Wax and bentonite blends for prototyping industrial clay development: preliminary results

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Abstract: The automotive design process and the materials in the automotive industry in recent years has caused great interest to the industrial and academic sector. In this study was to evaluate the effect of the amount of bentonite on the thermal and rheological properties of the compound bentonite / paraffin wax. Two bentonite ratios were used: paraffin wax (40:60 and 30:70). The paraffin was characterized by Fourier transform infrared spectroscopy (FTIR), the bentonite was characterized by means of x-ray diffraction (XRD), thermogravimetric analysis (TGA), X-ray fluorescence (XRF). The bentonite/paraffin wax composite was characterized by differential-scanning calorimetry (DSC) and rheology. The sample that contains a higher amount of bentonite shows a lower latent heat, and this could cause a greater heat transfer. Finally, the sample that has a lower amount of bentonite evidenced a lower viscosity, and it could be related to a lower interaction between the particles. The sample S1 due to its lower latent heat compared to S2 could represent an interesting alternative to develop prototyping clays, since these materials are characterized by their low working temperatures and easy malleability.

Keywords: automotive, prototyping, latent heat, bentonite, paraffin.

Mezclas de cera y bentonita para el desarrollo de arcilla industrial de prototipado: resultados preliminares

Resumen: El proceso de diseño automotriz y los materiales en la industria automotriz en los últimos años ha despertado un gran interés en el sector industrial y académico. En este estudio se evaluó el efecto de la cantidad de bentonita sobre las propiedades térmicas y reológicas del compuesto bentonita / cera de parafina. Se utilizaron dos proporciones de bentonita: cera de parafina (40:60 y 30:70). La parafina se caracterizó por espectroscopía infrarroja por transformada de Fourier (FTIR), la bentonita se caracterizó mediante difracción de rayos X (XRD), análisis termogravimétrico (TGA), fluorescencia de rayos X (XRF). El compuesto de cera de bentonita / parafina se caracterizó por calorimetría de barrido diferencial (DSC) y reología. La muestra que contiene una mayor cantidad de bentonita presenta un menor calor latente, y esto podría provocar una mayor transferencia de calor. Finalmente, la muestra que tiene menor cantidad de bentonita evidenció una menor viscosidad, y podría estar relacionado con una menor interacción entre las partículas. La muestra S1 debido a su menor calor latente en comparación con S2 podría representar un interesante alternativa para desarrollar arcillas de prototipado, ya que estos materiales S3 caracterizan por sus bajas temperaturas de trabajo y fácil malleabilidad.

Palabras clave: automóvil, prototipado, reología, bentonita, parafina.
I. INTRODUCTION

Recently, the smart and connected car is creating a new ecosystem of opportunities and competition between different companies. Driven by shared mobility, services, and feature upgrades, new business models could expand automotive revenue pools by about 30 percent, adding up to $1.5 trillion [1]–[3].

Along with this appear new challenges that must be faced. From manufacturing issues, implementation, development of new technologies and the restructuring of automotive design processes. Being the automotive design process and the materials involved in the process of great interest to the industrial and academic sector [4], [5].

Currently in the South American market there are not many local alternatives of Industrial and prototyping clays and its components. Our continent is committed to importing different automotive clays from abroad, such as Chavant, STAEDTLER, Tools INT' L, among others. Therefore, the import prices are much higher due to their dimensions and weight. There are a number of international formulations and alternatives for these materials. However, south America falls short in these developments and there are not many alternatives in our markets. Consequently, is of great interest to generate local alternatives with competitive prices for the South American market.[6][7]

Among the materials used to develop these compounds are paraffin wax, bentonite, Calcium stearate and kaolin have value-added functions, for instance, mechanical properties, heat stability, lubrication, filling capabilities, low cost, among others. Kaolin provides tensile strength, tear strength, abrasion resistance, improve air retention, among other benefits considering that if used it could affect the compound color. Kaolin is one of the best materials to improve surface smoothness for better print quality while being very cost efficient [8]–[10]. However, It is known that prolonged exposure to materials such as kaolin can cause structural and functional damage to the lungs and deterioration to the respiratory system [11]. In addition, sulfur compounds and other similar materials are avoided due to environmental and health implications. Exposure to these types of materials can cause health damage ranging from respiratory problems, skin problems, among others [12].

Otherwise, bentonite is a native, colloidal, hydrated, non-metallic mineral of the Smectite Group composed of montmorillonite. Bentonite have gained much attention because of their high sorption properties, high surface area and high porosity. Bentonite its abundant in many countries and its cost remains significantly low [13], [14]. Paraffins are white, translucent, tasteless and odorless solids composed of hydrocarbons of high molecular weight. Paraffins are the most promising phase change materials because they are available in a large temperature range, have higher heats of fusion, chemical inertness, stability, and they are commercially available at very low cost [15]–[17].

To the best of the authors knowledge and belief, the influence of bentonite and paraffine wax on thermal and rheological properties has not been studied. Accordingly, the main objective of this study was to evaluate the effect of bentonite: paraffin wax ratio (40:60 and 30:70) on rheological and thermal properties of composite.

II. DEVELOPMENT

Car designs do not change radically from one model to another. Aspects such as the number of wheels, the seating positions, etc., do not change, and this has allowed the industry to structure its design in the manufacturing processes in a very compartmentalized and sequential way, with the participation of a number of specialized suppliers. In 1927 General Motors ushered in a new era in the field of automotive design thanks to their flexibility in the process, and they developed the method to create designs on paper as various types of sketches, turning them into full-size orthogonal illustrations, using them to create templates, etc. [18]. For full-size or reduced-size three-dimensional models, clay enables car designers to present and model the geometry of a car's body [19].

Industrial clays became a modeling material primarily used in automotive design studios. It was developed as an industrial version of play dough or hobby clay and they are wax-based and generally contain sulfur, which gives most artificial clays a distinctive odor. Clay models are essential for finding new concepts and drafts; this material is used in augmented prototyping methods to analyze proposed designs [20].

In recent years, computer-aided design technology has generated so much interest, but it has failed to completely displace clay-based prototyping. On the contrary, the industry has found a way to take advantage of both methodologies, the automotive industry in Japan performs simulations in computer-aided engineering system before making the first prototype in order to identify and eliminate problems in advance. This makes it possible to transition from the first prototype to the production prototype quickly [21].

Although prototyping clays continue to be used, the requirements have varied over the years. Some materials used to make these materials are dangerous for the environment and people. This has caused interest in less polluting and economically accessible materials such as
bentonite and paraffin to grow in recent years.

III. METHODOLOGY

A. Materials and methods
Paraffin waxes and bentonite technical grade were used. The characteristics of each material are summarized in table 1.

| Material   | Parameter          | Unit | Specification |
|------------|--------------------|------|---------------|
| Paraffin wax | Melting point     | °C   | 58-60         |
|             | Oil content       | %    | 1.5 max       |
|             | Color             | Saybolt | >17 min |
| Bentonite  | humidity          | %    | 12 max        |
|             | pH                | -    | 10.5 max      |
|             | Swelling          | mL   | 23            |

B. Methodology
The paraffin was crushed until a powder was obtained using a plastic mill (POKSPC400). Different mixtures of bentonite and paraffin were prepared (see table 2). The quantities required for each of the formulations were weighed on a digital scale (JADEVER JWN-30K). The two components are heated to 80 °C under continuous stirring during 10 minutes. The mixtures were placed in a container (30 cm x 30 cm x 30 cm) and stored at 23 °C for 5 hours.

Table 2. Formulation composition

| Nomenclature | Material  | Wt.% |
|--------------|-----------|------|
| S1           | Paraffin wax | 60   |
|              | Bentonite      | 40   |
| S2           | Paraffin wax | 70   |
|              | Bentonite      | 30   |

C. Characterization
Rotational rheometer AR 2000 ex (TA Instruments) was used to measure the viscosities of the formulations according to ASTM standard D4440-15. Additionally, the formulations were studied within the range of 56–70 °C. The melting temperatures and the latent heat storage capacity of the bentonite / paraffin formulations are measured by DSC analysis method according to ASTM D3418-15 standard. The equipment used was a differential scanning calorimeter with modulated heating MDSC Q200 (TA Instruments). General operating conditions and results tables for each formulation will be presented below. The heating program used consists of raising the temperature from 10 °C to 90 °C, at a heating rate of 10 °C/min. Then, an isotherm was applied for 5 minutes, and the material was cooled to 10 °C/min. All the analysis was carried out under a nitrogen atmosphere (99.995%, 50 mL).

IV. RESULTS
The figure 1 shows the FTIR analysis of the paraffin sample used in this study. The band around 2953 cm⁻¹, 2915 cm⁻¹ and 2850 cm⁻¹ correspond to C-H functional group [22]. The band around 1464 cm⁻¹ and 1378 cm⁻¹ is due to the vibration of the functional group -CH₂ and -CH₃, respectively [23]. The band around 720 cm⁻¹ could be related to the vibration of the functional group CH₂ [24]. These bands are characteristic for paraffin wax [24].
Figure 1. FTIR analysis of paraffin wax material.

The figure 2 shows the TGA analysis of commercial bentonite. The first weight loss (11.3%) is evidenced up to 200 °C, and could be related to degradation of the water molecules present on the surface and in the bentonite intercalations [25]. Additionally, the weight loss (3.9%) between 350 °C and 800 °C corresponds to the degradation of organic material [26].

Figure 2. TGA analysis of bentonite.

The table 3 shows the chemical composition of bentonite obtained from X-ray fluorescence (XRF). This material is mainly composed of SiO2 (50.8%), Al2O3 (16.8%) and Fe2O3 (7.9%). Additionally, bentonite shows other components in lesser amounts such as MgO, CaO, Na2O, TiO2 and K2O. The amount of the main components of bentonite used in this study are similar to those found by Rabie et al. [27].
Table 3. Chemical composition of bentonite

| Bentonite | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | MgO | CaO | Na$_2$O | TiO$_2$ | K$_2$O | Others |
|-----------|---------|-------------|-------------|-----|-----|---------|---------|-------|--------|
| Wt.%      | 50.8    | 16.9        | 7.9         | 3   | 2.2 | 1.1     | 0.8     | 0.8   | 0.6    |

The figure 3 shows the XRD analysis of the bentonite used in this study. The diffraction peaks at 6°, 17°, 20°, 35°, 73.8° corresponds to the montmorillonite [28], [29]. The peaks at 21° and 27° are related to the presence of silica [28]. The presence of kaolinite is confirmed by the presence of diffraction peaks at 12°, 34°, 59° and 94° [29]. Additionally, the peaks at 34.9°, 56.6° and 50.2° are due to the presence of calcite [30], [31]. Finally, the peak at 28.2° is associated with the presence of feldspar [32].

The figure 4 shows the DSC analysis for bentonite/paraffin wax composite. All the materials show two peaks of phase change: The endothermic peak between 40 °C and 43 °C is related to the solid-solid phase change of the paraffin [33]. The second peak is due to the solid-liquid phase change of the paraffin, and corresponds to the main peak. The latent heat for S1 and S2 samples are 119.8 J/g (59.26 °C) and 59.3 J/g (59.3 °C), respectively. Li et al. [34] reported that the thermal conductivity of paraffin is around 0.12 W/m K, while the conductivity of bentonite is around 1 W/m K. This suggests that the sample with a higher amount of bentonite (S1) shows a lower latent heat, and this could be related to a higher heat transfer caused by the bentonite. The latent heat of sample S1 is lower than sample S2, suggesting that less energy is needed to melt the compound, and could be beneficial in the prototyping process.
The figure 5 shows the effect of shear rate on viscosity of composites. The figure 5a and 5b correspond to S1 and S2, respectively. All samples show a shear-thinning behavior, which consists in the reduction of the apparent viscosity with increasing shear rate. As the shear rate increases, the weak bonds between particles are broken and the viscosity decreases. In addition, in the sample F5 that has a lower concentration of bentonite, a lower viscosity is evidenced, and it could be related to a lower interaction between the particles [35]. Finally, by increasing the temperature it is possible that the phase change of the compound occurs and the viscosity is reduced.

**V. CONCLUSION**

This study evaluated the effect of bentonite/paraffin wax on thermal and rheology properties for prototyping industrial clay. Sample S1 shows less latent heat compared to sample S2, and this could be related to a higher amount of bentonite. The bentonite could be increasing the heat transfer of S1 sample. In addition, the S2 sample exhibit a lower viscosity, and it could be related to a lower interaction between the particles. The sample S1 could be represent an interesting alternative to develop prototyping clays, since evidenced a low working temperature.

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