



## A Thermal Analysis Study on Blended Ternary Cement Paste

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### Abstract

Pastes containing High Alumina Cement (HAC) and Ordinary Portland Cement (OPC) were prepared using Ground Water (GW) and 5, 10, 15 and 20%SF. The setting time and compressive strength of these admixed cement pastes were measured. The hydrated HAC blends were subjected to DTA/TG and DSC analysis. The recorded spectra were compared with the observed mechanical measurements of these blends. The hydration kinetics is well explained through these results. It is evidenced that 10%SF addition is optimum for this blend.

**Keywords:** OPC, HAC, Admixture, TG/DTA

### 1. Introduction

High Alumina Cement (HAC) is one type among the non-Portland or Special cement. An increase in usage of HAC is extensively observed in recent past combining it with other binder systems even for day today application. An Ordinary Portland cement (OPC) and one or some mineral/chemical admixture usually serves as a mixer binder.

The replacement of HAC by OPC may develop a low strength. The substitution of admixture in this mix may develop a compressive strength higher than or equal to that of HAC under normal circumstances. Silicafume (SF) is preferred because it is highly pozzolanic due to its particle nature and improve the properties of paste/concrete in fresh as well as

hardened state. Generally the addition of SF increases the strength and improves the resistance to sulfate attack. (Ramachandran *et al.*, 2002)

Advanced materials research has recently focused on ettringite rich products (Brooks *et al.*, 1990). One use of HAC is as a precursor to the formation of ettringite ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 6\text{H}_2\text{O}$ ). Blending HAC with anhydrite or gypsum is required for ettringite development. (Lamberet *et al.*, 2005)

In the present investigation it has been planned to mix HAC, OPC and SF in different concentrations. A particular permutation and combination of this blend is expected to bring a maximum strength development, which can be identified by its mechanical properties. The hydration processes can be identified and explained using any analytical tool. In the present study as heat energy plays a vital role, it has been planned to explain the hydration process through TG/DTA, DSC and compare it with the mechanical studies.

## 2. Experimental techniques

The materials used in this work were Ordinary Portland Cement (OPC), High Alumina Cement (HAC) and Silica Fume (SF) supplied by Coromondal Ltd, Chennai, Ace Refractory, Chennai and Polygon Chemicals Ltd, Mumbai respectively. The chemical composition of the materials is given in table 1.

Blended cement mix was initially prepared with 85% HAC + 10% OPC + 5% SF and well mixed with the help of a mini vibrator. Then HAC was substituted by 10, 15 and 20% SF. Ground Water (GW) was used as medium. The water analysis is given in table 2. The admixed cement pastes were prepared in a water/cement ratio of 0.4. The initial and final setting time of the blends were measured using the Vicat's apparatus (Fig. 1). Their compressive strengths were also measured using a Techno Scient Trading Corporation machine (Fig. 2). These procedures were well explained by Shetty (2004) and Sakkary *et al.*, (2004). The samples were hydrated to 1 day, 3 days, 1 week and 4 weeks. Proper curing was done for samples hydrated to more than one day. After dehydration as per the standard procedure (Moises Frias *et al.*, 2002), the samples were powdered and analyzed using thermal analysis technique (TG/DTA, DSC). The TG/DTA and DSC were recorded from room temperature to 1000°C at a heating rate 10°C/min. The facilities available at CECRI, Karaikudi, Tamilnadu, India is made use of. For the sake of convenience HAC-control, 90% HAC + 10% OPC, 80% HAC + 10% OPC + 10% SF and 70% HAC + 10% OPC + 20% SF thermograms at 28th day are shown in fig 3, 4, 5 & 6.

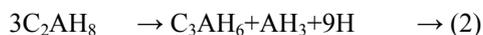
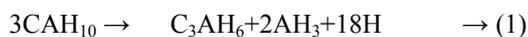
## 3. Results and discussion

DTA endothermic peak seen at around 130°C, 200°C, 275°C and 300°C may be assigned to  $\text{CAH}_{10}$ ,  $\text{C}_3\text{AH}_6$ ,  $\text{C}_2\text{AH}_8$  and  $\text{AH}_3$  respectively (Bradbury *et al.*, 1976).

Hydrated HAC (one day) spectra show an endothermic peak at around 130°C the decomposition of  $\text{CAH}_{10}$  may be responsible for this.

In our present work a delayed set compared to other mixtures is observed. According to (Watson *et al.*, 1990) the process of setting and of nucleation and growth of the first hydrate are intimately linked. For a retarded set the nucleation is lower than at higher or lower temperatures. The significance is that the temperature range coincides with that at which formation of  $\text{CAH}_{10}$  becomes less favorable thermodynamically.

The formation of  $\text{C}_2\text{AH}_8$  is sluggish and  $\text{C}_3\text{AH}_6$  could be formed via conversion of one of the hexagonal hydrates. The present results are in accordance with this hypothesis and the retarding set is associated with the difficult nucleation of  $\text{CAH}_{10}$  and  $\text{C}_2\text{AH}_8$  producing a longer dormant period. An endothermic peak is seen around 275°C. The phase formation may be due to the decomposition of  $\text{CAH}_{10}$ . The phase formation ( $\text{C}_3\text{AH}_6$ ) can be identified by the following reaction (Ana Hidalgo, *et al.*, 2009).



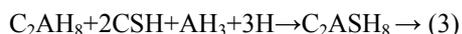
These dehydration mechanisms are accompanied by micro cracking and porosity formation. This explains the decrease in compressive strength at 28<sup>th</sup> day. (Chotard *et al.*, 2005)

In fig (4) due to the replacement of HAC by OPC, the setting time is accelerated as compared to that of control. In any cement binary the sulfates and aluminates composition plays an important role in formation of ettringite (Sivakumar *et al.*, 2008). Since the availability of sulfate in HAC is less, the formation of ettringite observes to be with lesser strength. This deficiency can be compensated by the addition of Silica fume (Ping Gu *et al.*, 1997)

The Differential Thermal Analysis (DTA) thermogram of the composite with 5% SF shows an endothermic peak centered at around 200°C due to  $\text{C}_2\text{AH}_8$ . It is observed that the additions of SF accelerate the setting time and increase the compressive strength at 28<sup>th</sup> day. This may be attributed to the formation of calcium silicate hydrate which gives higher strength than the hydrate of calcium aluminate and sulphoaluminate.

An addition of 10% SF to the composite shows an endothermic peak at around 200°C and 230°C which may be due to the formation of  $\text{C}_2\text{AH}_8$  and  $\text{C}_2\text{ASH}_8$  respectively. An increase in strength at 28<sup>th</sup> day is due to this formation of

stratlingite instead of  $C_3AH_6$  and the formation of CSH (Midgley et al., 1978). The formation of this phase can be quoted by the following equation (Mohamed Heikal et al., 2004)



An addition of 15%SF composite shows a decreasing endothermic peak centered at around 300°C. As the time increases it could be noted that the formation of  $C_2ASH_8$  decreases and  $C_3AH_6$  became dominant at the 28<sup>th</sup> day. Hence there is an accelerated setting time with lower compressive strength compared to that of 5% and 10%SF. According to (Ding et al., 1995) higher amount of SF keeps the non reacted SF particles as residual on the surface of products which may be responsible for lower strength.

Similar results were observed from the thermograms of composite 70%HAC+10%OPC+20%SF. The decreases in compressive strength with an addition of 15 and 20%SF are less significant than that of the control cement paste. This may also be contributed to lesser  $Ca(OH)_2$  content found in blended cement pastes because of pozzolanic reaction consuming free lime disposable of  $Ca(OH)_2$  formation (Mohamed Heikal., 2006)

The Differential Scanning Calorimetry (DSC) thermograms shows only two endothermic peak located at around 275°C and 562°C with an enthalpy of 358.3J/g and 40.23J/g. For the replacement of 10%OPC shows the peak being shifted and gives an enthalpy of 102J/g, lower than the control. For the addition of 5%, 10%, 15% and 20%SF the enthalpy values are 139,157,152 and 120J/g respectively. An increase in enthalpy value is due to the pozzolanic reaction of SF with the liberated  $Ca(OH)_2$  to produce  $C_2AH_8$  and  $C_4AH_{13}$  and then react with CSH to form  $C_2ASH_8$  (Morsy et al., 2007). On the other hand the enthalpy decreases with an increase in SF content.

The Thermogravimetric Analysis (TG) is commonly used with DTA to follow the hydration reactions. From the TG curve the variations in weight loss with the temperature of properly cured cement pastes at 28<sup>th</sup> day are shown in fig 3, 4, 5, and 6. The physically sorbed water at 110-120°C, the peaks at 200 and 400°C are due to the dehydration of C-S-H and C-A-H hydrates. The mass is increased between 500 and 600°C because of the carbonation of  $Ca(OH)_2$ . The result of TG/DTA and DSC serves as a complement in each other and compared with mechanical observations. Addition of 5 and 10%SF shows an increase in the mass loss than the other mixes of 15 and 20%SF. This may be due to the principal reaction between SF and Calcium hydroxide from cement additional, cementitious aluminium containing C-S-H gel, together with crystalline products which include calcium aluminate hydrates and aluminosilicate hydrates (ie  $C_2ASH_8$ ,  $C_4AH_{13}$  and  $C_3AH_6$ ) (Heikal et al., 2005).

From the earlier discussion in the presence of SF, OPC in the hydration of HAC results in the formation of stratlingite compound. The formations of these hydrated phases remove  $Ca^{2+}$  ions from the pore solution and hence restrict the conversion of  $CAH_{10}$  and  $C_2AH_8$  to the stable cubic hydrate  $C_3AH_6$  i.e suppressing the extent of the conversion reaction. This is reflected by the strength development of 10%SF.

#### 4. Conclusions

From the above findings it can be concluded that

- The addition of Silicafume increases the strength and decreases the setting time (i.e) it accelerates the reaction.
- The 10%SF addition is supposed to be moderate as the strength increases uniformly. This is also supported by the DTA/TG and DSC study.
- The incorporation of SF in these systems contributes to the reduction of waste materials and therefore to a better sustainability development.
- The addition of SF reduces the cost to a suitable extent.

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Table 1. Percentage Chemical composition of Materials

Materials	Oxides							
	CaO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub> +FeO	MgO	Na <sub>2</sub> O	SO <sub>3</sub>	Others
HAC	38.5	39	4.5	14	0.4	0.1	0.15	3.15
OPC	63.41	5.45	21.45	3.42	2.59	0.38	2.39	0.91
SF	0.45	1.17	93.14	3.13	0.98	0.30	0.10	0.73

Table 2. Contents of the Ground Water

Content	Ground Water
Total Dissolved Solids	1401
Total Hardness	158
Chlorine	55
Sodium	120
Magnesium	12
Calcium	66
Potassium	15
Sulphur	7.1
Fluoride	0.08
Electrical conductivity	500
p <sup>H</sup>	7.8

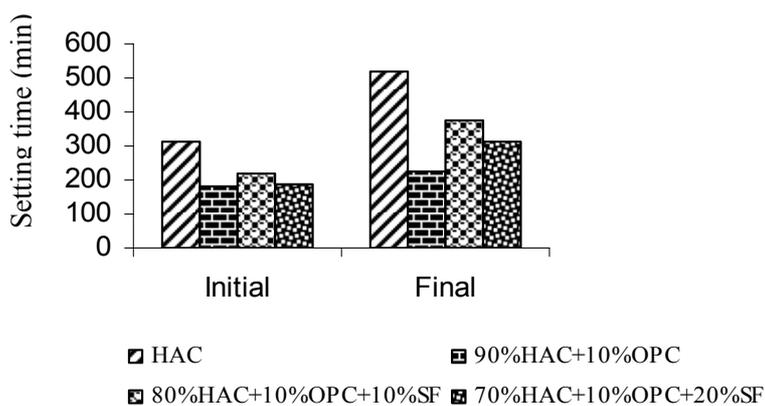


Figure 1. Setting time of the admixtured cement paste

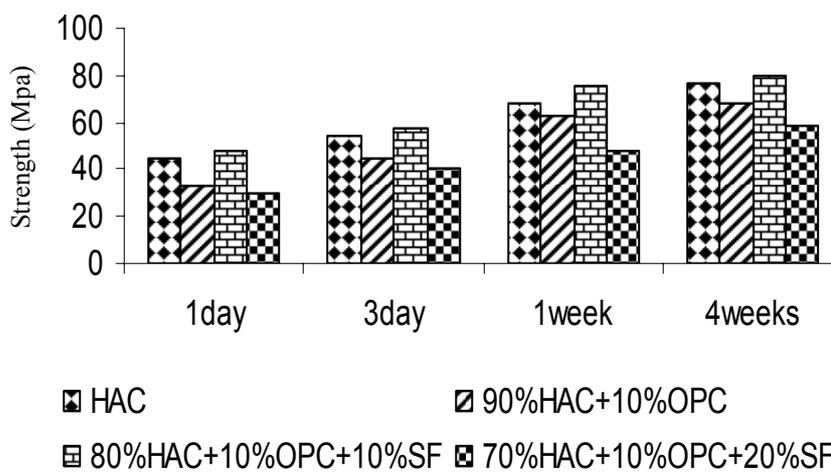


Figure 2. Compressive strength of admixtured cement paste

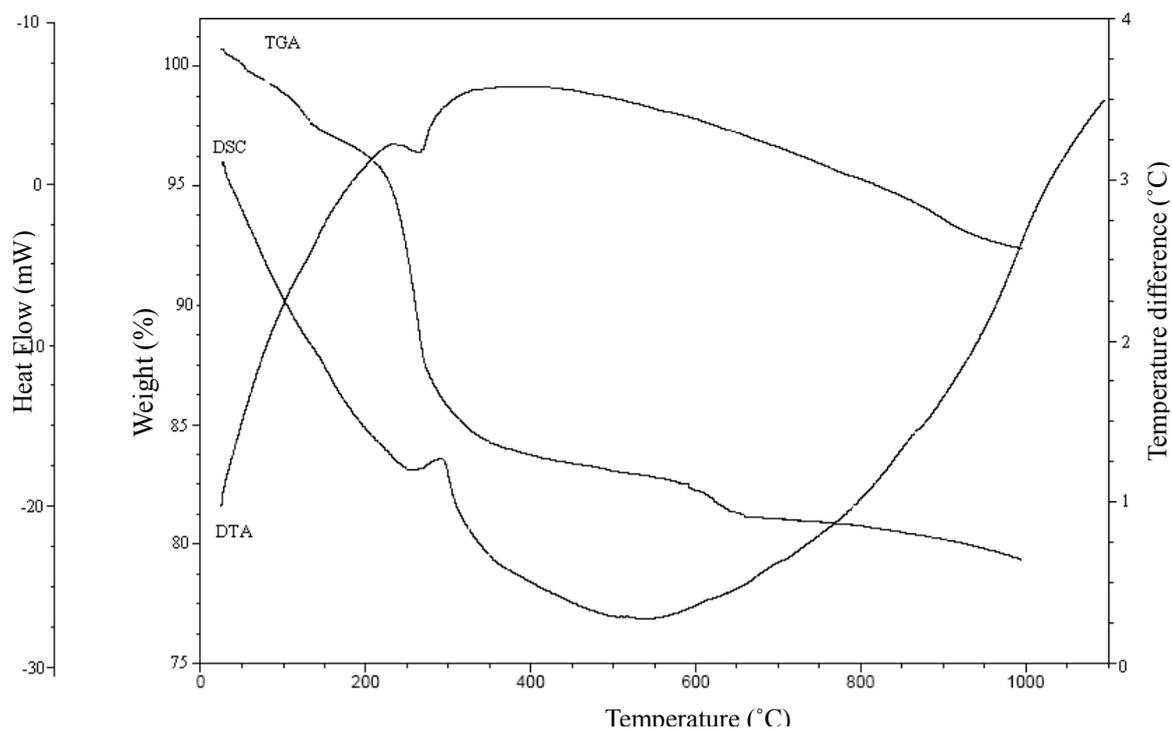


Figure 3. DTA/TG and DSC Spectrograms of Hydrated HAC

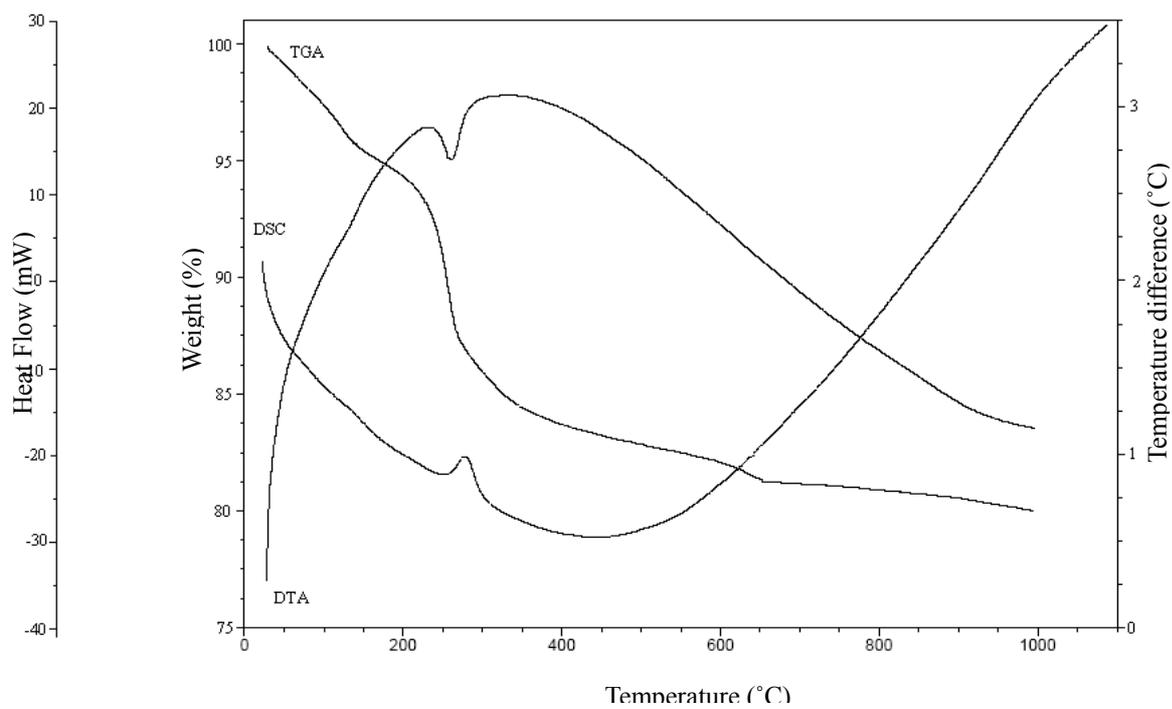


Figure 4. DTA/TG and DSC Spectrograms of 90%HAC+10%OPC

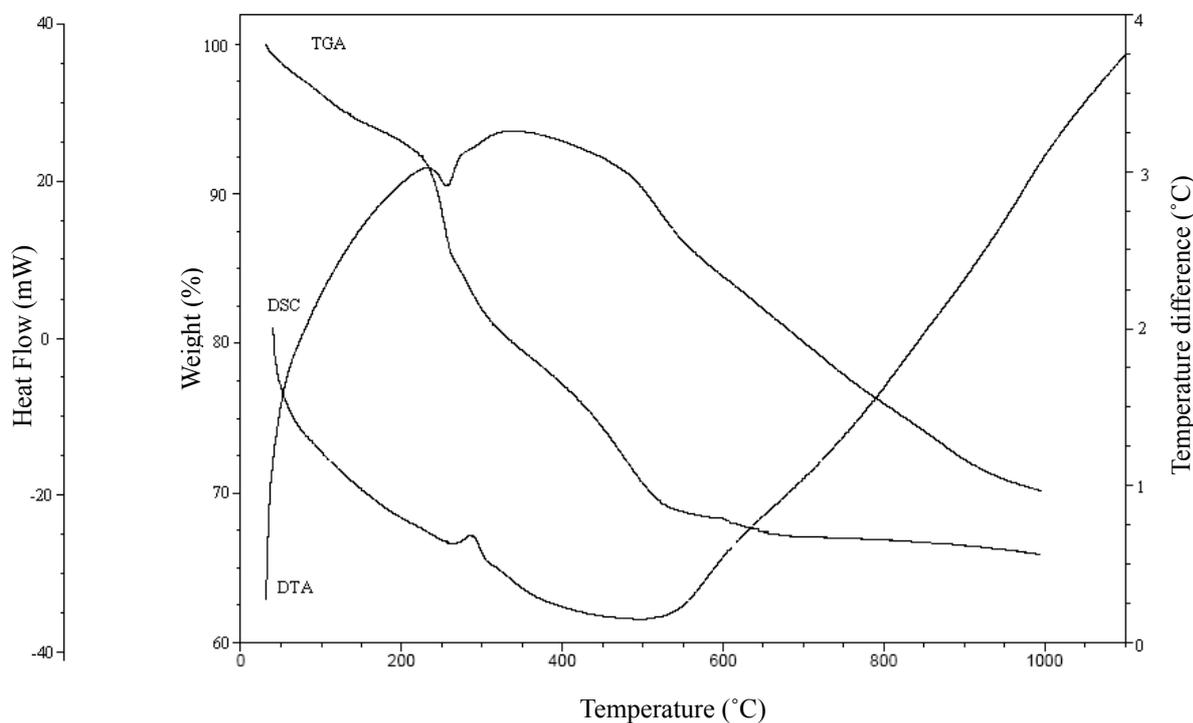


Figure 5. DTA/TG and DSC Spectrograms of 80%HAC+10%OPC+10%SF

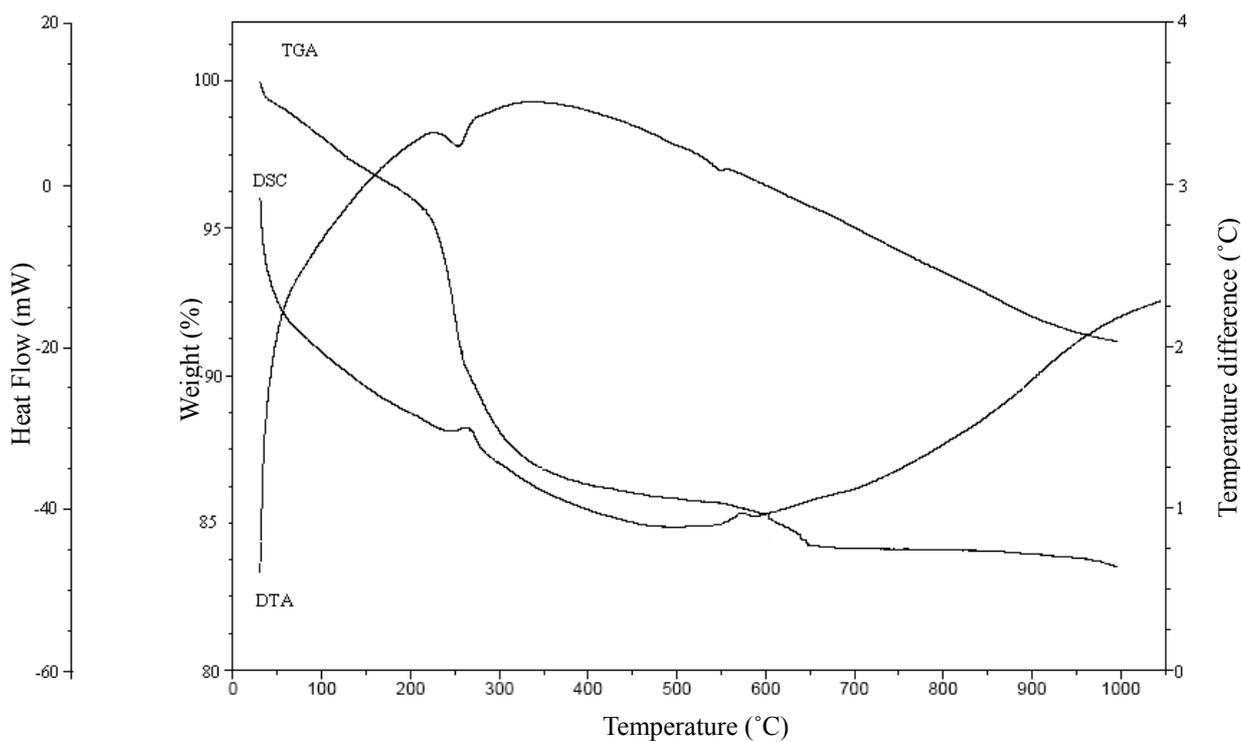


Figure 6. DTA/TG and DSC Spectrograms of 70%HAC+10%OPC+20%SF