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TG/DTG/DTA/DSC AS A TOOL FOR STUDYING DEPOSITION BY THE SOL–GEL PROCESS ON MATERIALS OBTAINED BY RAPID PROTOTYPING

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In rapid prototyping (RP), building 3D physical prototypes involves the addition of material in layers. The sol–gel route is an alternative to produce multicomponent oxide materials with chemical, physical and thermal properties that cannot be obtained by other processes. The sol–gel method allows for the preparation of coatings on several kinds of materials, directly influencing the materials' properties. In this work, metal oxides were prepared by the sol–gel process and deposited further by dip-coating technique on ABS and Nylon substrates obtained by RP. The resulting coating presented good adhesion to the substrates. The obtained materials were characterized by scanning electron microscopy (SEM) and thermal analysis (TA).

Keywords: *coating, dip-coating, rapid prototyping, sol–gel*

Introduction

Rapid prototyping (RP) defines a set of technologies that retain as a common characteristic the building of 3D physical prototypes via a process involving material addition in thin layers obtained from the material's analogical, virtual prototypes. RP makes use of organic polymers to build computer-designed parts [1]. RP machines take virtual designs from computer aided design (CAD); transform them into thin, virtual, horizontal cross-sections; and then create each cross-section in the physical space one after the other, until the 3D solid is complete [2]. The cross sections are built by the action of a laser beam, ink jet or extrusion heads on the target materials, which are in the form of powder, liquid, wire or sheet. Construction of a new cross-section and its adhesion to the previous one occur simultaneously. All these techniques lead to the preparation of pieces with complex geometries.

The sol–gel process allows one to obtain coatings for the coverage of complex 3D structures, and the target compound is deposited on the surface of the substrate from a colloidal suspension (sol). The sol–gel route directly influences the properties of the substrate. The sol–gel process is based on the hydrolysis and polycondensation of alkoxide precursors in solution at low temperature leading to the formation of a polymer network that allows for the incorporation of a variety of compounds [3–13]. It is an alternative for the production of stable multicomponent oxide materials displaying chemical, physical and thermal properties that cannot be obtained by other processes [14–17]. This method is utilized to obtain materials with optical applications, which is based on the inorganic polymerization of molecular precursors involving the evolution of a polymer through a colloidal (sol) suspension with the formation of a net and passing through the continuous liquid phase (gel). The molecular precursor used in the sol–gel process is essentially $M(OR)_z$ alkoxide, where M is silicon or a metal and R is an alkyl group [18]. Different combinations of alkoxides and organo-alkoxide silanes have been prepared to produce materials with better mechanical properties such as abrasive strength and/or high chemical stability [19]. The reactivity of alkoxides depends strongly on the nature of the central ion (silicon or metal). Alkoxides and their organic derivatives, for example play an important role in the synthesis of glasses, ceramics and hybrid organic-inorganic materials [20] in which the materials present a high degree of purity that is preserved throughout the production phase [21].

In this work multicomponent oxide coatings were deposited by the dip-coating technique on the organic polymers ABS and Nylon, obtained by RP. The goal by use the sol–gel method is due to this process can work at low temperature and the precursors in solution.

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Table 1 Chemical composition of the prepared sols (in molar ratio)

SOL	EtOH	TEOS	isoTi	isoAl	isoV	$Ca(NO_3)_2$	HAc	HCl	H_3PO_4	NH_3
1	10	1	1	1	1	–	1	0.1	–	–
2	10	1	1	–	–	–	1	–	–	–
3	10	1	–	–	–	1	–	–	–	–
4	10	1	–	–	–	1	–	–	0.1	0.1

Experimental

Sample preparation

Four different sols were prepared by the sol–gel process by dissolving the ethanol (EtOH) as solvent. SOL 1 was obtained from hydrochloric acid (HCl), acetic acid (HAc) and aluminium (isoAl), vanadium (isoV) and titanium (isoTi) isopropoxides, and tetraethylorthosilicate (TEOS) as source of silicon.; SOL 2 was prepared from acetic acid, titanium isopropoxide and silicon alkoxides; SOL 3 was produced from calcium nitrate ($Ca(NO_3)_2$) and silicon alkoxide; and SOL 4 was obtained from calcium nitrate, phosphoric acid (H_3PO_4), ethanolic ammonia (NH_3) solution and silicon alkoxide (molar ratio are shown in Table 1). For all samples the aging time was 1 h. These sols were deposited on Nylon and ABS by the dip-coating technique using 150 mm min^{-1} speed submersions for 20 min.

Characterization

Thermal analysis (TG/DTA) was carried out in a thermal analyzer (TA Instruments – SDT Q600 – Simultaneous DTA-TG) in nitrogen atmosphere, at a heating rate of 20°C min^{-1}, from 25 to 1000°C, 10 mg of samples with size of 3×3 mm were used. The morphology of the system was investigated by scanning electron microscopy (SEM) using a Jeol JSM-T330A microscope.

Results and discussion

Thermal analysis (TA) was carried out in order to verify the thermal properties of the materials. There was an increase in the thermal stability of the material after it was coated. The coatings were well adhered to the substrate mainly to the ABS samples. TA revealed that the coated materials decomposed at higher temperatures. In case of the organic polymer ABS there was no significant difference in the initial decomposition temperature when the non-coated and coated materials were compared. However, changes in the maximum and final decomposition temperatures reached 20°C, as depicted in Figs 1–3.

The DTA and DSC curves obtained for the ABS samples revealed that an endothermic process takes place in the 450°C region ascribed to sample decomposition.

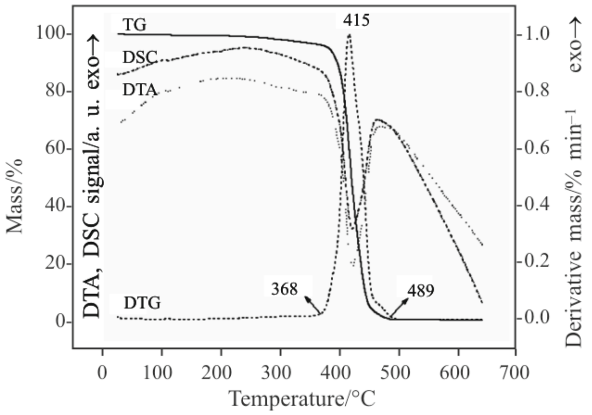

Fig. 1 Thermoanalytical curves of the organic polymer ABS before coating

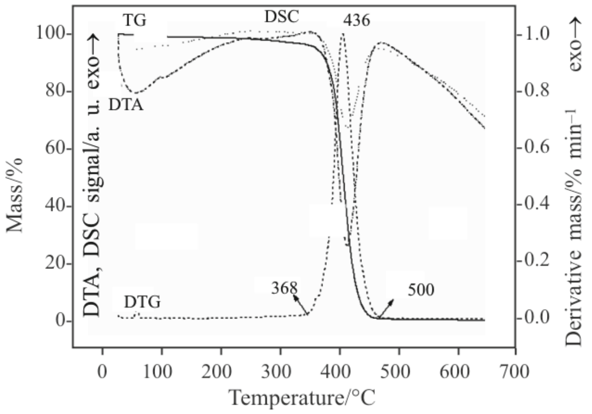

Fig. 2 Thermoanalytical curves of the organic polymer ABS after coating with SOL 1

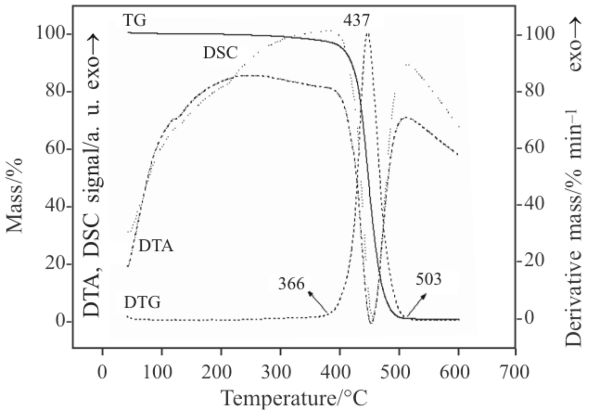

Fig. 3 Thermoanalytical curves of the organic polymer ABS after coating with SOL 4

Table 2 Decomposition temperature of coated and non-coated samples

Samples	Initial decomposition temperature/°C	Maximum decomposition temperature/°C	Final decomposition temperature/°C)
ABS	368	415	489
ABS+SOL 1	368	436	500
ABS+SOL 1 (oxi)	370	425	460
ABS+SOL 2	363	431	506
ABS+SOL 3	368	433	492
ABS+SOL 4	366	437	503
Nylon	345	448	500
Nylon+SOL 1	362	439	503
Nylon+SOL 2	350	442	522
Nylon+SOL 3	359	445	511
Nylon+SOL 4	359	448	506

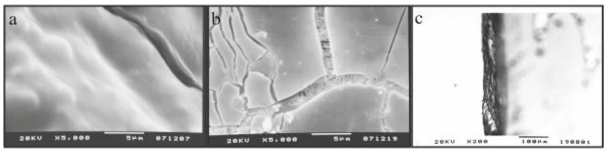

Fig. 4 SEM of ABS a – before coating, b – with SOL 1 coating and c – thickness

For the Nylon samples there was an endothermic peak at 100°C indicating the loss of water molecules adsorbed in the porous structure of the samples. Results of the thermal analysis are summarized in Table 2.

Thermal measurement was carried out under oxidative atmosphere (in air flow) for the sample ABS+SOL 1(oxi), the difference appears in the maximum of decomposition and in the more one event. This event occurs from 510 to 575°C can be due to metal-oxide.

SEM clearly showed the coating on the substrate surface (Fig. 4a) coating SOL 1 (Fig. 4b) and coating thicknesses SOL 1 (Fig. 4c) were larger on ABS, approximately 30 μm, and thinner on Nylon, approximately 5 μm. The presence of cracks (Fig. 4b) can be due to shrinkage effect during gelling and aging steps or a poor anchorage of the sol–gel layer on the sample surface due to low affinity. By dip-coating procedure thin films of 0.1–1 μm, but in this case the high thickness is due to the time of immersion substrate (20 min).

Conclusions

The materials prepared in this work display interesting properties for future application as complex 3D geometries that require low density and large resistance. Coating consisting of different components can promote changes in the physical, chemical and thermal properties of the ABS and Nylon samples. The 30 μm thickness corresponds to a 3% increase, being probably responsible for the 20°C rise in the degradation temperature. The heating ratio shown difference between the initial and final temperature of decomposition but the temperature interval is the same (20°C).

The sol–gel method is an efficient process for the preparation of substrates with new properties and thermal analysis is an important tool for studying changes in sample properties. Several parameters can be studied to obtain sol–gel coating, such as molar ratio of reagent, viscosity and others.

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