this latex yielded the best compressive strength. In addition, KT 3935 and PB 260 with second and third highest sludge contents gave rise to the next two best compressive strength values. On the other hand, RRIM 937 and RRIM 926 which contains least quantities of

sludge were related to the lowest compressive strengths. Thus, higher sludge content seems to favor strength development.

By virtue of the fact that sludge normally consists of fine particles of heavier characteristics especially when compared with hydrocarbon particles, this could lead to void and microstructural fillings as these fine particles occupy spaces between larger aggregate particles in concrete phase. Obviously, this action might result into higher material compaction with eventual increase in the compressive strength of the concrete. However, where sludge is relatively high in quantity its presence in between aggregate particles may cause aggregate particle displacements with eventual decrease in compressive strength. For instance, the use of ready-mixed concrete plant sludge water in making concrete was observed to cause "4-8%" reduction in the compressive strength of control concrete (Chatveera & Lertwattanaruk, 2009).

Considering the pH results, RRIM 2015 and RRIM 937 were observed to have highest and lowest values respectively. Concretes modified with these two clonal latexes depicted first and last compressive strengths accordingly. These outcomes therefore suggest that compressive strength concrete modified with NRL is favored by relatively higher pH values. This could be a result of contributions due to precipitation of metals particularly zinc. In fact, according to Boardman (1999) zinc is amphoteric and the optimum pH it will precipitate is about 9.45. Above this pH, hydroxide precipitates would re-dissolve in an excess of hydroxide ions to form soluble zincates (ZnO₂) and the solubility increases with increase in pH. Therefore, the higher pH values in RRIM 2015, KT 3935 and PB 260 might have aided the solubility of zinc, hence, less precipitation in the form of hydroxides. Thus, the retardation effect on cement hydration due to metal precipitation is minimized under the higher pH conditions.

RRIM 937 with its outstanding quantity of VFA stands a good test for the impact of fatty acids on the concrete strength. Indeed, concrete modified with RRIM 937 yielded the least compressive strength, which indicates strong possibilities that VFA have contributed to its poor performance. Statistically, RRIM 937 suffers "12.4%" and "15.8%" losses in compressive strength when compared with control concrete and RRIM 2015 respectively. In fact, acidic substances are known to harm cement products (Bala et al., 2012; Ali et al., 2005; Bertrona, Escadeillasa, & Duchesn 2004).

Zinc content seems to play a role in the strength decrease observed among the modified phases. For instance, while RRIM 937 and RRIM 926 which contain high zinc contents yielded concretes with the lowest compressive strength values, PB 260 and KT 3935 with low metal contents gave rise to concretes with relatively high compressive strengths. In fact, RRIM 937 depicted "14.1%" loss in compressive strength when compared with PB 260. Thus, presence of metals in NRL appeared to impair compressive strength of the modified concrete. Indeed, in a study conducted on the hydration of tricalcium silicate, zinc seems to be the most severe hydration retardant among the metals considered in the study (Chen et al., 2007).

Even though, protein which is popularly known to exist in NRL basically consists of large molecules of one or more chains of amino acids, but correlating protein contents in the individual latexes with the compressive strengths results, it appears that protein has little or no impact on the strength. Similarly, the trend in compressive strength of the modified concretes does not reflect that of molecular weight distribution among the latexes. Indeed, modified-concretes associated with strong or weak strengths values do not show any preference to high or low molecular weights. However, according to Ramakrishnan (1992), concrete modified with latex of lower molecular weight particles may not have the same strength as that modified with latex of higher molecular weight.

4.3. Performance of NRL on flexural strength of concrete

Figure 6 presents results of flexural strength test. The optimum latex/water ratio was "4%". The corresponding increase percent of this optimum value over control strength was "4.7%".



Figure 6. Effect of latex content on the flexural strength of NRL concrete

Maximum flexural strength was observed at higher latex content when compared with that of the compressive strength. This could be related to the nature of the applied force during test. The applied bending stresses in flexure are invariably causing elongations most especially in the lowermost layers of the section, and this act synonymous to a direct test on the elasticity of the latex-films. Thus the higher amount of the latex became an advantage as it will provide additional elastic capabilities. In fact, strength development in flexural parameters of latex modified concrete as observed by (Ramakrishnan, 1992) is the combined actions of cement hydrate-aggregate bond and elastic strength of latex-films. Furthermore, NRL has been credited for this specialty property, where according (David & Richard, 2002), NRL still dominates rigid elasticity applications such as; production of dipped goods, extruded threads and water based adhesives for its high strength characteristics. However, increase in latex beyond "4%" resulted in significant decrease in the strength, an indication of elastic performance limit by the latex-films.

Another interesting observation arising from these results is in relation to artificial latexes; unlike most of the synthetic latexes where optimum strength can be attained only by adding "10%" or more of latex-cement ratios (Ramakrishnan 1992; Ohama, 1995; Barluenga, 2004; Abdullah, 2008), in this case it can be seen that peak value is readily possible by adding a smaller amount. However, optimum values in mechanical capacities are generally greater when synthetic latexes are used as modifiers. The reason for this is to do with the polymerized contents in synthetic latexes which are usually predetermined as against natural polymerization in NRL.

4.4. Performance of NRL on water exclusion of concrete

Based on the fact that durability relates to the ability of concrete to withstand environmental factors of destruction while serving its purpose, the main gateway to aggressive attack was investigated and the findings were displayed in this section. Moisture being the chief transporter to destructive agents was evaluated in both unmodified and modified phases. Meanwhile, Figure 7 presents SEM captions for NRL, unmodified and modified phases of mortar mixes. These captions revealed the microstructural nature of the material orientation in all the three phases.



(a)

(b)

(c)

Figure 7. Microstructural units: (a) NRL, (b) normal mortar, (c) NRL modified mortar

Microstructural details of the NRL portrayed impervious characteristics which is quite suitable for moisture exclusion. On the other hand, microstructural unit of the normal mortar phase describes the porous nature of the matrix. In fact, hardened cement paste alone is known to have capillaries and pores initially occupied by mixing water. Introduction of aggregates therefore give rise to additional voids through gaps between the larger particles and microcracks. However, inclusion of NRL into the normal mix yielded the fairly cementitious phase shown in Figure 7 (c). Fragments of latex-films are seen scattered on the caption and this shows how blended the mortar was with the NRL.

Indeed, the modified mortar caption suggested a much denser matrix and since presence of voids in the unmodified mix renders the product more vulnerable to aggressive attack,

better moisture exclusion capacity is expected from the modified phase. Figure 8 presents results of moisture absorption of normal concrete (NC) and concrete modified with three clonal latexes. The assessment was based on modification with "5%" latex/water ratio. This percentage was observed as the optimum content of NRL to be added into concrete in order to yield maximum exclusion of moisture (Bala et al., 2012).

In a similar manner to assessments on mechanical properties, modification with clonal latexes also resulted in different levels of water absorption. Furthermore, concrete modified with PB 260 excelled the other two modifications by marked reductions. Even though, this clone has the least DRC, its presence in the concrete however yielded the most effective blockage to the water passage. One obvious advantage which PB 260 has over the other two clones is higher sludge content and this has been manifested in Table 3. Possible effect of sludge in cement aggregate conglomerate has been explained in section 4.2. An important role could be that of void and micro-structural fillings as sludge occupy spaces between larger aggregate particles in concrete phase with eventual increase in water tightness.



Figure 8. Effect of clonal latexes on water absorption of NRL concrete

4.5. Performance of NRL on chemical resistance of concrete

Physical appearance of specimens subjected to H₂SO₄ is presented in Figure 9. The originally gray colour of the specimen was observed to turn white with eroded fragments especially at edges. However, Figure 10 shows compressive strength results of concrete modified with different percentages of NRL after the aggressive attack. From the results, low content of latex has shown mechanical superiority over higher contents. Indeed, modification with "2.5%" latex/water not only exceeded higher modifications in quality but also the NC.

The entire compressive strength values were observed to be low. This was understood to be the consequence of early subjection of specimens into the aggressive curing medium. For instance, at 28 days old, the NC should have reached the designed concrete strength, but the impact of attack coming from the sulfuric acid clearly hindered this normalcy. Instead, strength reduction was registered not only in NC but also among all modifications. In fact, this is similar to real situations where concrete is cast in-situ particularly aggressive environments.



Figure 9. Effect of sulfuric acid on the surface of NRL modified concrete



Figure 10. Compressive strength of NRL-MC due to sulfuric acid attack; 84 days

The improvement associated with "MC-2.5%" is an indication of the impact of NRL at that particular amount. Higher amount appeared to attract severe attack through destruction of latex by the acid. Indeed, physical observations in the event of carrying out experimental processes revealed a high volume change of relatively more than "100%" in the affected latex. Previous findings regarding acidic substances coming into contact with polymeric materials have indicated possible harm on the polymeric Si-O-Al bonds with consequence strength weakening. This is probably the main reason behind the greater strength reductions witnessed in the higher modifications, "5 – 10%" (Allahverdi, 2005).

However, it worth noting that while a positive volume change accompanied the attack on the latex, a negative volume change was entertained in the concrete matrix. Close inspections on the attacked specimens discloses leaching of the cement, gradual disintegration of the fine aggregate particles and protrusions of the coarse aggregates. This indeed correlates the findings of Eglinton (1987), where the author pointed out that the action of acids on Portland cements is to leach calcium hydroxide from the cement paste. Thus, when the acid first comes into contact with the concrete it reacts with the calcium hydroxide of the cement to form calcium sulfate, or gypsum which then attacks the hydrated calcium aluminates to give ettringite. Meanwhile, in the present case, measurement on weight change was generally obscured as the expanded latex contains moisture which compensates for the lost in cement and fine aggregate particles.

Figure 11 shows the compressive strength results of concrete subjected to sodium sulfate environment. Unlike in the sulfuric acid test, the compressive strength values of all specimens were comparatively higher. In this case, higher strength values were observed due to mainly the initial normal curing of 28 days given to specimens before immersion into the simulated sodium sulfate environment. Also, contrary to the foregone assessment, all modifications were observed to yield greater strength values than the NC. But, just like the previous case, lower latex content ("1.5%") proves to be the best modification. Usually, the optimum content for maximum compressive strength is less than "2%" depending on the concentration of the NRL (Bala, 2009).



Figure 11. Compressive strength of NRL-MC due to sodium sulfate attack; 84 days

Superior performance observed in NRL modified concretes was a result of the inclusion of the elastomer. Thus, as the latex coats the aggregate and blocks the passage of the Na₂SO₄ particles into the hardened paste, development of expansive forces from high volume increase which normally evolves when calcium sulfate reacts with tricalcium aluminate was discouraged (Vedalakshmi et al., 2005). In fact, while sign of attack in the form of leaching

was manifested on the surfaces of specimens subjected to acidic environment, similar sign has not been witnessed on the surfaces of specimens introduced into the sulfated environment. In other words, surface erosion does not occur in the later. Henceforth, variations in weights of specimens at the end of the curing exercise were also noticed to be insignificant.

4.6. Performance of NRL concrete at elevated temperatures

Physical appearances of specimens during the entire heating range (27 – 1300 °C) are shown in four stages in Figure 12. Prior to heating, the specimens are perfectly cubic in shape with smooth surfaces and straight edges. However, during the process of heating many physical changes took place. These include colour changes, crack formations, distortions and spallings. Indeed at 1300 °C, the concrete is not only so week to be tested for compressive strength but also not strong enough to resist pressure from forefinger and thumb as indicated in the disintegration stage.



Figure 12. States of concrete in the process of firing; (i) before firing, (ii) during firing, (iii) after firing, and (iv) disintegration

Compressive strength test results after heating at various temperature levels particularly within 27 – 800 °C are presented in Figure 13. Continuous increase in temperature is seen to

have caused corresponding decrease in compressive strength to both categories of concrete. However, least drop in the compressive strength was entertained by NC and the highest was associated with "MC-10%". In fact, the more the latex percent added into the concrete the higher the strength loss. From this, it shows that inclusion of latex into concrete has a negative impact on the compressive strength of concrete at elevated temperatures and the impact increases with increasing latex content.



Figure 13. Effect of high temperature on compressive strength of NRL modified concrete

"MC-1.5%" surpassed NC by "6.8%" at the initial stage and this superiority was maintained up to 300 - 500 °C where the MC dropped below NC. The temperature at the intersection point between NC and "MC-1.5%" was about 390 °C. Thus, the critical limit of superiority of NRL-MC over NC is 390 °C. Nevertheless, up to 500 °C the difference in strength between these two categories is only "4.4%", which may be considered as insignificant.

Categorically, NRL-MC suffered more strength loss than NC. The main reason behind higher strength depreciations in the NRL-MC could be the early degradation of the latexfilms which gives rise to undue formation of unacceptable cracks during the compression test. To this regard, the temperature limit at which these cracks were formed was postulated to be related to the superiority limit of "MC-1.5%" over NC as indicated in Figure 13. Eventually, the temperature limit was realized to be about 390 °C. However, this hypothesis was investigated further using TGA.

Thermal degradations which accompanied temperature rise in latex-film and cement-latex blend are presented in Figure 14. While the latex-film in its entity suffers a single major weight loss, the cement-latex blend entertained relatively two minor and one major weight losses as witnessed in its TGA. Latex-film lost more than "95%" of its weight within 340-460 °C. This marked the softening point and the main degradation limit of NRL. The remaining decomposed content afterwards represents the filler. Previous works have also indicated similar weight losses in polymeric substances at temperatures above 300 °C. For instance, more than "95%" weight loss was observed on polyethylene between 380 and 510 °C (Zhengzhou et al. 2003).



Figure 14. Thermal degradations of HCP and NRL-film

On the other hand, the TGA presented by cement-latex blend also entertained its major weight loss within the range 350-430 °C. This forms an interesting part of the result since it indicates the impact of the blended latex. Indeed, out of the overall weight loss of about "39%" as witnessed in the blend, this degradation was observed to be about "29%", which amounts to "74%" of the overall degradation. This amount of degradation could possibly be the main factor responsible for the significant fall in the compressive strength of MC at temperatures within 300-500 °C.

This observation was further strengthened by the fact that the mean of the temperature at which the sudden weight loss was registered in the cement-latex blend (350-430 °C) is 390 °C, a temperature value which corresponds to the superiority performance limit of MC over NC. In other words, cement-latex blend lost much of its strength at the softening point of the NRL. Therefore, the critical limit of performance of elastomerically modified cement mix should be expected at the softening point temperature of the latex involved.

4.7. Recent trend in research activities and challenges facing applications of elastomers

The act of directing great sources of power in nature for the benefit of man has been described as 'Civil Engineering' (Navin, 2000). Since the beginning of this profession several

efforts have been made by research individuals, groups, private organizations and statutory parastatals in order to identify materials of potential qualities. Consequently, numerous materials have so far been classified as civil engineering materials, particularly in the last three decades during which the profession experiences dramatic changes in the way of thinking about process engineering, modification technologies and innovative material evolutions. Thus, construction industry is already in a new era where not only there exist interest in the expansion of mankind's frontiers enabling new technologies to be developed, but also the need for a harmonious co-existence with the eco-sphere through optimization of material technology and infrastructural creativity, so that a healthy life in harmony with nature is fully enforced.

Indeed, the cement industry, in its effort towards evolving befitting products for the new era has taken a positive step by developing 'eco-cement', a product that helps to clean the environment by utilizing municipal solid wastes in its manufacture and is even said to have the potential of absorbing carbon dioxide (CO₂) from the environment as it hydrates (Ampadu & Toni, 2001). However, even before the concept of eco-cement is matured enough to make impact in the present world of advancing technology, global worries over the existing environmental threats, have triggered a tremendous force towards the search for eco-friendly materials in all respects. Thus, frantic efforts towards inclusion of eco-friendly materials into OPC mixes originated from the rising concern and worries over environmental degradations such as; global warming atmospheric pollutions and waste disposals. These coupled with the recent worldwide economic recession have indeed strengthened the inspiration for the continuous efforts towards the search for durable and sustainable infrastructures [Walter, et al., 2004; Dionys, 2007].

At present, the act of directing great sources of power in nature has dramatically turn to redirecting waste materials as well as agricultural byproducts to construction materials. Even though, polymers have contributed immensely on the performance of cement mixes but the rush towards consuming waste materials and agro-based substances may open an entirely new challenge to the world of polymer concrete. Meanwhile, pozzolans from agricultural waste are receiving more attention since their uses generally not only improve the properties of the blended cement concrete but also reduce the environmental problems.

Therefore, sooner or later, research activities in the world of polymer concrete may face compounding challenges. According to Lech (2006) the search for new research simulations and applications of polymeric substances is still essential in order to make their improvements more efficient and reliable. Like other advanced materials, polymeric substances need reliable theories based on firm scientific findings. In fact, elastomers which currently dominate construction applications are no exception in the dear need for scientific knowhow on their performance. This, together with the possible chemical metamorphism which could erupt when cement, elastomer and agricultural byproduct intermingled together in a single co-matrix system needs intensive investigations.

5. Conclusions

In this chapter, properties, application and performance of elastomers in cement mixes have been investigated. In particular, the roles of NRL in the two major properties of concrete; strength and durability have been examined. Based on the experimental framework adopted in this investigation, the following conclusions were drawn:

- Inclusion of NRL in concrete enhances its performance especially durability functions such as water tightness and chemical resistance. The improvement was achieved mainly through void and capillary fillings of the cis-1,4-polyisoprene particles.
- The dry rubber content of NRL is not the major factor responsible for strength development in modified concrete. Instead, sludge content and pH value are the chief factors contributing to strength development in the cement concrete.
- NRL consists of some non-rubber substances which are likely to cause damage to the mechanical properties of concrete. The chief substances causing strength impairment are volatile fatty acids (VFA) and metals particularly zinc.
- SEM captions expose the microstructural details of latex film, hardened cement paste and cement-latex co-matrix. Presence of latex in the hardened cement paste transforms the initially porous phase to a more cementitious matrix.
- Deterioration of concrete due to chemical attack, particularly those from acidic and sulfated environments is discouraged by the inclusion of NRL. However, efficiency of the latex was observed to be higher in sulfated environment rather than acidic.
- The critical limit of performance of NRL concrete at high temperatures was observed to be about 390 °C. Meanwhile, TGA result has shown that NRL softens and degrades to about "5%" at similar temperature. Therefore, as the NRL softens at this temperature significant loss in the compressive strength of the NRL modified concrete was observed.

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