

Influence of Castor Oil-Based Polyurethane on Physico-Chemical Properties of Calcium Silicate Cement

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Polyurethane from castor oil and toluene diisocyanate was activated in the presence of calcium silicate cement paste, with varying equivalent free isocyanate (NCO) to equivalent free hydroxyl (OH) moiety and cement to water ratio. It was shown that as the NCO/OH ratio and percent cement mixture were increased, the compressive strength and bulk density of the obtained polymer-modified calcium silicate cement materials improved significantly. The increase in the strength and density is explained by low porosity and the presence of polyurethane hard segments in the polymer structure. Moreover, the powder x-ray diffraction and surface morphology investigations of the castor oil-based polyurethane-reinforced cement composites revealed the interpenetration of the polymer macromolecules in the cementitious matrix. The Ca^{2+} from the portlandite phase was readily available to react with the hydroxyl groups from the polyurethane macromolecule and excess monomer resulting in calcium oxide-terminated diisocyanate.

Key Words: calcium silicate, castor oil, composite, polyurethane-reinforced cement

INTRODUCTION

One of the most widely used construction materials includes conventional cement and concrete. The materials have low flexural strength and failure strain as well as susceptible to chemical damage in spite of their good physical properties and relatively low cost. This problem can be solved by fabricating composite material wherein an organic polymer is added to the inorganic cement powder. The two different phases are continuously interpenetrated and can be optimized for producing lightweight components with interesting potential applications in the field of non-structural and construction materials (Verdolotti et al. 2008).

Polyurethanes (PUs) are commonly used as diffuse plastic materials in the construction industry and its addition to a

cement mixture can significantly enhance the properties of the polymer-modified cement-based composite (Chung 2004; Yang et al. 2004). There is an observed increase in the hardness, modulus of elasticity, and compressive strength of the polymer-impregnated cement (Odler et al. 2003; Zhong et al. 2002; Sujjavanich et al. 1998). Moreover, the presence of polymeric foam offers the advantage of improved resistance to corrosion, reduced water permeability and controlled rheology as well as stabilization of the cement slurry against segregation (Rastoul et al. 2003; Singh et al. 2001). Polyurethanes belong to a diverse family of important polymer materials with end use ranging from cast and thermoplastic elastomers, adhesives and coatings, to flexible and rigid foams (Oertel 1994).

The properties of polyurethane are dependent on certain factors such as the content of the reactive groups, the

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degree of crosslinking, and the entanglement of the reacting monomers. The polymer material is mainly produced by the isocyanation of diisocyanate (NCO) with polydiol (OH) of various molecular weights (Hepburn C 1992). It is possible to change the properties by using the same polyisocyanate with different polyols while maintaining a constant NCO to OH ratio or by utilizing the same polyol with variation in the quantity of the polyisocyanate. Castor oil-based polyurethane, which is a trifunctional polyol derived from a natural and renewable source material offers several advantages such as strong mechanical strength, easy handling, and strong resistance to water and ultra-violet rays (Claro Neto 1997).

In this investigation, the effect of castor oil-based polyurethane on the physico-chemical properties of calcium silicate cement was evaluated. The polymerization reaction was in contact with the actual cementitious powder during mixing process. The interpenetration of the polymer macromolecules into the inorganic cement matrix was explained through the observed surface morphology and chemical structure of the composite material. An improvement in the compressive strength and bulk density of the composite was determined with respect to the variation of the NCO/OH ratio in order to produce a lightweight hybrid polymer modified cementitious material.

MATERIALS AND METHODS

Ordinary portland cement (ASTM Type I) was used in this study. Commercial castor oil was utilized without further modification. Toluene diisocyanate (TDI) used in the polyurethane synthesis was donated by Resins Incorporated.

The type I portland cement was dissolved in distilled water and mixed with the castor oil while in continuous stirring. The mixture was reacted to toluene diisocyanate, after which the material was transferred into the mold and allowed to cure for 24 hours. The product was removed from the mold and again aged for another 24 hours. The synthesis of polyurethane was based on a 1:1 and 2:1 proportion (with the equivalent free NCO to equivalent free OH moiety). Figure 1 shows the general scheme involving the reaction of polyurethane (Khatu et al. 1997).

The amount used to produce the composite was based on the percent weight of the constituents. The different composition of the mixtures is shown in Table 1, following the factorial design of experiment with three replications for the response variables. Compression strength (ASTM C109-93 modified) and bulk density (Archimedes' Principle) measurements were determined for the obtained polymer-reinforced cement materials. Scanning electron microscopy (SEM) with electron backscattered diffraction images for surface morphology were obtained using Carl Zeiss ULTRA Plus and Leica S440. Powder x-ray diffraction (XRD) measurements for phases determination were carried out using Shimadzu XRD-7000.

Table 1. Composition of the mixtures.

Sample	TDI (%w/w)	Castor Oil (%w/w)	Water (%w/w)	Cement (%w/w)
PUa _{1:1}	40	40.1	10	9.9
PUB _{1:1}	37.9	38.1	10	14
PUC _{1:1}	36	36.2	10	17.8
PUa _{2:1}	53.3	26.8	10	9.9
PUB _{2:1}	50.6	25.4	10	14
PUC _{2:1}	48.1	24.1	10	17.8
Control	0	0	25	75

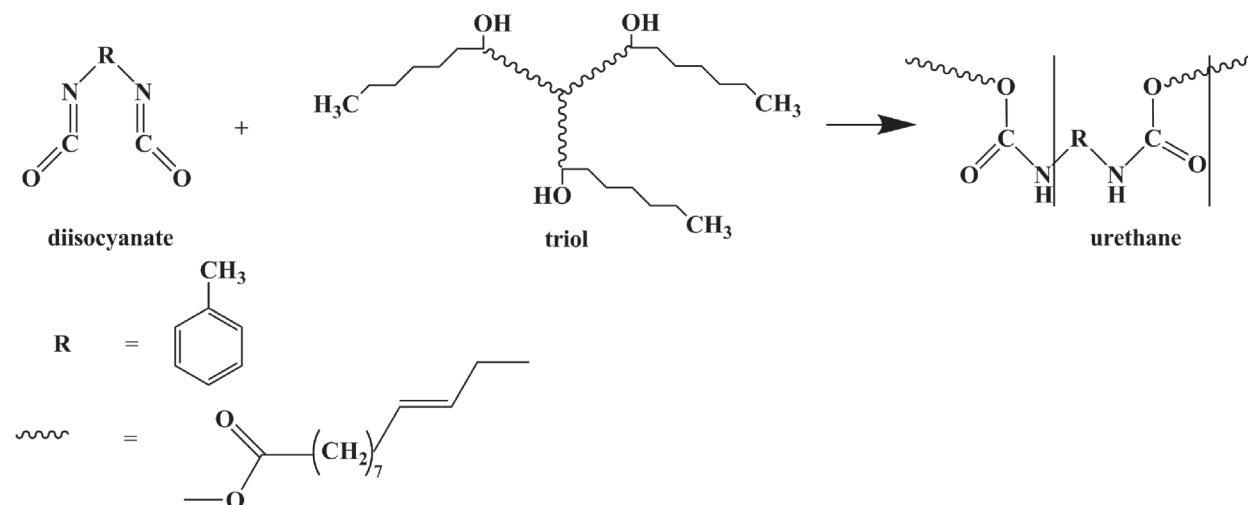


Figure 1. General reaction of diisocyanate with triol to form urethane linkage.

RESULTS AND DISCUSSIONS

The colloidal surface of the solid and porous phases of calcium silicate hydrate generally dominates the structure of hardened cement paste as shown in Figure 2A. Some exhibit platy crystallites for the ettringite phase (Figure 2B) and hexagonal-prism morphology for the portlandite

phase (inset Figure 2B). Using the backscattered electron imaging mode of the SEM, the surface morphology of the polymer macromolecule from the obtained castor oil-based polyurethane-reinforced cement material is clearly differentiated in the cementitious matrix (Figure 2D).

Scanning electron microscopy analyses of the composite

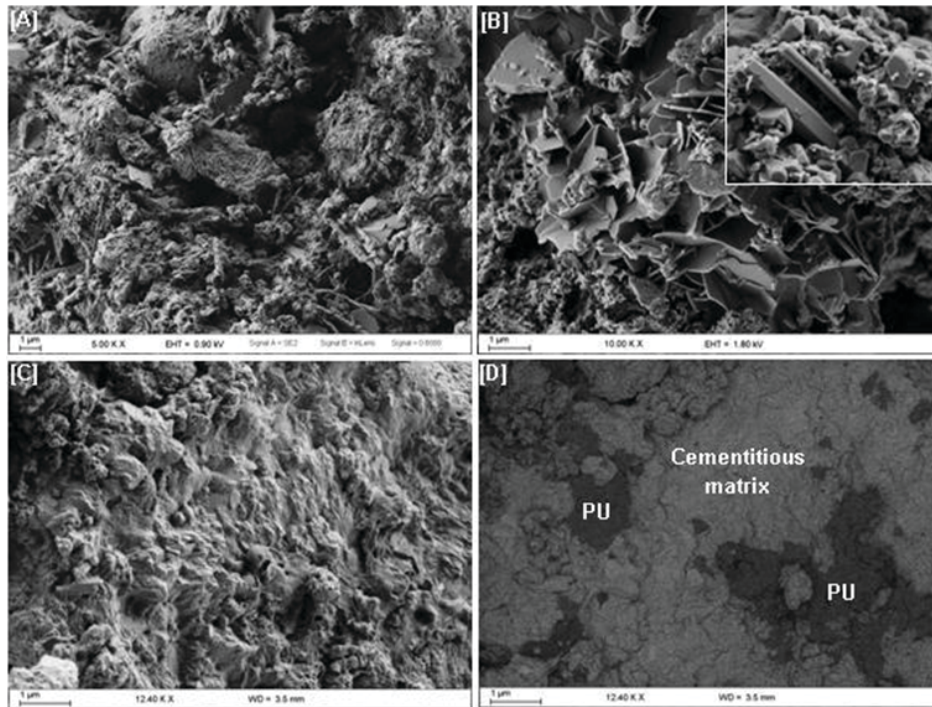


Figure 2. SEM morphology of cement (A & B) and representative sample of polyurethane-reinforced cement composite (C) with its corresponding backscattered electron imaging mode showing the contrast of the polymer macromolecule in the cementitious matrix (D).

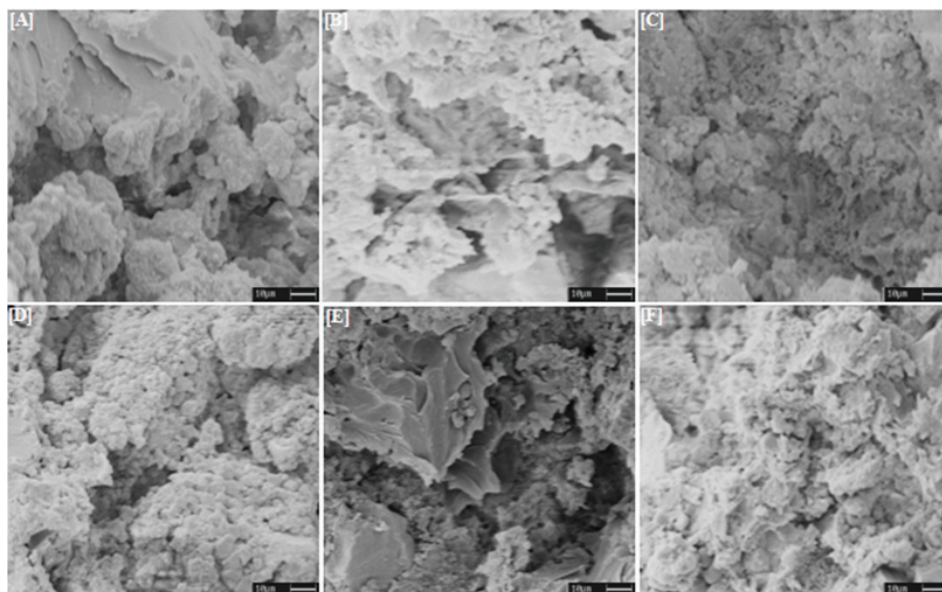


Figure 3. SEM morphology (2000X) of polyurethane-cement composite samples (A) PUa_{1,1}, (B) PUB_{1,1}, (C) PUC_{1,1}, (D) PUa_{2,1}, (E) PUB_{2,1}, (F) PUC_{2,1}.

material at different proportions shown in Figure 3 further revealed that an increase in cement content and NCO/OH ratio resulted in a more compact surface structure. This is due to less availability of the water which serves as a foaming agent in the polyurethane reaction. The water is absorbed and causes hydration of the calcium silicate cement. The reaction of water with the isocyanate component results in the production of carbon dioxide. Along with the heat generated due to the exothermic nature of the reaction, it helps in expanding the foaming reactants, thus giving the foam its cellular or porous structure (Herrington et al 1998).

Increasing the cement content led to a lesser foaming of the polymer phase, resulting in the production of more compact structure of the obtained composite material. The polyurethane-reinforced cement paste has shown that the densification of the calcium silica hydrates was significantly modified by the presence of the polymeric material.

Table 2 shows the data on the compression strength and bulk density corresponding to the treatment combinations of the castor oil-based polyurethane-reinforced cement material. Based on the given data, the relationship of the average values of the two responses is derived and shown in Figure 4. It was observed that an increase in the NCO/OH ratio and the amount of cement to water mixture resulted in a significant increase in the compressive

Table 2. Data for the compressive strength and bulk density corresponding to the treatment combinations.

Sample	Compressive Strength (MPa)			Bulk Density (kg/m ³)		
	R ₁	R ₂	R ₃	R ₁	R ₂	R ₃
PUa _{1:1}	11.94	10.54	10.63	350	345	349
PUB _{1:1}	13.43	12.82	12.21	525	513	349
PUc _{1:1}	14.58	15.01	13.88	530	536	539
PUa _{2:1}	12.38	12.18	12.73	410	415	408
Pub _{2:1}	18.09	18.44	17.13	862	859	856
PUc _{2:1}	16.59	15.9	15.54	528	531	531
Control	22.46			1882		

strength and bulk density. The corresponding regression equation between the compressive strength and bulk density of the polyurethane-modified cement composite is $y = 0.013x + 7.258$, with the coefficient of determination value R^2 of 0.86.

The relationship of the compressive strength to the bulk density of the obtained material can be attributed to the porosity and the air void content coming from the foaming activity of the polyurethane reaction. There has been a decrease in the porosity or presence of voids in

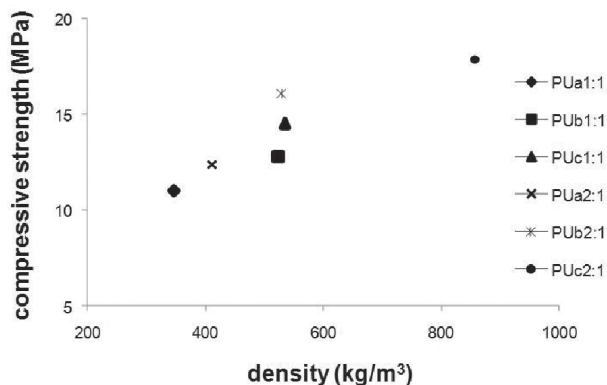


Figure 4. Compressive strength and density of the polyurethane-cement composite at different compositions.

the morphology of the obtained polyurethane-modified cement composite, as confirmed by the scanning electron microscopy analyses, with respect to an increasing compressive strength and bulk density properties. The influence of the higher amount of isocyanate also translates to higher amount of hard segments in the polymer chain. Hard segments existing between urethane linkages impart stiffness in the polymer chain. Having a high density of urethane groups causes polymer macromolecules to become more rigid (Mythili et al. 2004).

Table 3 shows the analysis of factorial design for the two response variables. A negligible p-value of the main effects and the interaction for both compressive strength and bulk density is a strong indication that the NCO/OH and cement to water ratio have a significant influence on the physical

Table 3. Analysis of variance for the compressive strength and bulk density of the obtained polyurethane-modified cement composite.

Compressive strength					
Source	DF	SS	MS	F	P
NCO/OH	1	31.84	31.84	89.54	0.000
Cement/H ₂ O	2	60.37	30.18	84.88	0.000
NCO/OH*Cement/H ₂ O	2	3.64	1.82	5.12	0.025
Error	12	4.27	0.37		
Total	17	100.12			
Bulk density					
Source	DF	SS	MS	F	P
NCO/OH	1	103361	103361	63.79	0.000
Cement/H ₂ O	2	309503	154751	95.50	0.000
NCO/OH*Cement/H ₂ O	2	66925	33462	20.65	0.000
Error	12	19445	1620		
Total	17	499233			

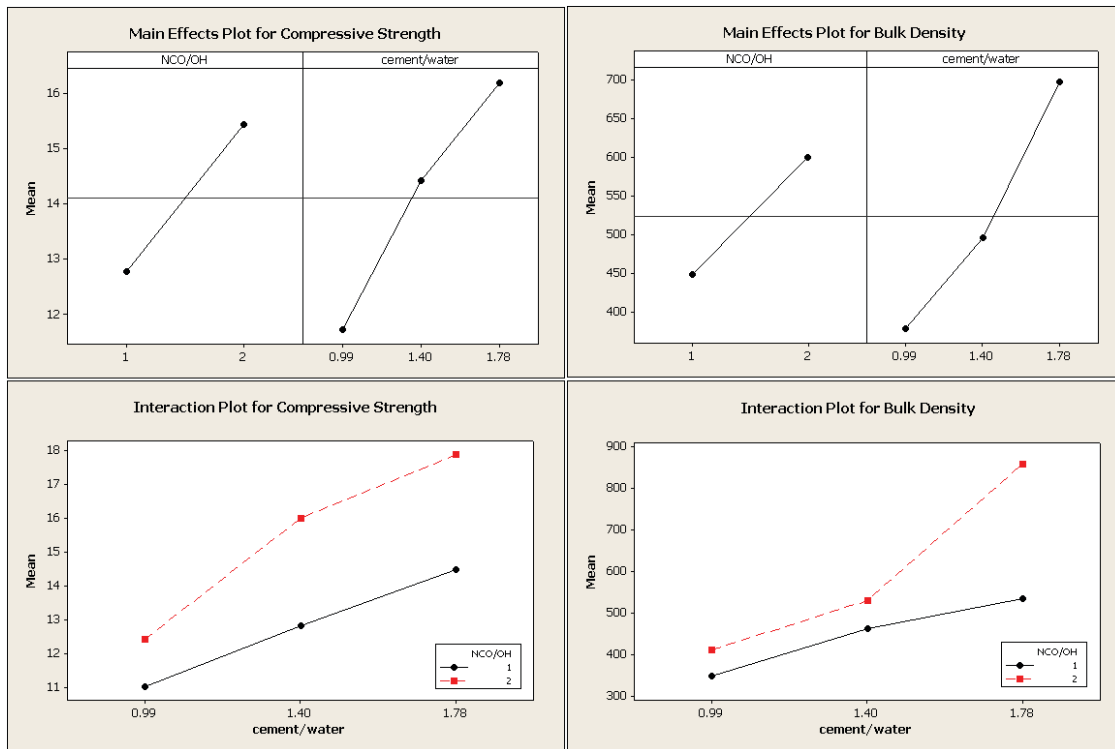


Figure 5. Plot of the main and interaction effects for compressive strength and bulk density.

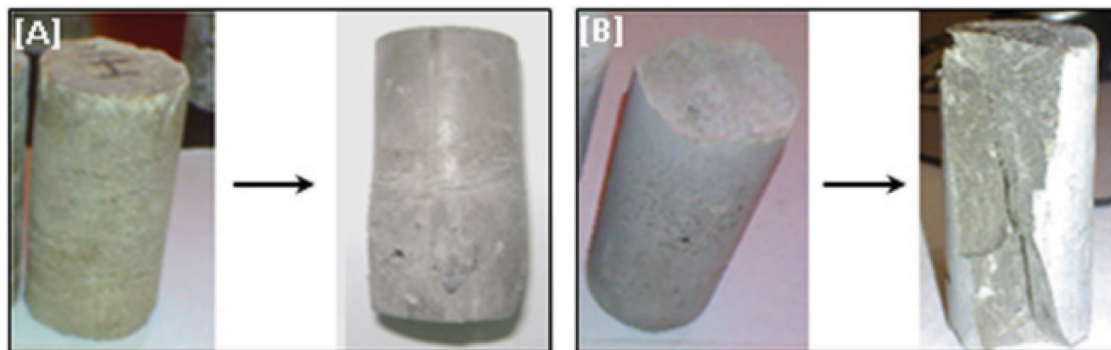


Figure 6. Fracture behavior for the polyurethane-cement composite (A) and pure cement (B).

properties of the obtained material. Figure 5 shows the plot for the main and interaction effects. The regression equations for the two responses were also derived:

$$\text{compressive strength} = 2.27 + 2.66 \text{ NCO/OH} + 5.65 \text{ cement/water}$$

$$\text{bulk density} = -260 + 152 \text{ NCO/OH} + 400 \text{ cement/water}$$

The strengthening mechanism of the polyurethane-modified cement material can be explained through the interpenetration of the polymer macromolecules in the cementitious matrix. Any propagation of microcracks in the cementitious matrix will be hindered by the polymer phase. Thus, the presence of polymer network further strengthens the bond strength between the silica grains and the hydrosilicate gel (Ismail et al. 1998). This is very

evident in the fracture deformation of the castor oil-based polyurethane-reinforced cement composite unlike of the pure cement of which the latter loses its material after fracture as shown in Figure 6.

The results of x-ray diffractogram evaluation in Figure 7 showed the formation of various crystalline phases associated with the different components of the calcium silicate cement and the hydration products. The most prominent peaks in the hardened cement paste material were tricalcium silicate (C_3S) at 29.4° , 32.5° , 39.3° , 43.1° , diffraction angles and dicalcium silicate (C_2S) at 22.9° , and 32.2° . Portlandite, which is essentially a calcium hydroxide $Ca(OH)_2$, was identified at 18° and 47.3° . The peak of ettringite was also observed at 34° .

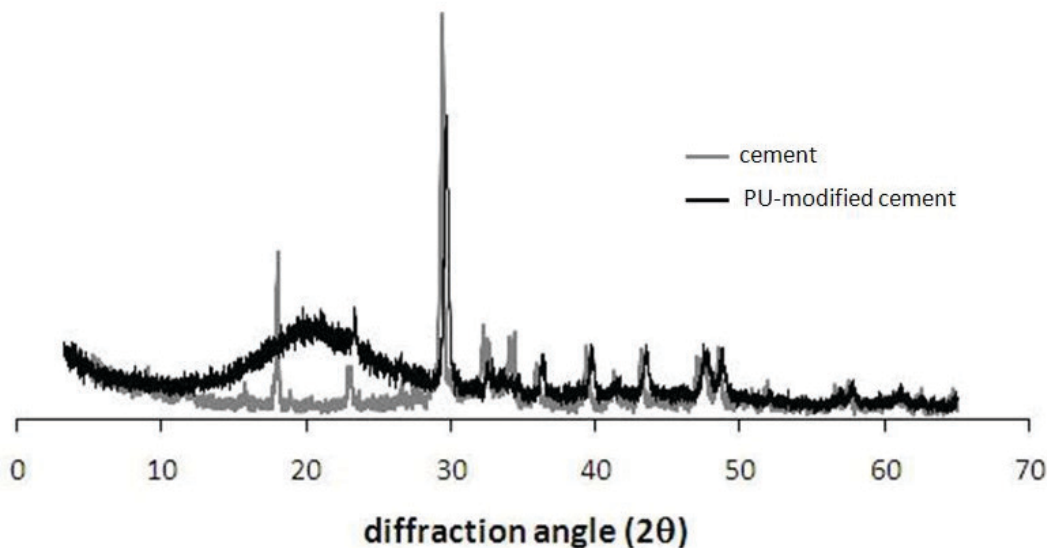


Figure 7. XRD patterns of pure cement and representative sample of the obtained polyurethane-cement composite.

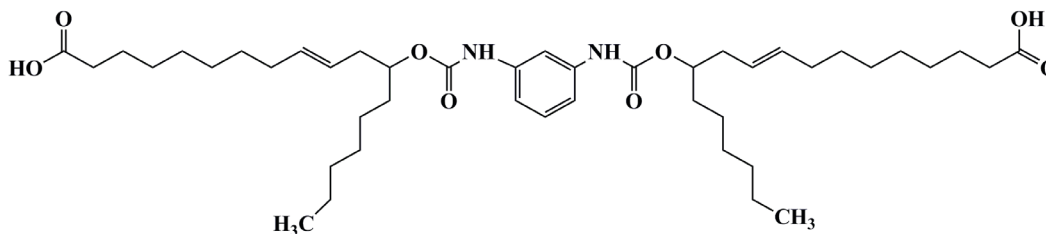


Figure 8. TDI-castor oil polyurethane backbone.

Table 4. Reactions of cement hydration (x represents chemically bound water content) and between portlandite and diisocyanate.

Cement Hydration Reactions					
$3\text{CaO}\cdot\text{SiO}_2$ <i>tricalcium silicate</i>	+	$(1.3 + x)\text{H}_2\text{O}$	\rightarrow	$\text{CaO}_{1.7}\cdot\text{SiO}\cdot\text{H}_2\text{O}_x$ <i>calcium hydrosilicate</i>	+ $1.3\text{Ca}(\text{OH})_2$ <i>portlandite</i>
$2\text{CaO}\cdot\text{SiO}_2$ <i>bicalcium silicate</i>	+	$(0.3 + x)\text{H}_2\text{O}$	\rightarrow	$\text{CaO}_{1.7}\cdot\text{SiO}\cdot\text{H}_2\text{O}_x$	+ $1.3\text{Ca}(\text{OH})_2$
Reactions between Portlandite and Diisocyanate					
$\text{Ca}(\text{OH})_2$		\leftrightarrow		$\text{Ca}^{2+} + 2\text{OH}^-$	
				<i>in cement water</i>	
$2\text{Ca}^{2+} + 4\text{OH}^-$	+	OCN-R-NCO <i>toluene diisocyanate</i>	\rightarrow	$\text{Ca}^{2+}\cdots\text{O}-\text{C}(=\text{O})-\text{R}-\text{N}(\text{C}=\text{O})-\text{O}\cdots\text{Ca}^{2+} + 2\text{H}_2\text{O}$	

There was a broadening of the peak width at 20° for the polyurethane-modified cement material compared with pure cement. This peak change may correspond to the interaction of the polyurethane to the portlandite phase. The reduction of the intensities of the different phases of calcium silicate gel resulted in the incorporation of the polyurethane phase in the cementitious matrix.

When portland cement is mixed with water, the hydration leads mainly to the formation of calcium hydrosilicates (CSH), portlandite, and sulfoaluminates, such as ettringite and other precipitates (Taylor 1997). Moreover, upon addition of the toluene diisocyanate in the cement pastes with castor oil, the reaction to form the urethane linkage between the diisocyanate and hydroxyl groups proceeds.

The toluene diisocyanate-castor oil polyurethane backbone is shown in Figure 8.

Dissolution of ions from the phases present within the cement grains in water occurs. Concentration of certain ionic constituents, such as calcium (Ca^{2+}) and hydroxide ions (OH^-) increases to a sufficient level at the time of induction period in order to favor the nucleation of calcium hydroxide. This subsequently encourages further dissolution of Ca^{2+} and OH^- ions into the solution before reaching supersaturation (Jawed et al 1983; Dalglish et al 1982). Due to the dissolution of calcium hydroxide ions, it is hypothesized that this in turn opens the possible reaction of Ca^{2+} with the hydroxyl anions from the polyurethane macromolecule backbone and the excess toluene diisocyanate to form a calcium oxide-terminated diisocyanate.

The interaction of the cement phase in the polymer with its degree of short-range order of molecular chain arrangement resulted in the broadening of the peak in the diffraction pattern at 20° for the polyurethane-modified calcium silicate. The simplified chemical reactions describing the hydration process of a cement powder and the reactions between the portlandite with the toluene diisocyanate are presented in Table 4.

CONCLUSION

Increasing the amount of castor oil-based polyurethane when incorporated in the calcium silicate cement was effective in increasing the compressive strength and bulk density of the polymer-reinforced composite material. The polymer macromolecule is interpenetrated in the cementitious matrix due to the hydrogen bonding between the hydroxide anions from the calcium hydroxide and the hydroxyl group from the castor oil-based polyurethane backbone. Given the versatility of the castor oil-based polyurethane in the composite material, it is possible to tailor the properties of the polymer-modified cement by changing the amount of cement and molar ratio of NCO/OH in order to attain specific applications as lightweight structural and non-structural materials.

ACKNOWLEDGMENT

The authors acknowledged the financial assistance of the University of the Philippines Engineering Research and Development Foundation Incorporated (UP ERDFI) through the Faculty Research Incentive Award (FRIA). The help and support of Willie Bisquera was highly appreciated and valued.

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