

QUALITY ASSESSMENT OF FULLERENE SAMPLES USING THERMAL TECHNIQUE

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Abstract

Thermal analysis could be used as a powerful technique to check the purity of the sample. In this paper thermogravimetric analysis (TG) and differential thermal analysis (DTA) have been used to check the purity of fullerene sample prepared by different techniques. Hence it is possible to compare the purity of the samples, too. The analyzed results have been compared and hence correlated with the other characterization techniques, e.g. FAB-Mass, FTIR, UV-VIS and SEM.

Keywords: fullerene, FTIR, mass spectra, SEM/TEM, thermal analysis, UV-VIS

Introduction

Following the breakthrough of the technique for macroscopic production of fullerenes [1], several research groups all around the world produce, extract and separate fullerenes. Fullerenes have been largely produced so far from graphite (by laser as well as by arc discharge) [1–4], burning of benzene [5], hydrocarbon combustion [6], pyrolysis of naphthalene [7], pyrolysis of camphor [8, 9]. The samples obtained were so far principally characterized by mass spectra, ¹³C-NMR and XRD methods, while using UV-VIS, FTIR, thermal analysis and SEM techniques secondarily [1–9]. In this paper we report the analysis of the quality of the fullerene samples (synthesized by different process conditions and methods) using thermal analysis as principal technique. The results are supported by FAB-Mass, FTIR, UV-VIS and SEM analyses.

Experimental

Fullerene samples (synthesized either by arc-discharge or by laser vaporization method using graphite (99.999% purity) electrode) were sent to us (each ~2 mg) after the removal of hydrocarbon, purification and separation, for characterization and checking the quality. Unlike others, thermal analysis has been used as principal technique and mass, FTIR, UV-VIS and SEM as supporting techniques.

Results and discussion

Figure 1 shows the thermal analysis graphs of all the fullerene samples. All the experiments have been carried out under identical conditions (heating rate $20^{\circ}\text{C min}^{-1}$ under N_2 atmosphere). For samples A and B, the initial degradation temperature (IDT) has been found to take place at 590.82 and 565.72°C , mass loss has been found to occur between 600 – 700°C (one step reaction). While in sample C, IDT has been found to occur at 291.06°C , mass loss occurs as early as between 250 – 400°C (two-step reaction). This is because of the presence of high degree low to medium

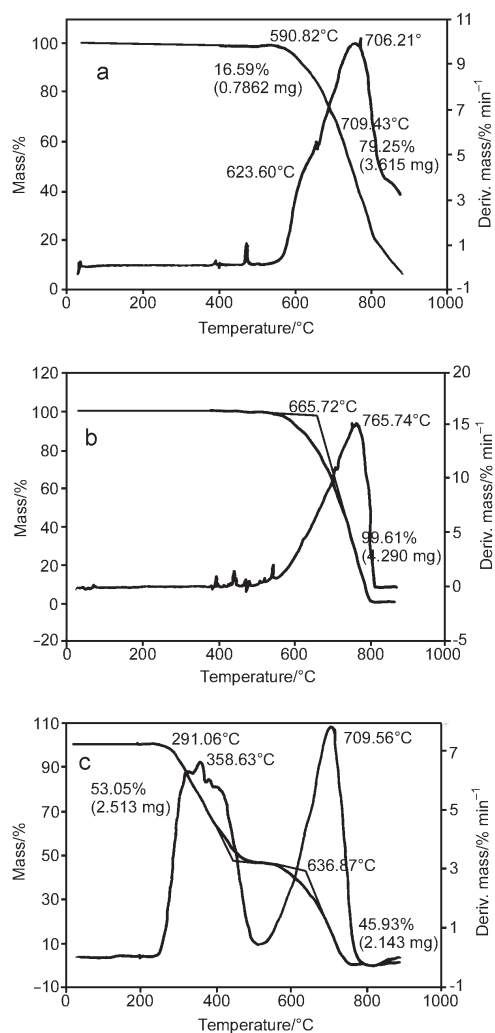


Fig. 1 TG along with the first derivative curves of the sample A in (a); B in (b) and C in (c)

molecular mass hydrocarbons in sample C compared to samples A and B. Furthermore, it has been observed that by changing the heating rate, the peak of vaporization of sample also changes. For example, by increasing the heating rate from 5 to 20°C min⁻¹ causes the temperature of maximum mass loss to increase from ~450 to 600°C. This result shows the need to define heating rates in any discussion of oxidation/sublimation temperatures for C₆₀. The observed dependence on heating rate is expected for any vaporization process, and in principal one can extract the heat of vaporization from these data as reported elsewhere [10, 11].

Evidently, the sample does not simply undergo a vaporization process, but also some other changes occur. The sudden change in the vapourization rate at high temperatures is the further evidence of a thermally activated transformation of the fuller-

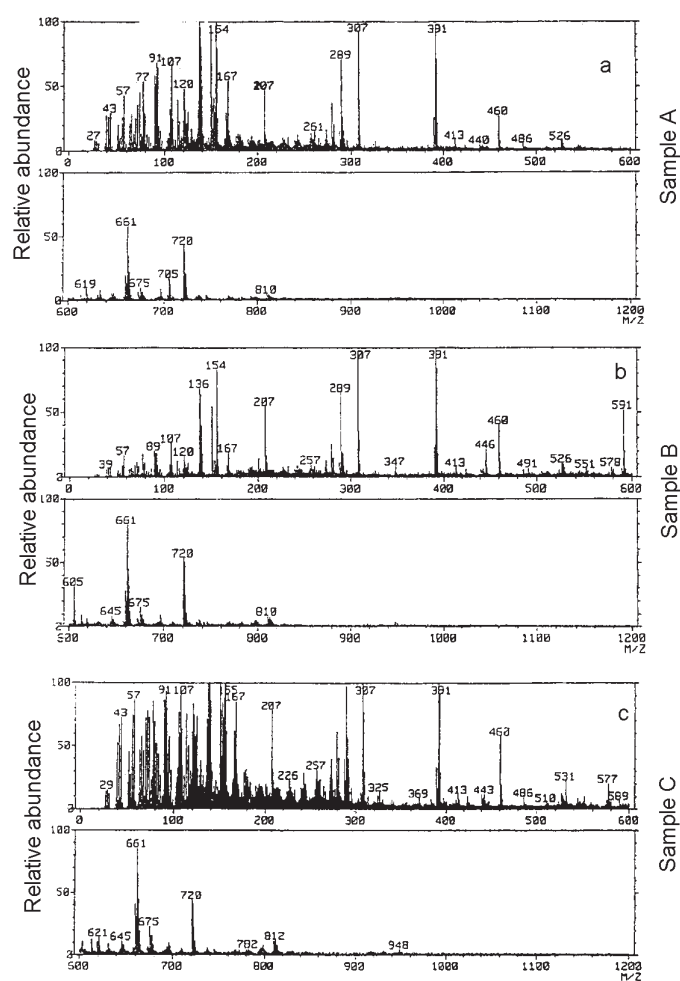


Fig. 2 FAB mass spectrum of the sample A in (a); B in (b) and C in (c)

enes into some new form of carbon. The new species is insoluble in toluene/benzene, slightly harder and granular. It is thought that this new carbon may be composed of larger fullerene structures that have thermally bonded together, possibly through Diels-Alder like adducts, as discussed elsewhere [12]. The effect of high temperature and high pressure (HTHP) treatment [13] may find an important use of this material and work is going on in this direction.

The thermal analysis results have been nicely supported by mass and FTIR results. The mass spectra of all the samples are shown in Fig. 2. It is clearly observed that in all cases the peak at 720 is clearly visible, suggesting the presence of C_{60} in all

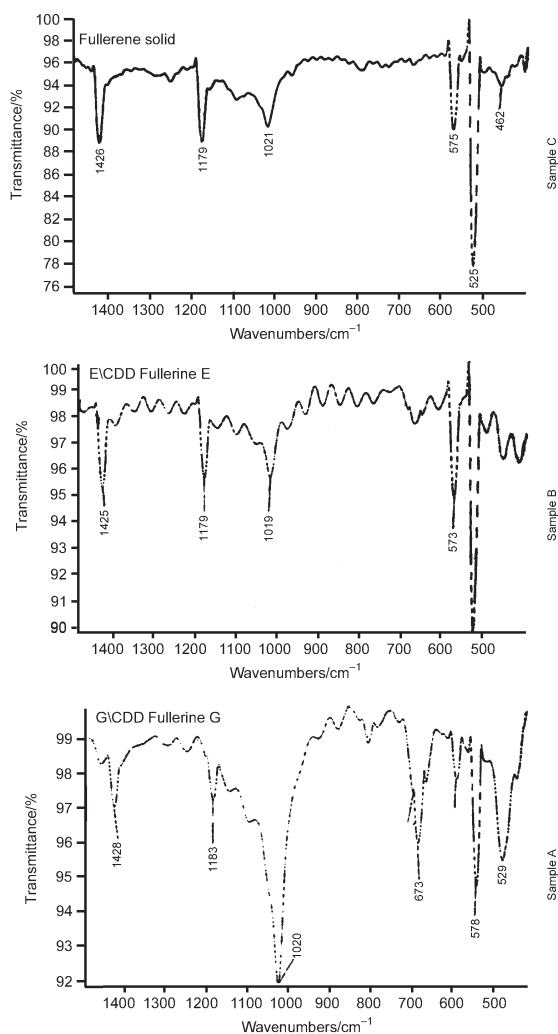


Fig. 3 FTIR spectrum of the sample A in (a); B in (b) and C in (c)

the samples. But there is no peak at 840, indicating the absence of C_{70} in all the samples. But the most interesting part is the appearance of the peaks within 600 amu. Except for sample B, for all other samples, it is too much crowded within 600 amu. This clearly indicates the presence of impurities, mainly low to medium molecular mass hydrocarbons in those samples. It is true that for sample B we also had some peaks within 600 amu, but the peaks are scattered and less dense indicating the much better purity of the sample B. The intensities of the impurity peaks within 600 amu are maximum for the sample C, followed by sample A and least in sample B. This fact is clearly supported when we compared with TG analysis of the samples. For sample C, these low-medium molecular mass hydrocarbons have been decomposed much earlier than fullerene ($\sim 300\text{--}400^\circ\text{C}$) and hence one break has been observed in the TG curve at around 350°C .

The same has been observed while comparing the results of thermal analysis and solid state FTIR. FTIR spectra of all the samples are shown in Fig. 3. It has been reported that the peaks at $\sim 525, 575, 1179$ and 1428 cm^{-1} region correspond to fullerene [14, 15]. For sample A and sample B, the clarity of the FTIR spectra and the absence of other peaks indicate the purity of the sample but for sample C, some peaks different from the reported peaks for fullerene have been observed. These peaks are due to the impurities present in the sample and are clearly visible in the mass and thermal analysis results, too.

From UV-VIS spectra of all the samples (not shown here) it is clearly indicated that the spectra of all the samples look identical. The reason may be that the spectra of

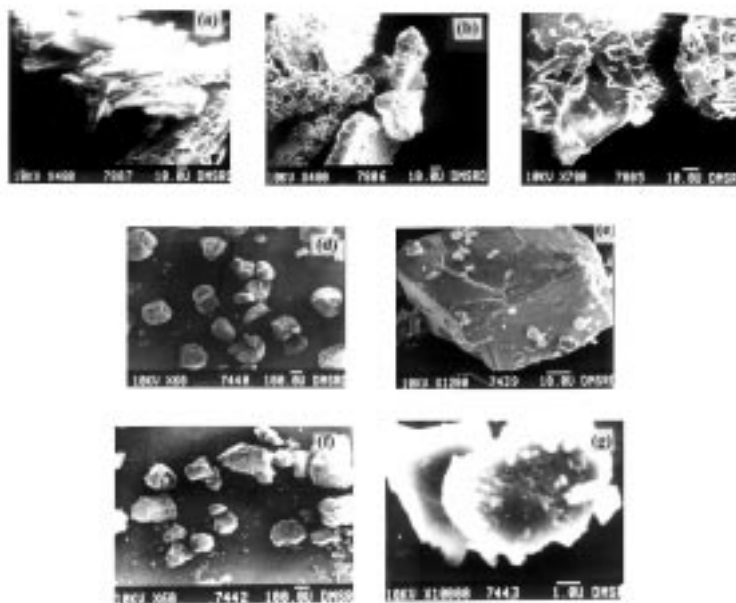


Fig. 4 SEM micrographs of sample A in (a, b, c); B in (d, e) and C in (f, g)

all the samples are recorded in a solution form where the spectrum of solvent is also playing a role. Another reason may be that in all the samples C_{60} is present. Since we have not made any quantitative analysis (i.e. the percentage of C_{60} present in the sample) of the presence of C_{60} , so the spectrum of C_{60} is predominant in all the cases, thus giving fewer indications about the impurity present in the sample. The same thing has been observed when we have made the FTIR analysis in a solution form.

SEM micrographs of all the samples are shown in Fig. 4. Although it is true that the samples are not 100% pure, hence whatever crystal/aggregates have been observed under SEM, will give impression of the mixtures. But here, too, the difference in crystallinity has been observed (ie. difference in the degree of crystallinity, shape and size). For samples A and particularly B, which have less impurity, beautiful shining crystals have been observed. Figures 4a–c show the SEM micrographs of sample A and Figs 4d–e show the SEM micrographs of sample B. It is clear from the micrographs that there is a difference in crystallinity of the samples. It is well reported that the crystal structure of the fullerene sample depends on the method of preparation of crystal, the solvent and the impurity present in the sample. Depending on these there could also be a difference on the shape of the crystal. It could be either rod shaped, star like, plate like etc. [16–18]. For example, the crystal of sample A is plate shaped while that of sample B is almost square. This kind of feature is almost constant for samples A and B. But for sample C, the impurities present play some role in the crystallinity and there is no fixed shape observed under SEM for sample C. Figures 4f–g will give some idea about this.

Conclusions

We can infer from our above mentioned analysis that quality of fullerene sample B is better than samples A and C. Further studies on using quantitative thermal analysis together with XRD analysis are underway. The correlation between the crystal structure and the thermal analysis data is going on, too.

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