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DESIGN AND APPLICATIONS OF A Curie point pirolyzer

THE TECHNIQUS of pyrolysisi analysis or analysis of the thermal decomposition products of a substance brought about by heat has been used successfully in the manufacture or the Pyroroil (Japan Analytical Industry Co., Ltd., Japan) Curie point pyrolyzer (PCPP) for the characterization or rubbers and industrial polymers (Figure 1).

The most important requirements or pyrolysis are: 1) Good reproducibility-the sample should be heated to a high and constant temperature with good reproducibility so that accurate analysis can be obtained; 2) Rapid rise time-the pyrolyzed sample should not be allowed to induce secondary reactions during the primary pyrolysis step: 3) Sample preparation-any form or sample may be analyzed directly without any sample preparation by simply wrapping and dipping the sample in the foil or wire; 4) Accurate temperature measurement-because the Curie point temperature is so accurate and reproducible. accurate quantitative analyses are ensured time after time.

Principle

To understand the operation of the CPP, it is necessary to understand the basic principle on which this operation is based. When a strong ferromagnetic material is placed inside a conducting coil, and a direct current is passed through the coil, the ferromagnetic material is transformed into a magnet, and a magnetic field is created. If the direction of the current is changed, the polarity of the magnet is reversed, i.e" N→S is reversed to S→N. When

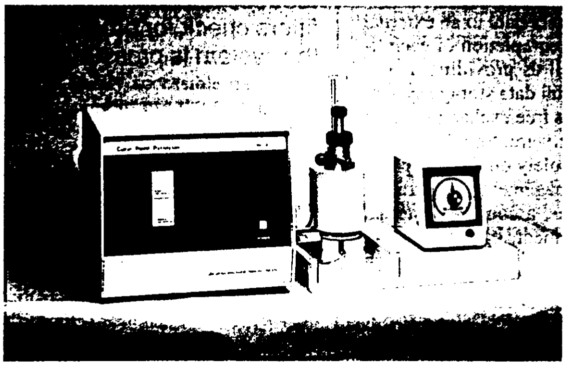


Figure 1 *Curie point pyrolyzer, Pyrofoil.*

the polarity of the coil is changed rapidly. heat is generated from the ferromagnetic material. Heat generated by this action causes the ferromagnetic material to reach its Curie point temperature. where the magnetic property is lost, and the temperature is maintained constant The time taken to reach the Curie point temperature is less than 0.2 sec. By varying the alloy or the ferromagnetic materials, it is possible to accurately choose different Curie point temperatures. Japan Analytical Industry offers a range or nineteen different temperatures from l60℃ to 1140℃.

System description

The Pyrofoil Curie point pyrolyzer meets and exceeds the above-mentioned requirements of pyrolysis. When each ferromagnetic pyrofoil reaches its Curie point. it maintains an exact temperature (Figure 2). No significant secondary reactions lake place because or

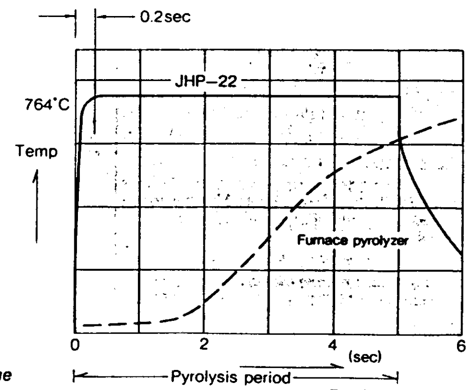


Figure 2 ***Rapid rise time of the Curie point pyrolyzer.***

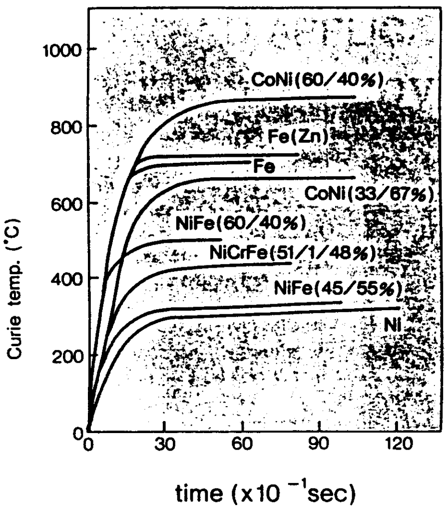


Figure 3 *Curie temperature vs ferromagnetic alloy on Curie point pyrolyzer.*

the extremely rapid rise time. A solid sample can be wrapped in a pyrofoil prior to being inserted into the pyrolyzer. Since Only a minute quantity of sample is needed for the pyrolysis, a liquid sample can be placed on the pyrofoil with a microsyringe. As each foil has its own Curie point temperature, it is not necessary to set the pyrolysis temperature. The Curie point temperature of the foil selected is already known (Figure 3).

A block diagram of the Pyrofoil Curie point pyrolyzer model JHP-22 is shown in Figure 4. It consists of a quartz tube and a pyrofoil or pyrowire in the middle of the system. Solid samples are simply weighed and wrapped in the pyrofoil. Liquid samples can be coated on a pyrofoil or pyrowire. Both can be reused after cleaning with solvents or acids.

Experimental

When a radio frequency (RF) field is applied to the coil, the ferromagnetic foil or wire reaches its respective Curie point temperature. The pyrolysis time is controlled by a timer. The pyrolysis products from the pyrofoil or the wire are then transferred to the gas chromatograph (GC-MS/GC-IR) via a heated transfer line by the carrier gas. The instrument has a long transfer line to interface it with any type of GC or GC-IR, or GC-MS. The quartz Sample tube can be cleaned by solvents, acids, or by firing.

Advantages of the Curie point pyrolyzer

The Pyrofoil Curie point pyrolyzer-GC (GC-MS/GC-IR) method is simple and very effective for the identification of synthetic polymers. The results give information on the structural composition, microstructure identification, thermal stability, and quantitative distribution of polymers. In order to obtain reliable data, the aforementioned criteria must again be emphasized. *Figure*

Main components (JHP-22)

1. Timer
2. Oscillator
3. R.f.coil
4. Septum
5. Sample tube
6. Pyrofoil®
7. Quartz filter
8. Valve
9. Purge gas valve
10. Purge gas inlet
11. Connection tube (transfer tube)
12. Gas chromatograph column
13. Carrier gas inlet
14. Injection port for identification

(Items No. 3—8 are contained in a thermostatically controlled oven to prevent condensation of pyrolyzed products.)

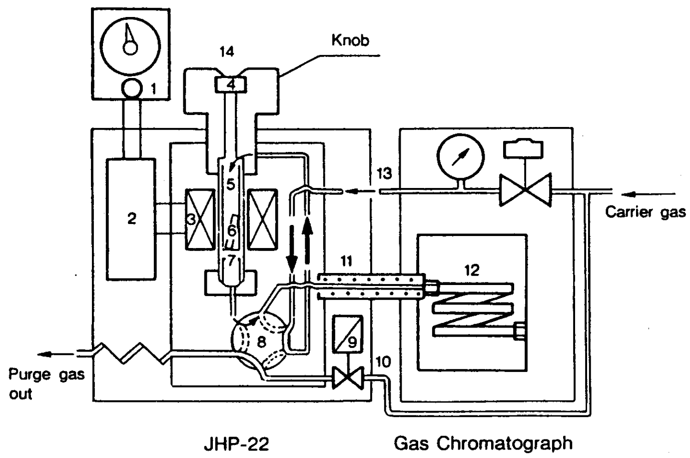


Figure 4 *Schematic diagram of the model JHP-22 Curie point pyrolyzer.*

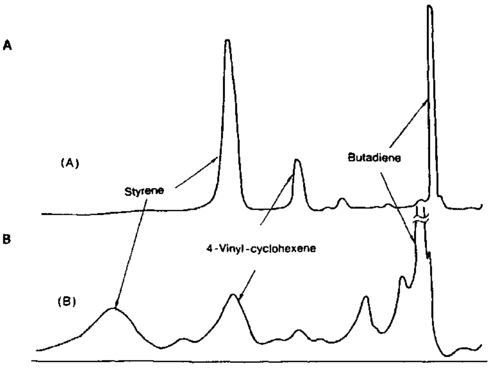


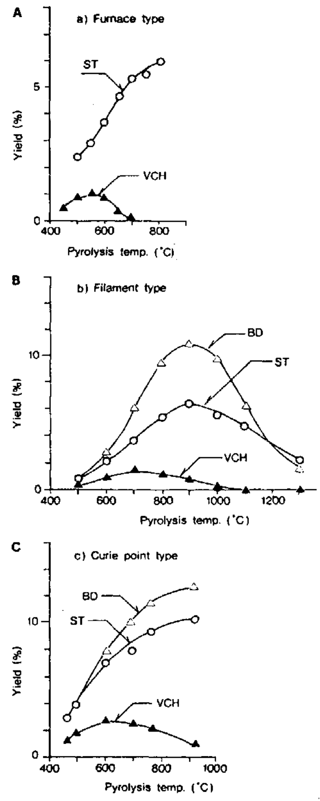
Figure 5 *Pyrogram of SBR with a) Curie point pyrolyzer and b) Furnace-type pyrolyzer.*

5a and b shows the difference in pyrograms obtained from styrene butadiene rubber (SSR) with the Curie point pyrolyzer and the furnace-type pyrolyzer. Figure 5a shows sharp characteristic peaks. Figure 5b demonstrates longer reten(ion times, broad peak shapes. and interference peaks at the shoulder of the butadiene peak. As a result. good quantitation cannot be expected from this pyrogram. Figure 6 shows the difference between three types of pyrolysis when NR/SBR is pyrolyzed. In the pyrolysis tube of the furnace-type pyrolyzer, the temperature distribution is large and therefore the reproducibility is not good. The pyrolysis temperature varies depending on the position of the sample insert.

In addition, lower molecular species are produced in the furnace-type pyrolyzer which may be due to the secondary reactions occurring in a long tube where the temperature distribution is large or the rise time is long. For the filament type and the Curie point type, reproducibility is good. But the yield of the pyrolysis products depends on the sample amount in the filament type.

Selection of the pyrolysis temperature plays an important role in the pyrolysis. Figure 7 shows the relationship between the pyrolysis temperature and the yield of the characteristic pyrolysis products of SBR. From Figure 7a (obtained from the furnace-type pyrolyzer), one can clearly see that one of the characteristic peaks, namely butadiene, is missing. and the yield is low. Figtlre 7b (obtained from the filament-type pyrolyzer) gives three characteristic pyrolysis products of

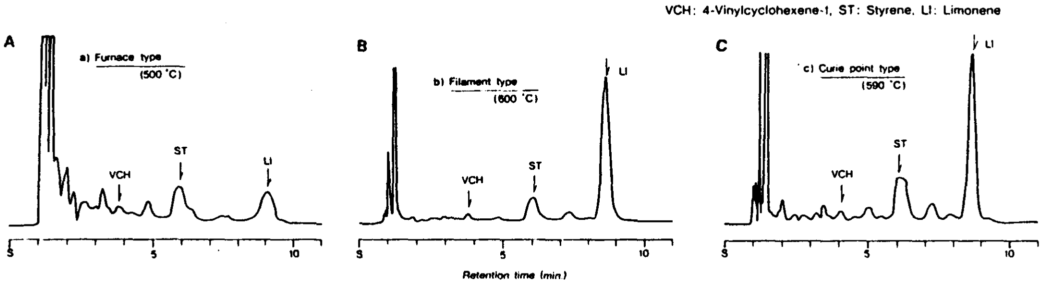
Figure 7 *Relationship between pyrolysis temperature and yield of characteristic pyrolysis products of SBR.*



BD: butadiene. VCH: 4-vinylcyclohexene-1. ST: styrene

Figure 6 *Pyrograms of NR/SBR (=80/20) blend rubbers.*

VCH: 4-Vinylcyclohexene-1, ST: Styrene, Li: Limonene



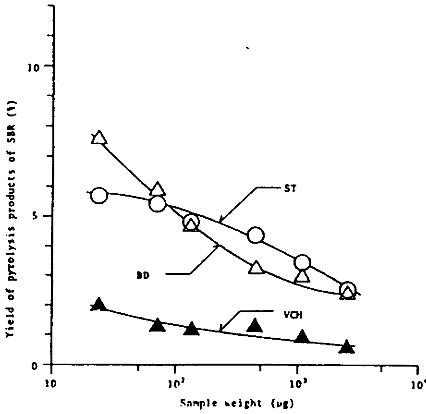


Figure 8 *Relationship between pyrolysis sample and yield of pyrolysis products (filament type).*

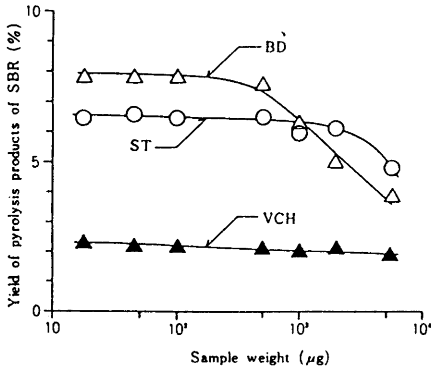


Figure 9 *Relationship between quantity of pyrolysis sample and yield of pyrolysis products (Curie point type).*

SBR, but the yield is somewhat lower than those seen in Figure 7c (obtained from the Curie point pyrolyzer).

In the pyrolysis of polymers, obtaining reproducible data is a problem. This problem is normally attributed to the reproducible pyrolyzing temperature, and the reproducibility of the sample preparation. In so doing, the quantity of sample pyrolyzed becomes an important factor. As we can see from Figures 8 and 9, the Curie point pyrolyzer demonstrates a constant yield of the pyrolysis products where the sample weight increases by a factor of 3, while the filament type pyrolyzer shows an immediate fan off of the yield as the sample amount increases. This fact is due to the poor heat transfer in the filament type when a large quantity of sample is placed on a thin film. while in the Curie point pyrolyzer a good heat transfer occurs as Ions as the sample contacts the large size of the pyrofoil.

The Pyrofoil Curie point pyrolyzer when coupled with a GC (GC-MS or GC-IR), demonstrates a superiority to other analytical techniques. For the analysis of residual solvent in magnetic wire, thermogravimetdc analysis (TGA), differential scanning calorimetry (DSC), or cure test is commonly employed. However, none of these methods gives reproducible and accurate results. The Pyrofoil Curie point pyrolyzer was found to overcome the problems encountered in the above-mentioned methods.

A PGC (pyrolyzer gas chromatograph) was also found to be a useful tool to study the microstructures of copolymers.[3,4]

A few examples are given here. Random and alternating copolymer of vinyl chloride-methyl methacrylate and of vinyl vhloride-acrylonitrile were studied .[5] Similarly, five kinds of butadiene copolymers have been investigated.[6] The sequential distribution of copolymers was also studied on methyl methacrylate copolymers with styrene or α-methylstyrene.[7] The pyrolysis - gas chromatographic behavior of poly (3-methyl-1-butenes) and poly (3-methyl-1-perltenes) with different monomer units was investigated, and the microstructure of the polymers was obtained.[8]

Therml degradation mechanism[9] of aromatic polyesters[10] and the cross-link density of vulcanized polyisoprene[11] were studied using a Curie poirlt pyrolyzer and GC-MS. Pyrolysis can be utilized as a fingerprint of polymer materials and biological samples. It can also can be used for the quantitative analysis of these types of materials.

Conclusion

PGC is an effective tool for analyzing polymers and other types of material. The fact that a minute amount of sample composition can be analyzed makes PGC superior to other techniques. Ease of sample preparation, reproducibility, and accuracy of data are important in this kind of work. Qualitative analysis and quantitative analysis can be performed on the Pyrofoil Curie point pyrolyzer. The ease in interfacing the Pyrofoil Curie point pyrolyzer to a GC, GC-MS, or GC-IR also plays an important role.

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