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## Replacing Limestone and Linseed Oil in the Synthesis of Putty

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**Abstract:** Putty is a fairly cheap product widely used to act as a “glue” for fitting glass to frames. It is commonly prepared from any cheap limestone (LS), mixed with raw linseed oil (LO) before being applied as a soft amorphous mass. Fly ash (FA) and used cooking oil (UCO) are two waste products that could possibly be utilized for the same purpose as LS and raw LO. The use of these two materials in the preparation of putty was therefore investigated. Various mixtures of LS, FA, LO and CO (virgin and used) were prepared and kept under lab conditions or UV light. Virgin CO was acidified with conc HCl before being mixed with FA or LS. The addition of CaO (1% m/m) as a possible catalyst was also investigated. It was found that temperature and UV radiation did not accelerate the hardening of the putty to a significant extent. Used and acidified cooking oil mixed with fly ash instead of limestone yielded putties comparable to the current commercial product. FT-IR spectroscopy was employed to follow the changes in the materials with the time. Spectra were recorded at different periods after mixing the samples and normalized on the carbonyl group band. However, no qualitative distinction between the two oils used for making up the putty mixtures could be achieved with the IR spectra. Fly ash and limestone could be distinguished from each other and in the mixtures they were used. Mass loss tests together with thermogravimetric analyses were carried out for different mixtures as well as LO, CO, FA and LS alone, to try and find a quantitative method to measure the components in any one particular mixture. Good agreement between experimental and calculated values were obtained in all but one of the samples investigated. Mechanical features of the samples were investigated by measuring penetration with a Vicat needle at selected times. With at least two of the samples penetration behaviour comparable to that displayed by the commercial product was observed. The work showed that waste products could be used to manufacture a useful material with similar performance and behaviour as the current commercial one and thus created an alternative application for materials that would otherwise have to be disposed of.

**Key words:** Putty, fly ash, cooking oil, limestone, linseed oil

### INTRODUCTION

Putty is a cementing material, which is used to secure sheets of glass in sashes, to fill nail holes and to stop crevices in woodwork. It is made of limestone (LS, finely powdered whiting) and boiled linseed oil (LO). Putty is a very-well known commercial product. For example, in the beginning of the last century, about two dozen recipes for putties, lutes, or cements appeared to be used in the filling of worm-holes, wind-shakes, splits and similar imperfections in wood. They were made mainly of different binders (rye flour, varnish, glue, etc.) and various fillers (chalk, paper pulp, sand, dust, etc.) (Kirk, 1993).

Proper putty should roll freely in the hands without exuding oil. Synthetic glazing and filling compounds have supplemented putty in many applications. The name putty is also applied to substances resembling putty, such as red-lead putty, mixtures of red and white lead and linseed oil. Certain dough-like plastics are also called putty. Drying oils and varnishes made from them, used to be the primary vehicles for paints, artists colours, printing inks, oil cloth and linoleum. Since the 1920s, drying oils have increasingly been replaced by other film-forming materials. Drying oil putties have been replaced to a large extent by glazing compounds made with polybutenes and polysulfides.

Today, putty is a broad term used for adhesive materials. It is used in many different applications such as: anti-corrosive putty for concrete and metals; electrical conductive putty; aqua putty with cold and heat resistance; putty powder for high strength emulsion paints, etc. Different materials can be involved in manufacturing of putties. Some of these putties (prepared from different materials) include (SANS, 1979):

- Putty based on powder metal matrix and chopped glass fiber and epoxy resin binder,
- Putty containing hydroxy or carboxy terminated liquid rubber,
- Unsaturated polyester resin putty,
- Machinable polymer alloy putty, etc.

Sunflower oil and cooking oil (CO) have the necessary unsaturated bonds to be used instead of LO in the manufacture of putty. Fly ash containing fine particles is cheap enough to use as a filler. The free lime in the fly ash furthermore has the potential to catalyse polymerization reactions through the action of the calcium ion. This is known to occur in the thickening of paints through the catalyzing effect of heavy metal cations (Rees, 1998). Thus two waste products can be potentially transformed into a useful commercial product.

Fly ash (FA) is defined as the powdery residue obtained by separation of the solids from the flue gases of furnaces fired with pulverised coal (SABS, 1989). Pulverised fuel ash (PFA) is the generic name given to the ash that arises when boilers are fired with pulverised coal. Mineralogically, the major non-crystalline component of FA is a silica-alumina glass, while the major mineral components are mullite, quartz, ferrite, spinel and lime, with minor amounts of hematite and portlandite (Kruger, 1999). If FA contains a sufficient amount of free lime (calcium oxide or calcium hydroxide), it may slowly develop some strength on its own (Nbri, 1984). Fly ash is normally used as a pozzolanic addition or mineral admixture to cement and concrete (Sear, 2001; Anonymous, 1996), a raw meal constituent in the manufacturing of cement (Canpolat *et al.*, 2004; Sahu and Majling, 1994) or as a filler in the polymer/plastics industry (Saxena and Parbhakar, 2000; Kruger *et al.*, 2001).

Linseed oil oxidizes easily upon exposure to atmospheric air, forming a tough organic film in the so-called drying process. This reactivity of the oil results from the esters of fatty acids with two or more non-conjugated double bonds separated by a single methylene group-CH = CHCH<sub>2</sub>CH = CH-, or those with two or more conjugated double bonds. The most common unsaturated fatty acids are linoleic ((Z,Z)-9,12-

octadecadienoic acid) and lineleic acid ((Z,Z,Z)-9,12,15-octadecatrienoic acid). Compositions of oils can vary greatly. According to the literature, the content of linoleic acid in used cooking oil can vary from 19 to 72% (Anelich *et al.*, 2000). These oils have a high content of glycerides derived from acids, which contain two or three double bonds (e.g. linoleic and linolenic acids). These glycerides undergo free-radical polymerization reactions upon reaction with oxygen to form tough organic films in the so-called "drying" process. Currently there is not much use for used cooking oil, although efforts have been made to utilize it as a supplement for cattle feed or a feedstock for microbiological transformations into useful products (Anelich *et al.*, 2000; Hageman *et al.*, 1990).

Due to the variety of the putties mentioned above, the design of a new putty is very interesting from both a chemical as well as a technical point of view. No references could be found in the technical or open literature to assist with the formulation and characterization of such a putty from the proposed sources. The general aim of this research was therefore to develop a methodology for the preparation of adhesive materials based on the utilization of waste resources, such as FA and used cooking oil (UCO), to create alternative outlets for these two waste materials.

## MATERIALS AND METHODS

Three types of oils were used for making the putties: raw linseed oil (Herpsa), sunflower cooking oil (Helios) and used sunflower cooking oil, obtained as a waste from a process of frying potatoes. Limestone (LS) was obtained from the PPC Lime (Pty) Ltd plant at Lime Acres in the Northern Cape. Calcium oxide used was of 96% purity (Riedel-de Haën). Concentrated hydrochloric acid (32%) was purchased from "Saarchem". Fly ash was supplied from the Lethabo power station in unclassified form by Ash Resources (Pty) Ltd. The work reported here was carried out in the laboratories of the Tshwane University of Technology during the period June 2004 to July 2005.

**Preparation of the samples:** The methods for preparing paste, consisted in essence of mixing the oily phase with the solid phase. The ratios of these components are presented in Table 1. The specific sequence of preparing the various pastes, is shown in Fig. 1 for linseed/cooking oil and limestone/fly ash mixtures and was similar for the rest of the mixtures employing acidified cooking oil and additional free lime (calcium oxide). The obtained suspensions were exposed to air for five months in all cases, at room temperature, with and without irradiation by UV light of 254 nm.

Table 1: Proportions of the components (m/m) used for the preparation of the different mixes, which have been tested over a period of six months<sup>a</sup>

Sample No.	Proportions of materials used in different compositions (m/m)					
	Lime	Limestone	Fly ash	Linseed oil	Acidified cooking oil (ACO) <sup>b</sup>	Used cooking oil (UCO)
1/1A <sup>a</sup>		1.50		1.00		
2/2A			3.70	1.00		
3/3A			2.20		1.00	
4/4A			4.40			1.00
5/5A	0.03		2.47		1.00	

<sup>a</sup> The samples were exposed to air at room temperature (samples 11; 12; 13; 14; 15) and also to UV-irradiation at 254 nm (samples 11A; 12A; 13A; 14A; 15A); <sup>b</sup> ACO was made by addition of 20% of conc. HCl to commercial cooking oil

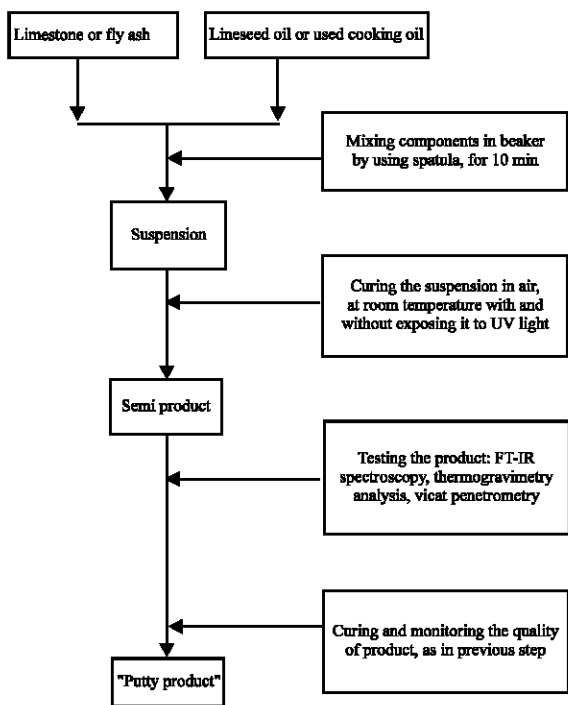


Fig. 1: Flowchart for preparation of putty from limestone and linseed oil; fly ash and linseed oil and fly ash and used cooking oil

The influence of temperature was investigated on selected samples by exposing them to 55 and 110°C and comparing it with a reference sample prepared at room temperature. All experiments were performed with about 500 g of material.

### Characterization of Putty

**Hardness measurements with Vicat needle:** In this study, the physical properties of putty, was estimated by measuring hardness with a penetrometer, such as a Vicat apparatus. The results obtained are summarized in Fig. 2. The measurements have been performed over the period of five months (after 7, 14, 28, 56, 91 and 147 days) and readings were taken from the bottom of the sample (the higher the reading the less the penetration was). A standard UV lamp with wavelength radiation of 254 nm

was used for curing the various mixtures in ultraviolet light.

### Cure monitoring of the putties sample by FT-IR spectroscopy:

Qualitative evaluation of the vibrational spectrum of complex samples may proceed on several levels. The simplest approach is that of generic identification followed by empirical pattern matching. A putty mix was considered as a collection of functional groups or sub-structural units, for which the observed adsorption bands were assigned using group frequency correlation tables (Lin-Vein *et al.*, 1991).

IR spectra were recorded using an evacuated chamber of a Bruker IFS113 v FT-IR spectrometer. A disk was prepared by mixing 2 mg of each sample with 100 mg of KBr and pressing it under a pressure of 6 tonnes for 3 minutes. Acceptable mid-IR spectra were obtained with 32 scans using a spectral resolution of 2 cm<sup>-1</sup>. A potassium bromide disk was used to record the background, which was subtracted automatically, while the baseline was manually corrected afterwards, since it was heavily influenced by the distribution of the sample in KBr matrix. All the corrections (baseline, sometimes smoothing) and the fitting of peaks were done with OPUS 2000 software.

### Compositional analysis by volatilization/gravimetric analysis:

A sample constituent that forms a gas or vapor by heating or by chemical reactions can be determined by volatilization (Stanley, 1986). In this work the sum of volatile constituents was determined indirectly by measuring the loss of mass of the sample as a result of the loss of the volatile constituents (water, carbonate, hydrogen and carbon). The approach was adopted from the standard specifications for putty (SANS, 1979) and fly ash (SABS, 1989) and the work described by Wunderlich (1990).

Different masses of commercial putty as well as the starting materials (FA, LS, CO and LO) were exposed to high temperatures (500 and 900°C) for 2 h and mass-loss of the samples determined. Mass-loss experiments were done on all cured samples during the five months of exposure. A temperature of 900°C was chosen to ensure

that all organic components are volatilized completely. The aim of the mass loss tests was to find a way of quantitative estimation of the oily components in the putties made by mixing the fly ash and the oils. The mass loss on ignition, in percentages, is shown in Table 2 together with the theoretical mass loss calculated from the amount of oil and fly ash or LS in the putty paste (LS was taken as pure CaCO<sub>3</sub> and amount of CO<sub>2</sub> which was supposed to be lost calculated).

**RESULTS AND DISCUSSION**

**Penetration/hardness tests:** Comparisons have been made between the putty pastes prepared and commercial putty (glazing putty), which have been exposed to the same curing conditions. From the results obtained it was concluded that the sample 1 (prepared from LS and LO) hardened faster than commercial putty (prepared as mentioned earlier from limestone and raw linseed oil). When UV-conditions were applied to enhance curing, no significant difference has been noticed. Sample 1A (sample prepared from LO and LS and exposed to UV light) hardened faster than sample 0A (commercial putty).

In sample 2, prepared from LO and FA, no penetration occurred after 147 days of curing. However,

replacement of LS with FA resulted in “late hardening”-no penetration occurred only after 147 days, while the other readings (7-91 days) indicated complete penetration of the Vicat needle (Fig. 2). Samples 0 and 1 (commercial putty and sample prepared from LO and LS) hardened gradually although sample 1 hardened faster than commercial putty, as already mentioned.

Sample 3 prepared from FA and ACO behaved similarly to sample 2 (LO+FA). No penetration occurred after curing the sample for 147 days. Hardening of the sample occurred more gradual than for sample 2. Addition of a small amount of lime (1%) to the sample prepared from FA and ACO (sample 5) resulted in a sample which still displayed complete penetration of Vicat needle even after 147 days of curing. The quality of the sample 5 was improved by using a slight modification of the method of preparing acidified cooking oil. The mixing of concentrated hydrochloric acid and cooking oil was prolonged from 2 to 30 min. When this ACO was mixed with calcium oxide and fly ash in the ratios mention earlier, a better quality of putty was obtained.

When ACO was replaced with UCO (sample 4) the penetration test showed that the sample was very similar to commercial putty and to sample 1 (prepared from LO+LS). It was concluded that the sample hardened

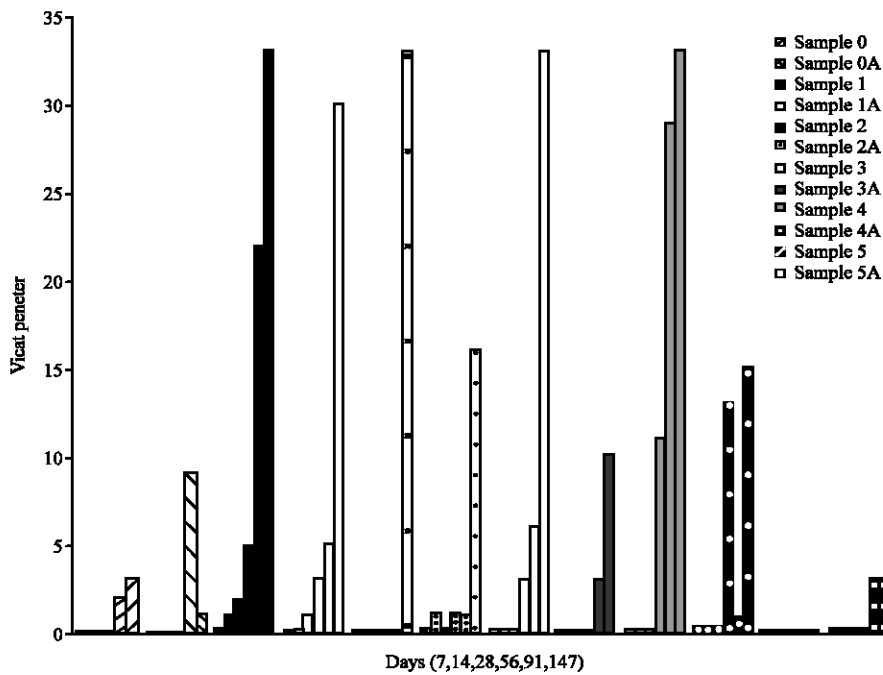


Fig. 2: Vicat penetration test of consistency of putties in mm (reading from the bottom of the samples)

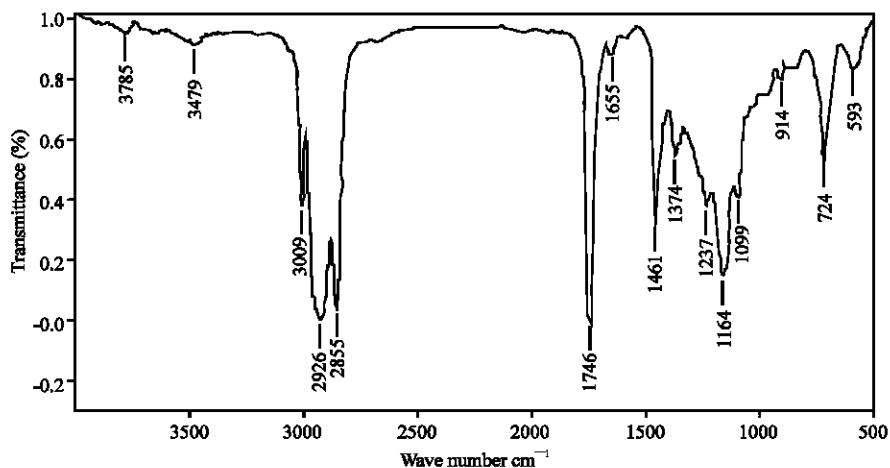


Fig. 3: IR spectrum of cooking oil

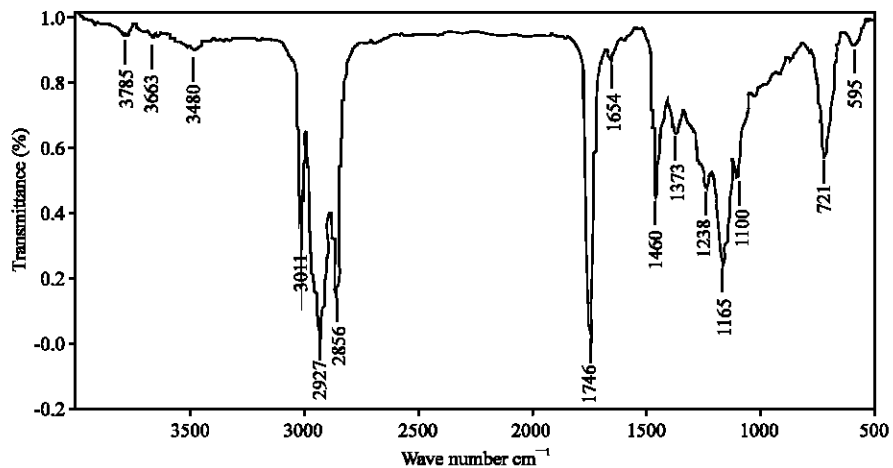


Fig. 4: IR spectrum of linseed oil

gradually and was not as hard as the sample prepared from LO and LS (sample 1), but was still much harder than commercial putty (sample 0).

When samples were cured under the UV light (samples 0A, 1A, 2A, 3A, 4A and 5A), results obtained followed the same trend as those of the samples exposed to air at the room temperature (samples 0, 1, 2, 3, 4 and 5). The general conclusion was that hardening of these samples under the UV light was slower than hardening of the samples in the air at the room temperature.

It was noticed during the experiment that the samples were not always homogeneous and that samples 2A and 4A had a layer of oil on the top. After 91 day of curing, penetration of Vicat needle was measured in the center of the mould and 2-3 mm away from the wall of the container to ensure repeatable measurements. Figure 2 is a graphical summary of the results obtained on all five the mixtures discussed above.

**Spectrophotometric measurements:** The IR spectra of components used for preparation of the putty are shown in Fig. 3-6. It is easy to distinguish fly ash from limestone and linseed oil or cooking oil from fly ash or limestone, but the two oils are not easily distinguishable from each other. It can be seen from IR spectrum of limestone (Fig. 5), that this sample presents a mixture of  $\text{CaCO}_3$  (1430, 876, 712  $\text{cm}^{-1}$ ) and  $\text{Ca(OH)}_2$  (the strong sharp band at 3643  $\text{cm}^{-1}$  is characteristic of the O-H stretching vibration for monomeric form of  $\text{Ca(OH)}_2$ ) (Legodi *et al.*, 2001).

The IR spectrum of commercial putty is consistent with the fact that limestone is the main component of that putty (three bands at 1433, 875 and 712  $\text{cm}^{-1}$ ). The organic part of the sample contains sub-structural units of the type:  $\text{H-C=C}$ ,  $\text{CH}_2$ ,  $\text{CH}_3$  (3010-2854  $\text{cm}^{-1}$ ),  $\text{C=O}$  (1745  $\text{cm}^{-1}$ ). The carbonyl absorption is weak in comparison to the corresponding absorptions of the C-H groupings. The

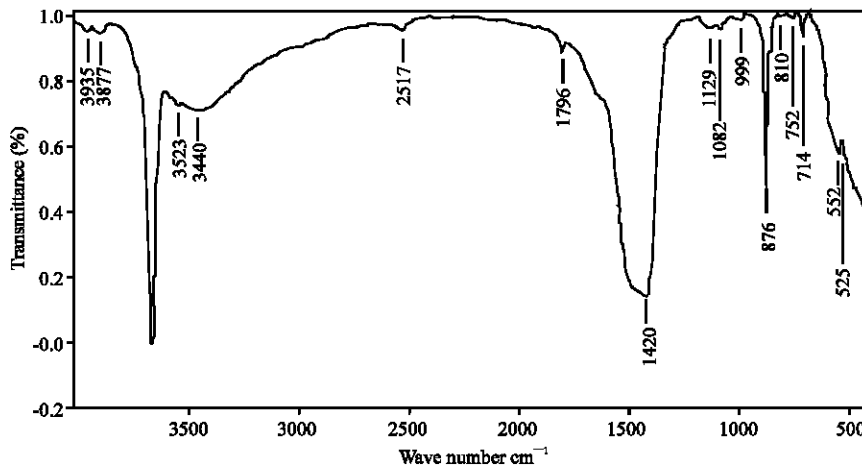


Fig. 5: IR spectrum of limestone

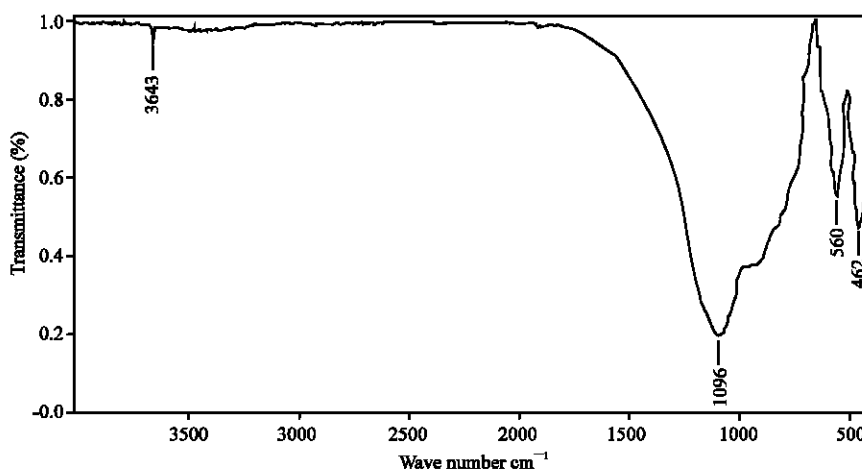


Fig. 6: IR spectrum of fly ash

spectra were taken after 3, 9, 16, 30, 57, 92, 127 and 147 days. On the basis of these spectra the samples were not easily distinguishable.

In all the relevant cases the presence of water was distinguishable when comparing samples and calcium hydroxide peaks could be identified when lime additions were made, but the two oils and changes occurring in them during the exposure periods were not distinguishable from each other on the basis of the IR spectra.

Four types of putties were prepared and exposed to air in the form of a thin layer, at three different temperatures: room temperature, 55 and 110°C. No significant differences could be noticed on the bases of IR spectra of the samples cured at different temperatures.

**Thermal decomposition of putty paste:** The theoretical mass loss for sample 1 and 1A is 66% when calculating LS

as pure  $\text{CaCO}_3$ . If the value of 27.2% mass loss is taken for the LS and 100% loss for the oil, the calculated mass loss for sample 1 would be 56.3%, which agrees with the average value obtained for sample 1A-55.8±2.1. The mass loss for sample 1 is somehow lower (51.2±1.3) than expected, which needs further investigation.

It was assumed that values obtained for the mass loss on ignition for putty samples treated at 900°C, should be quite equal to the mass of the oily component(s) and any other volatile constituents (SANS, 1979; SABS, 1989; Wunderlich, 1990). It can be seen from the Table 2 that in most cases the average experimental value with its standard deviation overlaps with the theoretical calculated value. The only exceptions are sample 1 and 5. Slightly lower mass loss on ignition average values obtained for sample 5 (FA + ACO + CaO) can be explained by the presence of CaO.

Table 2: Mass loss on ignition (%) at 900°C for the different putty pastes

Day	Sample					
	Commercial putty		LS + LO		FA + LO	
	0	0A	1	1A	2	2A
7th	47.4	46.6	Nd	Nd	21.4	19.3
14th	46.4	46.5	nd	56.4	22.8	21.3
28th	47.1	46.3	nd	58.3	25.9	24.7
56th	45.8	46.7	51.2	55.8	21.2	21.0
91st	46.5	47.0	51.6	56.7	19.5	20.0
119th	43.6	46.1	49.4	52.0	18.3	16.6
147th	44.00	47.5	52.4	55.8	19.2	17.0
Average	45.8±1.5	46.7±0.5	51.2±1.3	55.8±2.1	21.2±2.6	20.0±2.8
Theoretical mass loss:						
Oil	-	-	40.0	40.0	21.3	21.3
CO <sub>2</sub>	-	-	26.4	26.4	0.0	0.0
Oil + CO <sub>2</sub>	-	-	66.4	66.4	21.3	21.3

Table 2: Continue

Day	Sample					
	FA + ACO		FA + UCO		FA +ACO +CaO	
	3	3A	4	4A	5	5A
7th	31.5	30.3	19.4	18.4	27.6	27.8
14th	29.6	30.6	21.3	20.3	27.5	27.0
28th	31.5	30.1	21.1	20.1	27.4	26.9
56th	32.2	29.9	19.5	19.9	26.7	27.1
91st	31.9	30.2	21.9	20.3	26.4	26.1
119th	14.2	29.5	17.7	18.6	24.2	26.3
147th	36.6	28.5	15.6	21.5	27.0	28.4
Average	32.2±2.3	29.9±0.7	19.5±2.2	19.9±1.1	26.7±1.2	27.1±0.8
Theoretical mass-loss						
Oil	31.3	31.3	18.5	18.5	28.9	28.9
CO <sub>2</sub>	0.0	0.0	0.0	0.0	0.0	0.0
Oil + CO <sub>2</sub>	31.3	31.3	18.5	18.5	28.9	28.9

Thermogravimetric studies of materials under oxidative atmosphere are not so frequent, in spite of the information about incineration processes that can be obtained from this technique. Thermogravimetric analysis under oxidative atmosphere has been used to characterize samples such as biomass charcoals (Varhegyi *et al.*, 1988) or elastomers in tires (Sircar and Lamod, 1975), different refuges such as wood (Caballero *et al.*, 1998), rye straw (Ghaly and Ergudenler, 1991), tannery wastes (Caballero *et al.*, 1998) and also fluoropolymers (Conesa and Font, 2001). In this project, only a few putty samples have been analyzed by using the thermogravimetric method. The characterizations of starting materials have been also done by this method.

Since combustion is the main type of reaction, the thermogravimetric curve for sunflower oil looks like the curve for a single step decomposition process. The total mass loss was 100%. The curve for linseed oil is similar to the curve for sunflower oil with a mass loss equaling 100%. The sample of partly oxidized raw linseed oil obtained by seven days exposure to air, yielded a thermogravimetric curve with the shape of a curve for a

double decomposition process. The total mass loss was again 100%. The curve for unclassified fly ash indicates a continuous decomposition with no stable intermediates. The mass-loss totaled 11.04 (%).

In order to calculate the ratio of fly ash and oil in the putty sample on the basis of the thermogravimetric curves the following was done (Wunderlich, 1990): Calibration was performed by using cooking oil as a standard. It has been shown that linseed oil or sunflower oil combusted almost completely. Therefore, it was assumed that the mass loss on ignition of the oil corresponds to a one hundred percentage value of the scale. It was also assumed that there was no interactions between the FA and the CO, in a way which would influence the following proportion

$$a/b = x/e$$

Where, a = mass loss for the fly ash, b = 10 0% - a, x = contribution of the fly ash with its mass loss value to the common value of the sample, e = 100%-mass loss of the sample and;

$$x + y = d$$

(y = contribution of cooking oil with its mass loss value, d = mass-loss of the sample)

In the case of a particular sample composed to test the feasibility of this approach, it was found that a =11.04, b = 88.96, d = 92.86 and values x and y could be calculated as x = 9.89 and y = 91.97. In addition, the mass of the fly ash for preparing the putty could be calculated as follows:

$$e + x = (100-92.86) + 0.89 = 8.09\%$$

So the mass ratio of fly ash and cooking oil was found to be 8.09/91.97, which is acceptably close to 1: 10, used originally for preparation of the sample.

## CONCLUSIONS

1. To improve the measurements on the hardening of the putty samples, the needle of the penetrometer has to be changed for the one with a needle of slightly extended diameter.
2. The qualitative evaluation of the vibrational spectra of the putty pastes has confirmed that it was easy to distinguish FA from LS and also LO or CO from FA or LS, but the two oils were not easily distinguishable from each other.



3. For all samples cured at room temperature, the IR analyses did not show any important changes throughout a period of six months, regardless of whether UV-light was used or not. No distinctive effect of temperature on the potential reaction was observed.
4. It was concluded that the minimum values for the mass loss on ignition, for putty samples heated at 900°C, were equal to the mass of starting oil component(s). It was also concluded that average experimental value with its standard deviation overlapped with the theoretical calculated value. The only exceptions were sample 1 and 5. It was useful to differentiate the samples, which had not been made from the same kind of components. Samples containing calcium hydroxide, distorted the mass loss calculations.
5. An approximate calculation for the fly ash/oil ratio has been proposed by using TGA, but it needs to be validated on a more extensive scale.

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