



Extraction and estimation of antistatic agent glycerol monostearate in polypropylene by gas chromatography coupled with flame ionisation detector

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Received 4 March 2022; accepted (revised) 2 January 2023

A new method has been developed for the estimation of an antistatic agent glycerol monostearate (GMS) in polypropylene (PP) over gas chromatography coupled with flame ionization detector (GC-FID). In the present work, selection of suitable sample specimen, sample weight, solvent mixture, extraction time, and temperature have been identified for the extraction of GMS in the PP resin. In-house polypropylene pellet has been used for study and the GMS extorted into n-hexane-ethyl acetate and quantified using GC-FID over 100% Dimethyl polysiloxane column. The method limit of detection is 1 mg/L and the limit of quantification is 5-750 mg/kg in PP resin with a correlation coefficient greater than 0.999. This method is accurate and has not found any interference with other co additives used in the propylene.

Keywords: Polypropylene, Polymer additives, Solvent extraction, Glycerol mono stearate, Gas chromatography with flame ionization detection (GC-FID)

Polymers are widely used materials and become an inevitable part of life, due to their flexible properties and affordability. These are used in various applications such as manufacturing, food packaging, household, medical, automotive, etc. Additives being added to the polymer¹ to attain desirable functional properties (physical, thermal, chemical), also gives the protection of external agents, ease of processability, and increase lifespan. Additives can broadly be classified as polymer functional agents and stabilizers. Stabilizers namely antioxidants (Irganox 1010, Irgafos 168, etc.), light stabilizers (like Benzophenones), metal deactivators (Hydrazide type, Amide type etc.). Functionalizing agents namely Plasticizers (Phthalic acid, epoxy type, etc.), Flame retardants (phosphorus & halogen type, etc.), Nucleating agents/Clarifying agents (Phosphate metal salts, sorbitol, fillers, etc.), Antistatic agents (Nonionic, anionic, cationic, etc.), and Lubricants (Hydrocarbon, metallic soap, etc.). Accurate quantification of additives is crucial during the production of polymers to achieve their desired properties in addition to regulatory reasons. Several analytical techniques were reported for the quantification of additives, among Liquid chromatographic²⁻⁴ and Gas chromatography-Mass Spectrometry⁵, X-ray fluorescence⁶ are the most popular methods.

Glycerol Monostearate is a widely used non-ionic antistatic agent⁷ that is compatible with polypropylene (PP), styrene polymers, and PVC. Glycerol monostearate (GMS) is classified into three types viz. GMS: 40 (GMS not less than 40%), GMS: 60 (GMS not less than 60%), and distilled glycerol monostearate GMS: 90 (GMS - not less than 90%). GMS-90 is being used in the plastic production industries as a foaming agent, lubricant, antistatic agent, anti-fogging agent. In addition to the antistatic properties, it also helps in improving the lubrication (being dual properties as hydrophilic and lipophilic) in the injection moulding and extrusion applications.

Polymers contain multiple additives which make a challenge⁸ in the accurate determination of additives due to matrix effect and co-additive interference, or degradation during sample preparation and extraction. The concentration of GMS in the polymer composition typically ranges from 0.02 wt% to 8.00 wt%. At concentrations below 0.02 wt%, the glycerol ester generally does not have a significant effect on the properties. At concentrations above 8.00 wt %, the glycerol ester tends to over-plasticize the polymer composition and cause undesirable softening⁹.

The test method for the determination of GMS in the PP product is developed over Fourier transform infrared (FT-IR) by Agilent Technologies¹⁰ measuring

the IR absorbance of the ester function group and this method has been validated over the range of 0.05 % to 0.80%. Ester functional group-containing additives such as Irganox- 1010 and zinc stearate, calcium stearate, have been found to interfere with GMS, therefore a correction factor is necessary for the accurate measurement of GMS in polypropylene. This correction factor decreases the reliability of the FT-IR test method for the analysis of GMS. The thin sheet is prepared and analyzed in the IR region and insignificant variation in thickness is having a significant impact on the test results especially when the analysis is required at a lower level (mg/kg). Other possible analytical strategies include High-Performance Liquid Chromatography (HPLC) with Evaporative Light Scattering Detector (ELSD). It is generally used only for semi-quantitative evaluations because the nonlinear dependence of the signal with the analyte concentration or short linear region in the calibration has been reported¹¹⁻¹⁴. Matrix-Assisted Laser Desorption/Ionization- Mass Spectrometry (MALDI-MS) is also an attractive emerging ionization technique that could be applied to qualitative identifications but it is not sensitive enough for a reliable quantification¹⁵.

In our current study, we have used a sonication liquid-solid extraction technique for extraction of GMS and quantified by using GC-FID in 1-150 mg/kg range of. This approach is more accurate and selective than the FT-IR method. It enables the qualitative and quantitative determination of GMS in PP resin.

Materials and Methods

Reagents

Glycerol monostearate (CAS number 123-94-4), In house Polypropylene resins standards (having Irganox -1010, Irgafos-168, Calcium stearate, Nucleating

agent and GMS90 additive approximate 520 & 550 mg/kg) Ethyl Acetate HPLC grade (CAS number 141-78-6), n-hexane HPLC grade (CAS number 110-54-3)

Instrumentation and sample preparation

Gas chromatograph

GC-FID conditions: Agilent -7890B with 7693A with liquid autosampler used for analysis. Injection port temperature set at 250°C with split ratio 1:2, Split flow 24 mL/min helium, separation was carried out using Agilent HP-1 capillary column (100% Dimethylpolysiloxane, 30 m x 530 µm x 5 µm, 60°C to 260°C) with an ultra-pure Helium carrier gas (99.999%) with a flow rate of 12 mL/min. Initial oven temperature was kept at 200°C and increased to 250°C with the rate of 13°C/min and hold for 25 min. FID temperature maintained at 250°C and Hydrogen flow at 30 mL/min, Air at 400 mL/min. 2 µL filtered sample was injected with Auto sampler. GC-FID Chromatograms are shown in Fig. S1-S3 in Supplementary Information.

GMS standards preparation and calibration

Calibration standards were prepared by dissolving commercially available GMS. A stock solution of 505 mg/L of GMS was prepared by dissolving 50.5 mg in 100 mL of ethyl acetate (75:25) solvent mixture. This stock solution was further diluted to obtain final concentrations 1.0, 2.5, 5.0, 10.1 mg/L (Fig. S4) and 50.5, 101.0, 151.5 mg/L (Fig. S5). Calibration curve was drawn for the lower range (1.0, 2.5, 5.0, and 10.1 mg/L) and higher range (50.5, 101.0, and 151.5 mg/L) of GMS. Average of triplicate analysis for each standard was used for drawing the calibration curve. R² value for lower and higher range of calibration for GMS is 0.99948 (Fig. 1) and 0.99985 (Fig. 2), respectively, and GC chromatogram is given in Fig. 3.

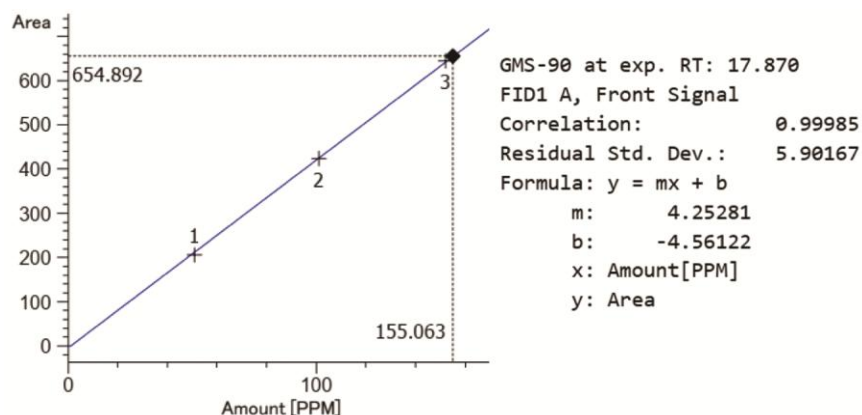


Fig. 1 — Low concentration curve for standards 1.0, 2.5, 5.0 & 10.1 mg/L

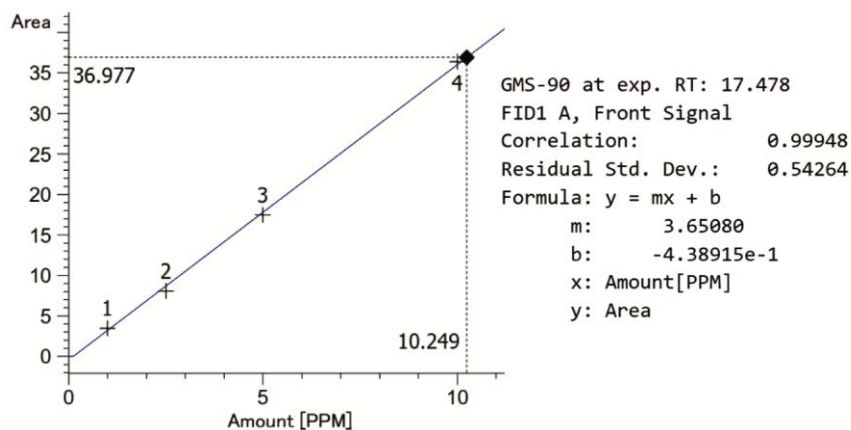


Fig. 2 — High concentration curve for standards 50.5, 101.0, and 151.5 mg/L

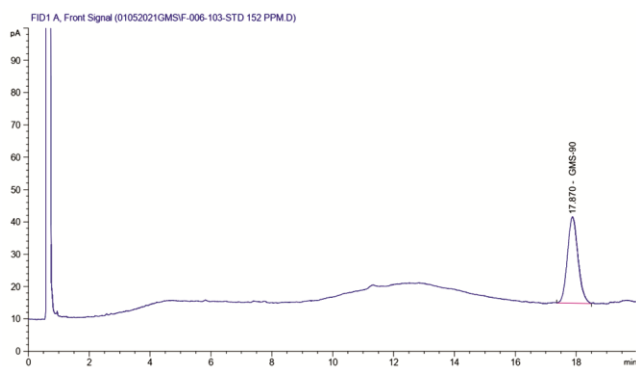


Fig. 3 — GC-FID Chromatogram of GMS

Preparation of 0.5 mm film specimen

0.5 mm thick PP film was prepared using a compression molding machine as per the standard test method¹⁶. Approximately 3.0 g of PP resin was placed in a mould of 0.5 mm thickness and sandwiched between 100 µm polyester films. Compression molding was performed using parting sheets of uncoated polyester film with a thickness of 100 µm and the obtained film was cut into small pieces. The temperature, pressure, time program used for the preparation of the film are given in Table 1.

Preparation of polymer powder sample

7.0 gram of PP pellets was cooled with 50 mL of liquid nitrogen. Cold PP pellets grinded in an ultra-centrifugal cryomill having distance sieve trapezoid holes diameter of 0.50 m (or 500 µm).

Extraction and analysis

2.5-10.0 g of sample specimen (grounded powder or film specimen) was weighted to the nearest 0.01 g, taken into an airtight 100 mL glass bottle, and 25 mL of solvent was added to it¹⁹. The content was subjected to ultrasonication for the extraction¹⁷⁻¹⁸ of GMS at 50°C & 60°C with different extraction times i.e. 60

Table 1 — Compression molding machine program for the preparation of film specimen

Molding steps	Temp. (°C)	Pressure (bar)	Time (sec)
Phase – I	210	150	350
Phase – II	210	200	350
Phase – III	30	240	600

min, 90 min, and 120 min. After ultrasonication allowed to room temperature, the extract was filtered through Whatman filter paper no. 541 followed by 0.45 µm nylon syringe filter before injection. Extracted samples are analyzed over Gas Chromatograph operated at similar conditions of calibration, final results were normalized with the applicable dilution factor.

$$GMS\ Content\ \left(\frac{mg}{kg}\right) = \frac{A \times R \times V}{W}$$

$$R = \frac{Concentration\ of\ additive\ \left(\frac{mg}{L}\right)}{Area\ of\ additive}$$

Where, A= area of GMS, R= response factor, V=volume of extraction solvent (mL) and W= weight of sample extracted.

Results and Discussion

Comparison of extraction efficiency between film and powder sample and optimization of solvent combinations

PP sample having 550 mg/kg GMS was used in this study and powder and film samples were prepared as per the above procedure. 5.0 g Film cut pieces, Powder sample specimens are separately taken into a 100 mL flat-bottom airtight bottle containing 25 mL solvent. Extraction carried by sonication for 90 min at 60°C. Test results with different solvent ratios are given in Table 2.

From the Table 2, it was evident that maximum extraction recovery was achieved with grounded powder samples as compared to film samples. Powder

specimen having more surface area than film specimen, the higher surface of the polymer is exposed to the solvent which in turn increases the swelling of polymer thus efficient extraction of additive molecule to a solvent phase. Better extraction efficiency (Table 2: S. No 4, 5) is observed in n-hexane : ethyl acetate mixture either in 75:25 or 25:75. To further optimize the sample quantity, we performed experiments with 2.5 g, 7.5 g, 10.0 g sample, test results are repeatable and showed that there was no significant impact on the sample quantity, therefore 5.0 g sample quantity and n-hexane-ethyl acetate (75:25) was chosen as optimal for further study so that saturation of extraction can be avoided and availability of extraction data at an upper and lower range of sample weight is available for further extraction study. To optimize the extraction temperature and time with n-hexane: ethyl acetate (75:25) solvent mixture was opted over (25:75) due to the lesser ratio of polar component (Ethyl acetate) in the solvent mixture.

PP is a non-polar polymer that allows the non-polar solvents to interact easily. GMS is a polar additive which easily attracted towards polar solvents. The combination of both the solvents (n-hexane and ethyl acetate) gives the efficient extraction. Extraction efficiency depends upon the temperature and sonication time. Detailed analysis report of PP grounded powder sample with n-hexane: ethyl acetate (75:25) solvent mixture extraction at 60°C with different extraction times in duplicate (Analysis I & II) was studied and test results are given in Table 3.

From the Table 3 experimental data, it shows that extraction recovery increased with time, decreased with temperature, and optimum extraction is achieved at 60°C and 90 or 120 min duration. For the completion of the test quickly, 60°C and 90 min duration are chosen over 120 min.

There are many experiments explaining the behaviour of n-hexane (non-polar) in the extraction of polymer additives. The higher percentage of hexane results in better extraction of the additive at lower temperatures. It is suggested that n-hexane works as a good swelling agent and this effect is especially important at lower temperatures. The solvent dielectric constant (ϵ) is an important parameter that affects the rates of chemical reactions and extraction processes. It may influence the extraction efficiency of a solvent depending upon the nature of the extractable material from the plastic. Non-polar solvents have both sides charged and are able to penetrate into the matrix of a feed. This is because they lack an O-H end which otherwise would interfere with the extraction process. Generally, non-polar solvents are better suited for extraction than polar ones, because the low presence or complete absence of charges allows penetration into the low polar matrix.

Reproducibility of the Test method

PP grounded powder sample (5.0g) ultrasonicated with n-hexane-Ethyl acetate (75:25) ratio at 60°C for 90 min and analysed over GC-FID by three different analysts in the duplicate run. Test results of the reproducibility tests are given in Table 4. Standard

Table 2 — Extraction results of Film sample and powder sample (PP GMS Standard sample 550 mg/kg)

S. No.	Solvent (25 mL)	Sample weight (g)	Film sample GMS (mg/kg)	Powder sample GMS (mg/kg)
1	n-hexane: ethyl acetate (100:0)	5.0	344	400
2	n-hexane: ethyl acetate (0:100)	5.0	398	472
3	n-hexane: ethyl acetate (50:50)	5.0	411	481
4	n-hexane : ethyl acetate (75:25)	5.0	422	536
5	n-hexane - ethyl acetate (25:75)	5.0	454	534
6	n-hexane - ethyl acetate (25:75)	2.5	407	512
7	n-hexane : ethyl acetate (75:25)	2.5	405	537
8	n-hexane - ethyl acetate (25:75)	7.5	434	528
9	n-hexane : ethyl acetate (75:25)	7.5	408	550
10	n-hexane - ethyl acetate (25:75)	10.0	415	548
11	n-hexane : ethyl acetate (75:25)	10.0	380	547

Table 3 — Optimization extraction time and temperature (PP GMS Standard sample 550 mg/kg)

S. No.	Sample weight (g)	Temp. (°C)	Time (min)	Analysis -I (mg/kg)	Analysis-II (mg/kg)
1	5.0	60	60	532	532
2	5.0	60	90	546	542
3	5.0	60	120	550	546
4	5.0	50	90	521	513

Table 4 — Reproducibility of the test method (PP GMS Standard sample 520 mg/kg)

S. No.	Observed value(x) mg/kg	Mean(\bar{x}), mg/kg	Standard deviation
1	509		
2	518		
3	497	513	8.92
4	495		
5	502		
6	497		

deviation of 1.72% (8.92 at 520 mg/kg) is observed for the extraction and analysis of GMS in PP resin.

Conclusion

It is concluded that the newly developed method for GMS in Polypropylene resin by ultrasonic extraction followed by analysis over Gas Chromatography (GC with FID and HP1 column) is an accurate method. This test method is not interfering with other co-additives and is better than the FT-IR technique. From the test results, it is evident that a temperature of 60 °C and 90 min time is optimum for extraction of GMS additive from Polypropylene. In place of digestion or any other high energy consumption extraction procedure, ultra-sonic extraction at a lower temperature is good enough for the extraction of additive even in less time. It will be one of the better in-process control tools for timely reporting of the results and to avoid loss in production. It is also evident from the test results that extraction in powder is much better than the extraction from film specimen in the case of ultrasonication. It is mainly due to enhanced surface area interaction with the solvent. With the minimum quantity of non-polar solvent in a polar-nonpolar solvent mixture of n-hexane : Ethyl acetate ratio, 75:25 is the optimum extraction of GMS-90 is also achieved even with very less quantity of sample i.e. 5.0 g. Usage of a minimum quantity of the sample also results in longer operational hours of the test equipment without any interruption. This analytical method will be useful for the quality control of PP resins and a better understanding of their behaviour in processing and final products, particularly in medical and food contact materials.

Acknowledgment

Authors are grateful to the management of Indian Oil Corporation Limited, Paradip Refinery for

providing infrastructure support and facilities to conduct the experiments at Paradip Refinery Quality Control Laboratory. Authors also acknowledge their thanks to Mr. Vinayagamurthi Murugesan and Ms. Sushree Sangita Acharya of M/s Gulf Bio Analytical for extending their support during the experiments.

Supplementary Information

Supplementary information is available in the website <http://nopr.niscpr.res.in/handle/123456789/58776>.

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