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Analysis of additives in polymers by thin-layer chromatography coupled with Fourier transform-infrared microscopy

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Abstract

A new, fast and convenient method based on coupled thin-layer chromatography (TLC) and Fourier transform-infrared (FT-IR) microscopy is developed to separate, detect and identify the additives in polymers. After the TLC development, the analytes were transferred on to a barium fluoride (BaF_2) salt plate via a special capillary technique and analysed by FT-IR microscopy. The additives used for stabilization of polypropylene and the plasticisers used for poly(vinyl chloride) were analysed as examples to illustrate this technique. The overall time taken for the experiment including transferring three marked spots and then identifying them was about 20 min. An amount as small as 0.5 μg can be easily detected and identified. It was a very convenient and reliable method to separate and evaluate complex additives for polymers without the interference from TLC adsorbent, because of a special transferring and identifying method, which is suitable to FT-IR microscopy.

Keywords: TLC; FT-IR microscopy; Polymer; Additive

1. Introduction

Identification of additives in polymers is important in forensic investigations, scientific research and quality control, etc. [1]. Currently, a range of additives is being used for protection during processing, increasing lifetime and improving the performance of products. Although high performance liquid chromatography (HPLC) is a very good method for separation of complex additives, there are some difficulties in identification of some components [2]. Gas chromatography coupled with mass spectroscopy (GC–MS) is very beneficial for isolating and identifying some additives but when dealing with antioxidants and stabilisers, it is not feasible in many cases owing to their decomposition or lack of volatility.

Thin-layer chromatography (TLC) remains one of the most widely used of all the chromatographic techniques for simple and rapid qualitative separation [3–5]. The use of a detection technique such as, Fourier transform-infrared (FT-IR) spectroscopy or nuclear magnetic resonance (NMR) spectroscopy arises from the need to reliably identify components or to obtain valuable molecular structure information of the components separated by TLC [6,7]. Therefore, combined TLC and FT-IR has been very attractive for the analysis of complex additive in polymers. The combination of TLC and FT-IR has recently been applied in two ways: in situ or transfer method with

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diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy as a method of the evaluation [8]. However, the major difficulty encountered with in situ DRIFT–TLC method is the strong background absorption of the adsorbent, which means that it can only be used in particular spectral regions according to the TLC adsorbent being used [9]. On the other hand, the transfer of analytes in DRIFT–TLC is usually time consuming [10].

Infrared microscopy is a powerful technique [11,12] that combines the image analysis capabilities of optical microscopy with the chemical analysis capabilities of infrared spectroscopy. The combination of these two techniques allows infrared spectra to be obtained from microspectroscopic-sized samples. With the assistance of microscopy, samples as small as 0.01 μg or even less (depending on the infrared absorption characteristics of the components of interest) can be easily located and detected. Therefore, with all of these characteristics, FT-IR microscopy is a good technique of identification for components separated by TLC.

The aim of this research is to apply FT-IR microscopy in combination with TLC for the identification of additives in polymers. It was very convenient and reliable because of the effective transferring technique and identifying method that were suitable to FT-IR microscopy. The advantage of this method is that it can be used to evaluate each separated component by various TLC sheets without the interference of TLC adsorbent. In addition, it is not a time consuming method. To the best of our knowledge, this coupling technique has not been previously published. In this study, we analysed antioxidants and ultraviolet stabilisers used for polypropylene (PP) and the plasticisers for PVC as examples to show how this technique can be applied. The technique can be extended to analyse various other additives in variety of polymers.

2. Experimental

2.1. Materials

TLC analysis was performed on TLC plates (5 cm × 10 cm) precoated with a 250 μm layer of silica gel 60 F254 on a glass support (Merck, Darmstadt, Germany). The solvents (methanol, acetone, formic acid, diethyl ether and toluene) and plasticisers (diisooctyl phthalate and dibutyl phthalate) were of analytical reagent grade and purchased from Science Supply, Vic., Australia. Antioxidant (Irganox1010) and ultraviolet stabilisers (Tinuvin770 and Chimassorb 119 FL) were from Ciba Specialty Chemicals Inc., Australia. Their chemical structures are shown in Fig. 1.

2.2. Analytical procedures

2.2.1. Preparation additive solutions, standards and other solutions for detection limit test

A simulated solution of a mixture of additives (I) was prepared by weighing 0.1 g of each Irganox1010, Tinuvin770 and Chimassorb 119 FL into a 10 ml volumetric flask and diluted it with toluene. The standard of solutions (0.5%) Irganox1010, Tinuvin770 and Chimassorb 119 FL were made by dissolving 0.05 g of each pure additive in a 10 ml toluene.

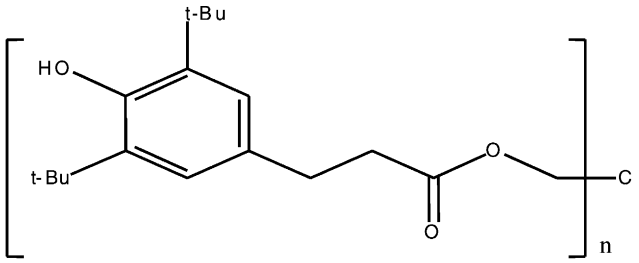
A series of dibutyl phthalate solutions were used for the detection limit test. A stock solution of dibutyl phthalate (0.5%) was prepared by dissolving 0.05 g dibutyl phthalate into a 10 ml of diethyl ether. The solutions of 0.1, 0.05 and 0.01% were obtained by diluting the stock solution with diethyl ether 5, 10, and 50 times, respectively.

2.2.2. Chromatographic procedures

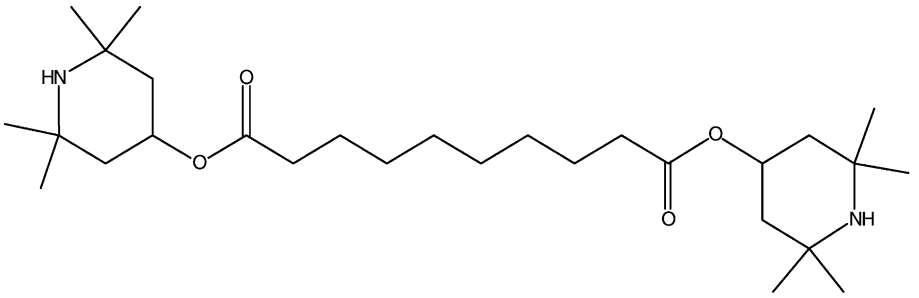
Before runs, the TLC plates were cleaned by developing in methanol–formic acid (1:1) solvent mixture. The plates were dried in air, heated for 3 h at 160 °C and stored in a desiccator until use. A 2.0 μl of solution (I) was applied onto the plates with 5 μl syringe. TLC sheet was then developed with a mixture of toluene–diethyl ether (10:1) as the mobile phase to a distance of 60 mm. The developed spot was marked under UV light and R_F value was 0.8. After the removal of $R_F = 0.8$ spot, the second development was carried out with the same TLC plate with a solvent mixture of acetone–formic acid (4:6) as the mobile phase to a distance of 60 mm. The separated substances were visualised by iodine vapour and marked. The R_F values were calculated to be 0.5 and 0.1, respectively.

2.2.3. Transfer of analytes

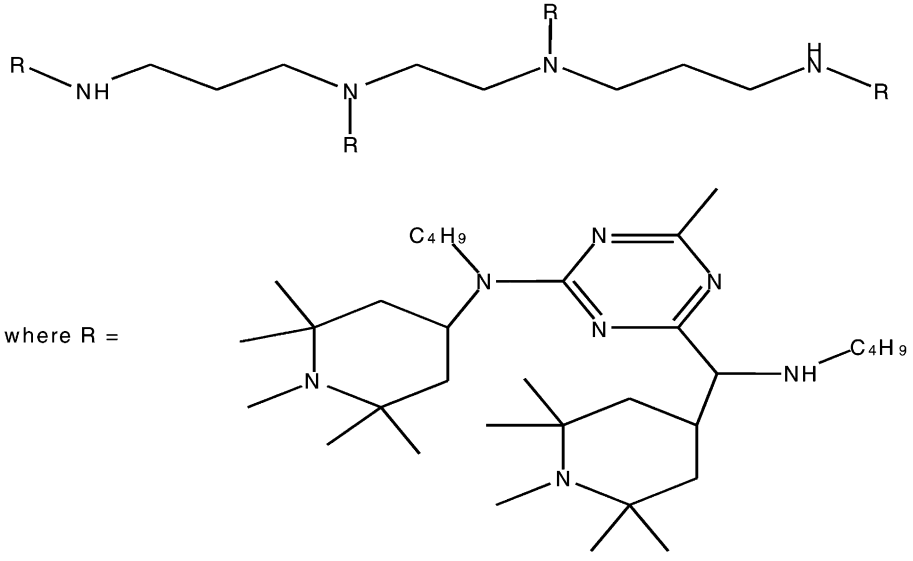
Melting-point glass capillaries of 8 cm long and 1 mm i.d., purchased from Selby-BioLab, Australia



(a) Irganox 1010 neopentyl tetra [3- (3, 5- Di- *tert* -butyl-4-hydroxy-phenyl)-propanoate]



(b) Tinuvin 770 Low molecular weight hindered amine light stabiliser, Bis-(2,2,6,6-tetramethyl-4-piperidyl) sebacate



(c) Chimassorb 119 FL (monomeric hindered amine light stabiliser [HALS]

Fig. 1. Chemical structure of: (a) Irganox1010; (b) Tinuvin770; (c) Chimassorb 119 FL.

were used to transfer the analytes. The 5 cm long piece was removed from the closed end of the capillary by breaking and the capillary (3 cm × 1 mm) was then packed with a small piece of facial tissue (Kimberly-Clark Australia Pty. Limited), as illustrated in Fig. 2a. The marked spot of the developed TLC plate was directly transferred to the capillary by lightly pressing and rubbing the capillary end on the marked

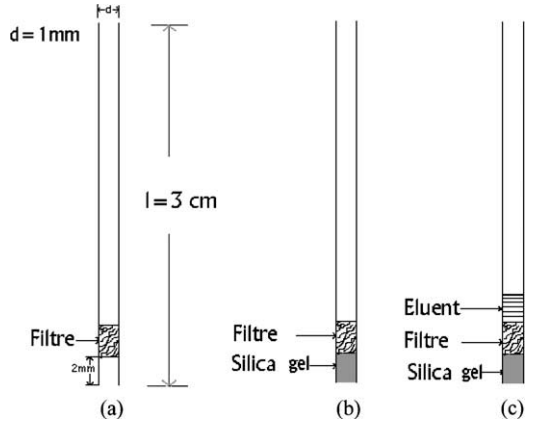


Fig. 2. Capillary transfer technique, showing the steps of transfer technique: (a) with the filter plug; (b) with filter plug and silica gel containing adsorbed compounds; (c) after eluting with the eluent, the upper eluent layer contains separated component.

area. After the silica gel containing the adsorbed compound was transferred to capillary (Fig. 2b), the capillary was placed into a 5 ml beaker containing the eluent. Then methanol was used as an eluent for the $R_F = 0.8$ spot and acetone–formic acid (2:8) for the $R_F = 0.5$ and $R_F = 0.1$ spots. Due to the capillary and penetration actions, the eluent travels upwards, allowing the component to rapidly elute from the adsorbent to eluent. When the eluent reached a level about 1–2 mm above the tissue position as indicated in Fig. 2c, the capillary was removed from the beaker.

A 3 μl glass capillary micropipete ($d = 0.5$ mm), made by Drummond Scientific Co., USA, was used to draw about 0.1 μl of solution from the capillary (taking care not to touch the facial tissue). Then, the 0.1 μl solution was dropped onto the BaF_2 plate, and the BaF_2 plate was placed inside a fume cupboard to evaporate the solvent. A stream of nitrogen was used to remove any trace of solvent. After the evaporation was completed, the position was marked with a fine pen. By following this method, all of the other separated materials were transferred onto the same BaF_2 plate. In order to remove any remaining formic acid, a small drop distilled water was dripped onto the corresponding positions of $R_F = 0.5$ and $R_F = 0.1$ components on the BaF_2 plate and distilled water was then taken away by removing it with a piece of tissue. This process was repeated three times to remove any remaining formic acid from the BaF_2 plate.

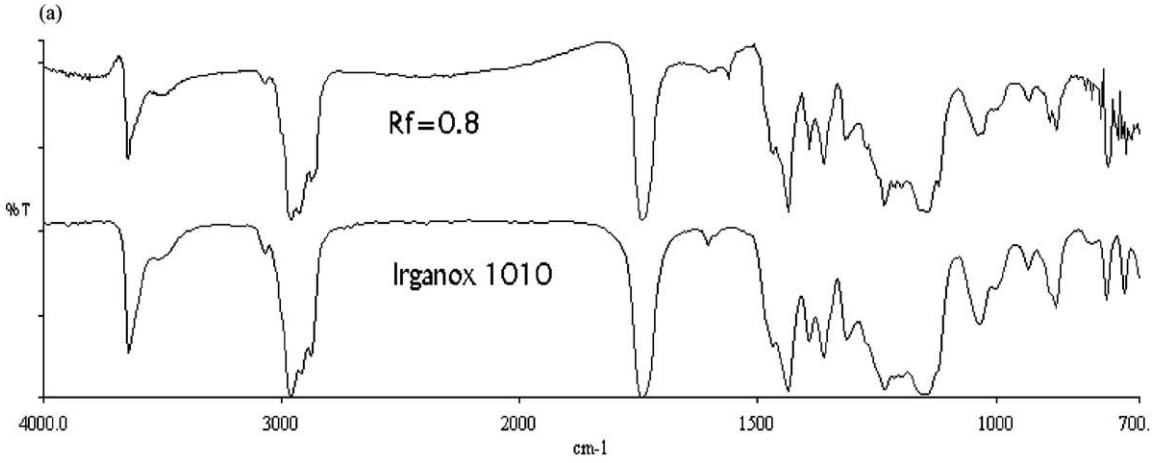
2.2.4. FT-IR microscopy measurement

A Perkin-Elmer Spectrum GX/2000 FT-IR spectrometer equipped with an Auto Image Microscope was used to identify the separated components. Perkin-Elmer Spectrum Search Plus software was used for library searching. The degree of conformity of the sample and the reference spectra is described by means of a hit quality, wherein the value 100 resembles maximum fit. About 0.1 μl of each standard additive solution was dripped onto the BaF_2 plate and the solvent toluene was removed by evaporating in air. After their FT-IR spectra were obtained (aperture 50 μm × 50 μm, no. of scan 32, resolution 4 cm^{-1}), the FT-IR spectra were added to the IR standard material library. Figs. 3–5 show $R_F = 0.8$, 0.5 and 0.1 component FT-IR spectra, their best matched standard spectra and corresponding microscopic zones which were chosen for measurement.

3. Results and discussion

The efficiency of the coupled TLC–FT-IR microscopy technique was investigated by analysing the PP additives. Outdoor PP products usually contain antioxidants and ultraviolet stabilisers and it is becoming more and more common to add complex ultraviolet stabilisers in order to obtain good performance of PP outdoor products [13]. In general, polymer additives are analysed after the extraction of additives from the polymer and there are extensive reports [1,14] dealing with how to extract additives from polymers. In these studies, a simulative extraction solution of complex additives for PP was selected to illustrate this technique. This complex additive mixture was made up of a mixture of Irganox1010, Tinuvin770 and Chimassorb 119 FL that are not easy to analyse qualitatively by other chromatographic method such as GC–MS or HPLC. Irganox1010 is a hindered phenolic additive, whereas Tinuvin770 and Chimassorb 119 FL are hindered amine additives.

The first step for this method is to separate each additive from the mixture by TLC development by choosing a suitable TLC plate and a mobile phase. TLC plates are available with a wide range of chromatographic supports such as normal phase silica gel, alumina (neutral, basic and acid), polyamide or cellulose, reversed-phase, ion exchange and chiral supports.



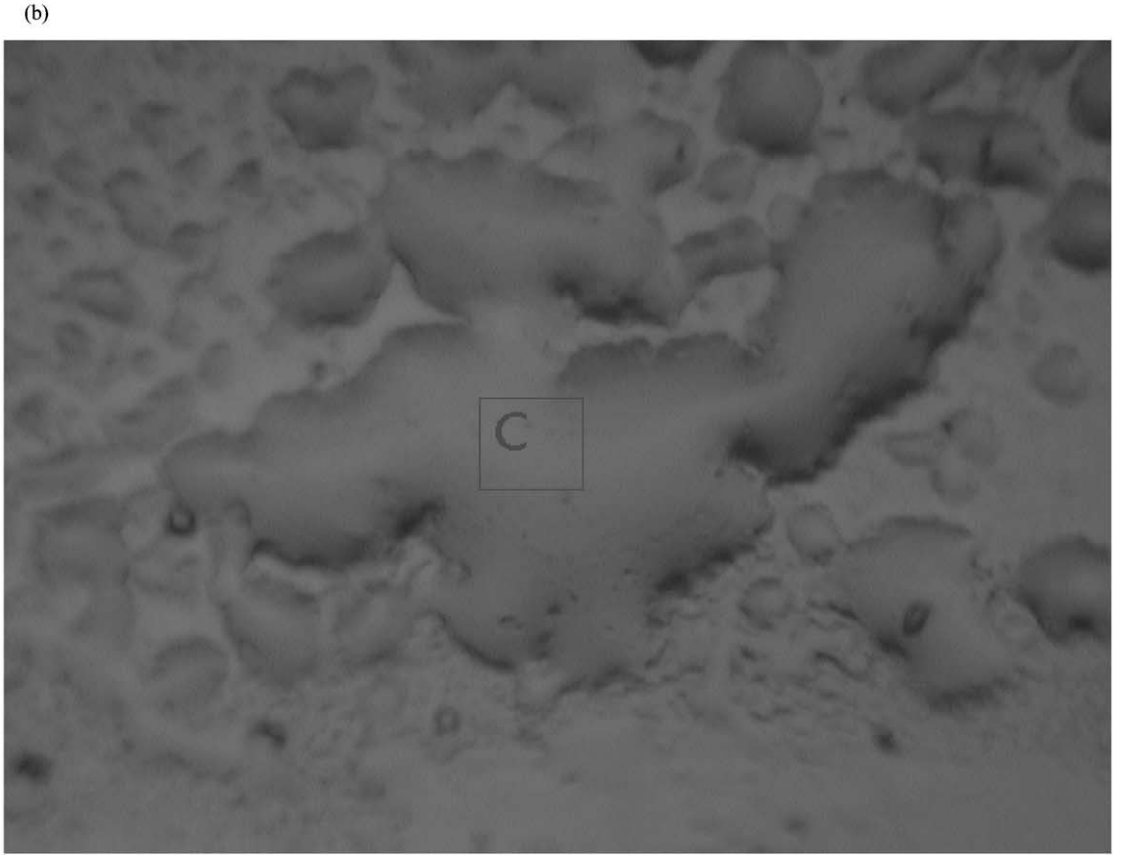
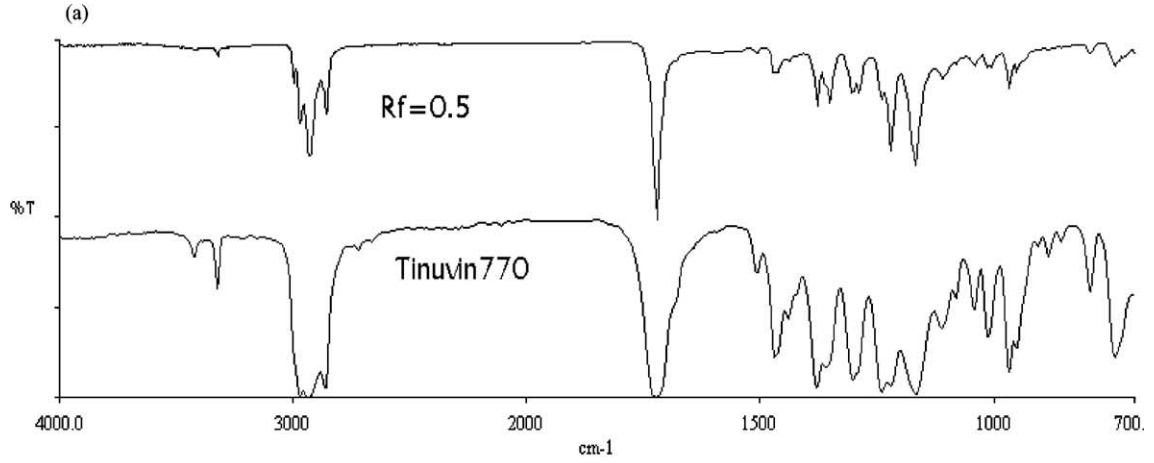


Fig. 3. (a) $R_F = 0.8$ spot FT-IR spectra (aperture 50 μm × 50 μm; scan times: 32; resolution: 4 cm^{-1}) and the hit quality of 96 matched Irganox1010 standard spectra (50 μm × 50 μm; scan times: 32; resolution: 4 cm^{-1}). (b) Microscopic picture of $R_F = 0.8$ spot on BaF_2 plate and selected zone marked as C for FT-IR analysis.



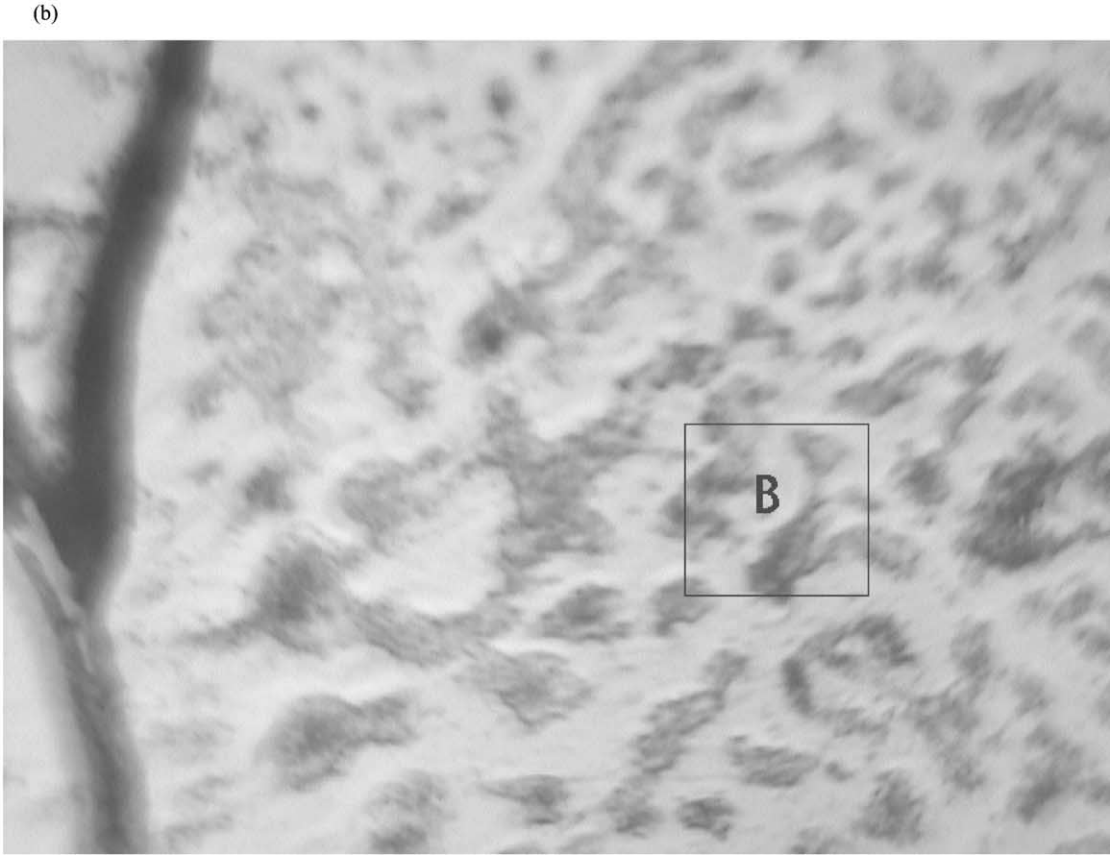


Fig. 4. (a) $R_F = 0.5$ spot FT-IR spectra (aperture: 100 μm × 100 μm; scan times: 32; resolution: 4 cm^{-1}), the hit quality of 95 matched Tinuvin770 standard spectra (50 μm × 50 μm; scan times: 32; resolution: 4 cm^{-1}). (b) Microscopic picture of $R_F = 0.5$ spot on BaF_2 plate and selected zone marked as B for FT-IR analysis.

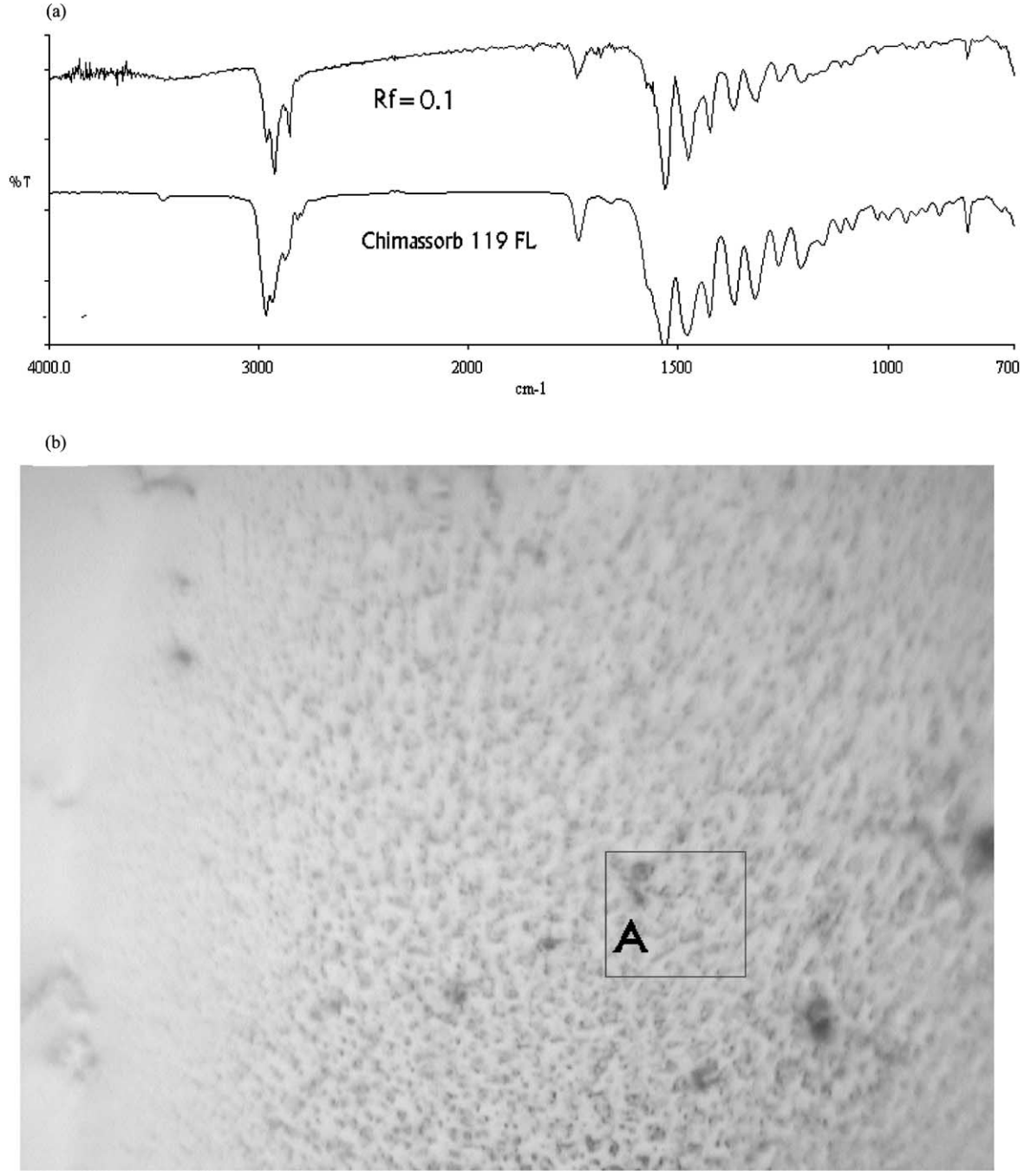


Fig. 5. (a) $R_F = 0.1$ spot FT-IR spectra (aperture: 100 μm × 100 μm; scan times: 32; resolution: 4 cm^{-1}), the hit quality of 95 matched Chimassorb 119 FL standard spectra (50 μm × 50 μm; scan times: 32; resolution: 4 cm^{-1}). (b) Microscopic picture of $R_F = 0.1$ spot on BaF_2 plate and selected zone marked as A for FT-IR analysis.

Nevertheless, a variety of solvents and solvent mixtures having different polarity are available as the mobile phase. The selection of TLC plates and the mobile phase mainly depends on the functional groups present in the analytes. In this study, silica gel plates were used with toluene–diethyl ether mixture (10:1) as the mobile phase for Irganox1010 ($R_F = 0.8$) and with acetone–formic acid (4:6) for Tinuvin770 ($R_F = 0.5$) and Chimassorb 119 FL ($R_F = 0.1$). Since Tinuvin770 and Chimassorb 119 FL are hindered amine compounds, the basic alumina plates are the best suitable TLC plates. However, the separation of hindered amine additives during the TLC development ($R_F = 0.1$ and 0.5) was successfully achieved with silica gel plates using a highly polar solvent mixture containing formic acid.

Since FT-IR microscopy with a nitrogen cooled MCT detector has very high sensitivity (0.01 μg is enough in most cases), dimensions of 1 mm × 3 cm capillary was chosen to transfer separated TLC components to the BaF_2 plate. During the process of transferring of analytes, it is important to prevent silica gel from being on BaF_2 plate, because silica gel will interfere with FT-IR determination. In order to prevent adsorbent from being drawn into micropipet during application onto the BaF_2 plate, use of a proper filter medium is essential. According to work done by Szekely [15], KBr was chosen as a filter medium. Although KBr powder itself is IR transparent, it is difficult to distinguish KBr powder from the real sample under the microscope. As a result, a high quality FT-IR spectrum cannot be gained. Then, a piece of cotton was chosen to block the adsorbent, but the result was not satisfactory owing to its fluffy volume, and the high absorbency capacity of the eluent. Since the eluting process was carried out by capillary and penetration actions, it can be estimated that just a small amount of adsorbent would be in the upper eluent. Therefore, a piece of facial tissue was used as the filter and it worked very well. The presence of adsorbent was not seen because the spectra displayed in Figs. 3–6 showed no Si–O peak at ~1100 cm^{-1}. No fibre of the tissue was found under the microscope. However, emphasis should be made not to contact the tissue with the micropipet during the transferring, since trace amount of adsorbent may deposit on the tissues.

After a marked spot was transferred to a capillary tube, the capillary was dipped into the eluent. At this stage, it is important to make sure that the separated component would not diffuse into the eluent in the beaker, instead it would elute from the adsorbent quickly. Thus, a pre-test experiment was carried out with a dye (bromophenol blue). The dye was applied onto a TLC plate and the spot was transferred into the capillary via the same method described previously. The capillary was placed in methanol. The upper eluent shown in Fig. 2c became blue and it was immediately apparent that instead of diffusion, the dye was eluted within a second from silica gel adsorbent to methanol. No colour change was seen inside the methanol container. Therefore, it is possible to transfer separated components easily and quickly with almost no diffusion, if the right eluent is chosen. As for the eluent, it also is very important to choose a solvent that is polar enough to elute the separated component quickly from adsorbent to eluent. Methanol was used to elute the less polar Irganox1010 and acetone–formic acid (2:8) was used for the amine additives. Since all eluent need to be completely removed from the BaF_2 plate before FT-IR determination, it is preferable to use a highly volatile solvent if it is possible.

The salt plate used for FT-IR microscopy should be hard, stable and resistant to most solvents. In addition, it should have as far as possible a wide spectrum range and a reasonable price. Of all window materials, a BaF_2 plate is the optimal one, because it has a relatively wide spectral range (50,000–770 cm^{-1}) and is resistant to almost all organic solvents, most acids, bases and moisture. Another advantage is its recyclability. After it was cleaned with a proper solvent, it can be reused. In this study, a BaF_2 plate of dimension 2 cm × 4 cm × 0.2 cm that could accommodate at least 18 samples was used. The separated components can be identified under the FT-IR microscope one by one, without being interrupted by transfer of samples prior to the FT-IR identification, saving much time.- After the transferring of each separated additive onto the BaF_2 plate, each spot was visualised under the microscope and the FT-IR spectra were taken at selective area as illustrated in images of Figs. 3b–5b for Irganox1010, Tinuvin770 and Chimassorb 119 FL, respectively. In order to obtain a high quality FT-IR spectrum, it is very essential to choose the correct area. Usually, if there is a single drop of liquid, or a crystal or powder whose area is larger than 2500 $μm^2$

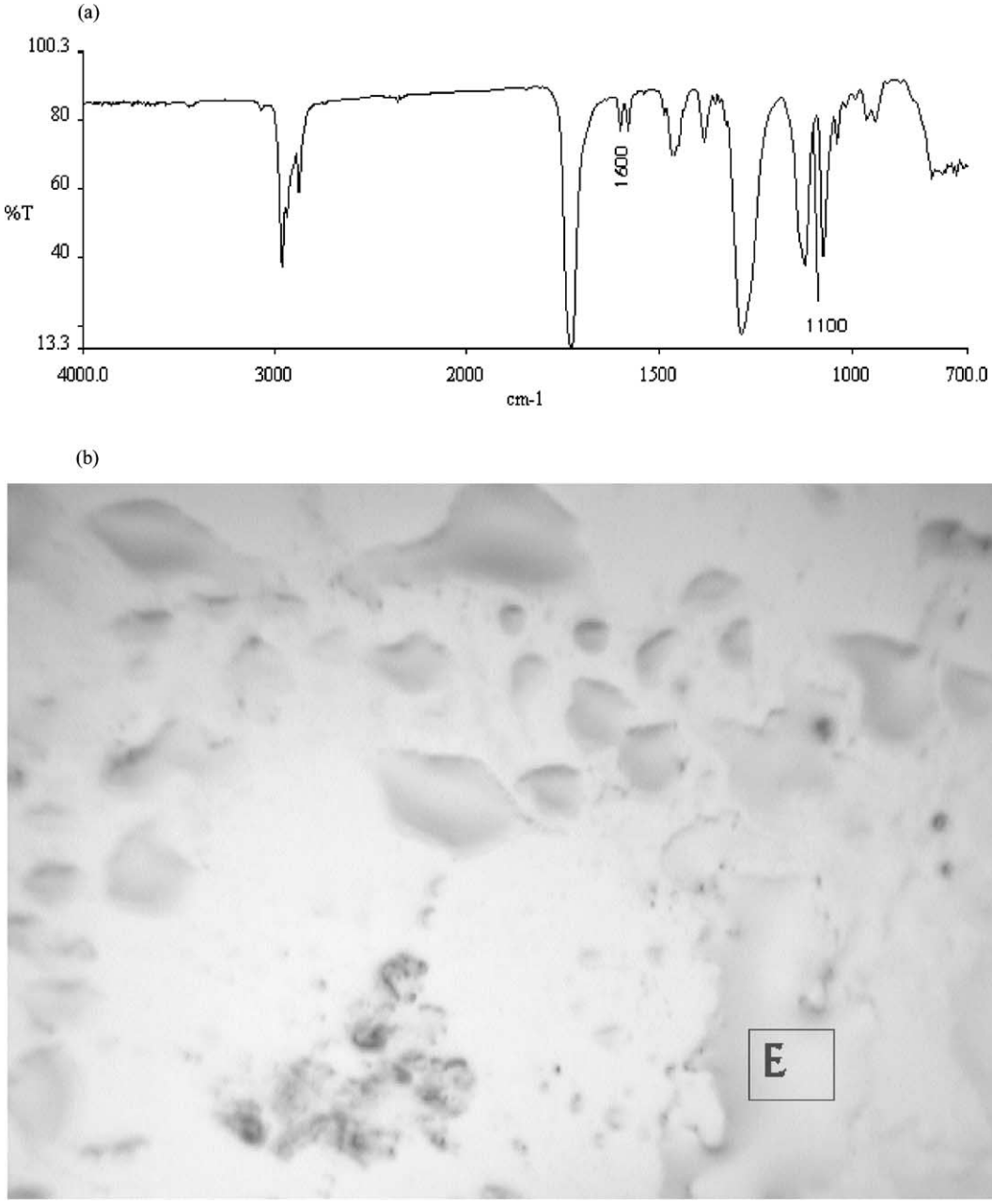


Fig. 6. (a) Dibutyl phthalate FT-IR spectrum (1 μl 0.05% dibutyl phthalate toluene solution was applied to TLC sheet and then dibutyl phthalate was transferred to BaF_2 (aperture: 50 μm × 50 μm; scan times: 32; resolution: 4 cm^{-1}). (b) Selected zone marked as E for FT-IR analysis.

(under the microscope it is very easy to locate the area), the areas (shown in Figs. 3b and 6b) are the best testing zones. If not, more concentrated sample area should be chosen as shown in Figs. 4b and 5b, with 100 μm × 100 μm aperture. As for the background position, the closer to the sample position, the better the spectrum will be. The collected spectra were matched with those of FT-IR library, and the hit

quality was 96 for Irganox1010 and 95 for both Tinuvin770 and Chimassorb 119 FL.

Dibutyl phthalate that is one of plasticisers for PVC, which has almost no absorption at 1100 cm^{-1}, however, shows a lot of weak characteristic absorbent peaks such as at 1600 cm^{-1}. We choose a series of dibutyl phthalate solutions for detection limit testing. The detection limit was assessed by applying 1.0 μl of 0.5, 0.1, 0.05 and 0.01% dibutyl phthalate in diethyl ether on the TLC sheet, and then using the same transferring and evaluating method. All the samples, except 0.01% dibutyl phthalate gave high quality spectra suggesting that even 0.5 μg dibutyl phthalate can be detected by this method without loss weak benzene ring stretch vibration peak at 1600 cm^{-1}, as can be seen in Fig. 6. For 0.1 μg dibutyl phthalate, the spectrum was not satisfactory owing to losing many weak characteristic peaks.

Furthermore, the applicability of this method was demonstrated by analysing the mixture of plasticisers used for PVC. The mixture of dibutyl phthalate, diisooctyl phthalate were separated using silica gel TLC sheets, diethyl ether–toluene (1:9) mixture as the mobile phase and methanol as the eluent. The R_F values were 0.6 and 0.5, respectively. Very high quality FT-IR spectra of dibutyl phthalate and diisooctyl phthalate FT-IR spectra were obtained after using above-mentioned transferring and evaluating methods. Thus, it is clear that the method described above can be applied to a variety of additives in various polymers qualitatively.

4. Conclusions

The results demonstrate that TLC–FT-IR microscopy coupling is very convenient and reliable technique to detect and identify additives in polymer without the TLC adsorbent interference. The total time for transferring three marked spots and then identifying them was about 20 min. The method has been applied to polymer additives including hindered amine light stabilisers, a hindered phenol antioxidant and complex plasticisers for poly(vinyl chloride). With a wide range of precoated TLC plates (silica gel and alumina supporters were tested in this paper) and a variety of mobile phases, a diversity of complex additives in polymers such as antioxidants, cure accelerators in rubber and additives for coating and so on can be analysed by this method. Moreover, a high quality infrared spectrum can be obtained with as little as 0.5 μg sample and the spectra are suitable for directly matching using spectral library search software. However, the shortage of this method is that it cannot be used to analyse sample quantitatively. After qualitative analysis, HPLC and GC are the best methods for quantitative analysis if it is required.

Acknowledgements

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