Detection of Inclusions and Degradation in Injection-Molded Thermoplastics

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Abstract: This work suggests a formal procedure to identify inclusions and anomalies in injection molded specimens. To find a suitable procedure, experiments with actual molded specimens have been tested. The specimens were injection molded blow preform of PET with inclusions and the PET preform degraded intentionally by controlling the residence time. By microtoming the inclusions have been exposed to the surface and then they have been analyzed by XRD, XRF, FTIR and DSC. Based on the results, this study have proposed a simple protocol for identifying visually observable foreign or unwanted substances. It starts with optical microscopy followed by SEM/EDS. Based on the result and amount of the inclusions, the procedure move onto conventional FTIR or micro-IR test. The XRF can be of aid especially when the inclusion is inorganic.

Keywords: Forensics, injection molding, inclusion, degradation.

1. INTRODUCTION

In the rapidly changing polymer processing industry, the manufactures are focusing on developing new technologies to gain a competitive edge. On the other hand, there is a lack of research data in terms of identifying and minimizing the causes of troubles that might prevent efficient production. In particular, defects of existing products are one of the serious concerns. Those in the products can cause enormous losses to the developers and manufacturers. Thus, it is necessary to respond quickly and properly to the anomalies that has already happen or will possibly occur. The cause of these anomalies must be identified from various fields such as tool design, production and raw materials.

Among many defects, inclusion of foreign or unwanted materials are one of the serious issues. The inclusions on the surface of polymer parts incurs visually inappropriate parts. Furthermore, this can result in earlier mechanical failure of the parts. To analyze various cases of foreign substances and defects from the polymer processing, especially injection molding, it is required to obtain information about the composition of the material. Here, efficient analysis with minimum time and cost is crucial to feasibility of it execution. However, it is very difficult to locate an institution or service agency that meets these requirements. In many cases, one has to deal with the inclusion on one's own. Since usual injection molders or extruders do not have such a capability, a formal procedure for solving this issue is needed. This is especially important when it has to do with identification of legal responsibility on the trouble. Therefore, this work will propose a simple protocol for identification of the foreign or unwanted materials that are visually noticeable. There are several test methods which are well-defined and allows actual tests by commercial devices. Although the test can be done in a reliable way, the test cost is quite expensive and time consuming. By the proposed test protocol, the inclusion and anomalies will be identified efficiently and economically.

This work will consider injection molded specimen because such parts are employed in foods, construction, automobile, electronics and defense industries. There have been tremendous amount of work about various defects found during injection molding processes [1-3]. However, there is almost no study regarding the inclusion detection. When inclusions are found in injection molded parts, its source should be identified. Where the inclusion is from is invaluable information. It can be from the raw material, injection molding machine and molds. As the source of the foreign inclusion can identify who is responsible, it can be legally crucial to each participant [4]. Sometimes without inclusions, visual appearance of the injection molded part can be abnormal. Especially yellowing is frequent and is also required to identify the cause. Yellowing is in most cases related to degradation. The organic properties of polymeric materials can damage material reliability by degradation under various conditions. This work is focused on thermal degradation induced during injection molding. The experimental method will be

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suggested first and then the protocol will be developed based on the test results.

2. EXPERIMENTAL

2.1. Test Methods

To establish protocols for identification of inclusion and visual anomalies, several experimental test methods will be considered. First, the optical microscope can be used to check the shape, structure and surface state of the foreign material and the anomalies. Next, SEM / EDS facilitates detecting specific X-rays for qualitative and quantitative analysis on small areas. Elemental analysis, which cannot be done in an optical microscope, can determine whether a foreign material is a metal or a nonmetal [5, 6]. In the case of metals, it is expected that more detailed analysis will be possible using XRF equipment. In addition, in the case of nonmetals, the design was divided into two cases, organic and inorganic. In particular, FTIR, which is commonly employed for foreign material analysis, can be used to identify polymer bonds and stretches. Moreover, thermal analysis methods such as DSC and TGA can further reveal the material characteristics [7, 8]. These are for thermal characterization but the results implicates more than that. Based on the teste results, the final protocol will be suggested through actual identification processes.

2.2. Injection-Molded Specimen

In injection molding, quite many sort of troubles can take place due to a variety of causes. The molded polymers are always evaluated in terms of cosmetics and performances. The problems of inclusions and unwanted colors are reason for outright rejection in production lines. What is worse is it can be a strong sign of possible problems in mechanical and physical performance of the parts. Thus, in molded parts, such anomalies should be analyzed appropriately in an acceptable range of time. Among those trouble that might possibly appear in the production lines, black specks that can be rasterized in a two dimensional domain as dots are of major concern. These can be from a foreign source or from polymer degradation. To investigate this, an injection molded specimen has been prepared, which is a preform for blow molding of drinking bottles. The preform in this work is the actual preform that is under mass production in a factory.

During the daily production, two different kinds of visual anomalies have taken place. The first one has several shiny pieces inside the polymer body as shown in Figure **1**. The second one has many black spots therein as shown in Figure **2**. Both of them are of course unacceptable as preforms and determined as faulty parts. Those two are under investigation for identification.

Figure 1: The first case: injection molded blow preform with foreign materials inside.

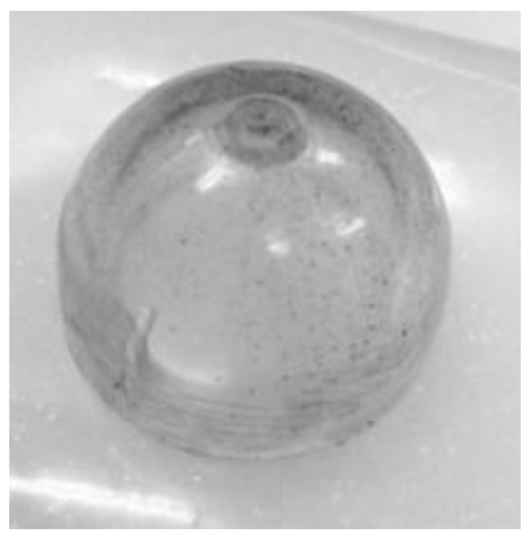

Figure 2: The second case: small inclusions in injection molded specimen.

2.3. Microscopic Inspection

Although initial inspection with naked eyes can provide a lot of information, microscopic visualization can expose deep details that has been unveiled. These days, microscopy is widely available to general people thanks to development of inexpensive USB-based handheld or simplified desktop devices. Thus, microscopic visualization has become nothing special to field engineers or any factory workers. This kind of easily accessible devices should be utilized in the initial phase of the inspection prior to further investigation with microscopy of higher resolution. If the material could not identified initial microscopic imaging, the procedure has to be performed with an equipment with higher resolution such as SEM (scanning electron microscope). With the inclusions exposed on the surface, the object can be easily magnified using an optical microscope. This step is very important since unnecessary usage of expensive imaging with SEM can avoided by doing so. However, note that there always is certain limit that the magnified image alone can identify the substance.

2.3. SEM/EDS Test

When the presence and location of the foreign matter can be clearly identified, the substance investigation can be relatively simple in comparison with embodied matter case. Thus, it will be necessary to surface the inclusion or the target material of interest. For the materials on the surface, there are several tools to identify its constituents. Amongst them, SEM/EDS is the most powerful method in identifying foreign materials. SEM turns out highly magnified features on the material surface. However, it does not aid scrutinizing inclusions embedded internal to the surface that SEM can access. When destruction of the sample is allowed, sectioning of the sample can be performed. Cutting, grinding and breaking by various instruments can all be adopted as for careful analysis in SEM. Especially microtoming facilitates obtaining thin planar section without noticeable contamination of the cross-section. Cryogenic environment sometimes should be prepared for polymers of low glass transition temperature (Tg) since sectioning is more easily conducted under Tg. However, care should be taken to examination of polymers with fibers.

Scanning electron microscopy (SEM) is valuable for forensic inspection in polymers especially in plastics. However, it is primarily elemental information usually attained through energy dispersive X-ray spectroscopy (EDS). This can work in coordination with a variety of SEMs available in market and research fields. From this, essential information in forensic polymer study can be extracted. EDS can be used to measure the elemental composition of any polymeric systems with minimal amount of samples.

SEM/EDS allows quantitative detection of elements such as Fe, Cr, Ni, O, C, P, and Si. By breaking the sample shown in Figure **1**, the foreign material has been taken out for SEM/EDS. As a result of the test, the contents of major elements has been analyzed as Fe- 67.63 wt.%, Cr – 18.28 wt.%, and Ni –7.98 wt.%. The target regions in the sample are shown in Figure **3**. Sometimes identification of the inclusion can be in a commotion but the result in this case is conspicuous. It is required to pay attention to the chromium and nickel content. Since chromium and nickel are commonly found in alloys for metal parts fabricated for molds and injection molding machine. Thus, these are possibly from the mold or the injection molding machine.

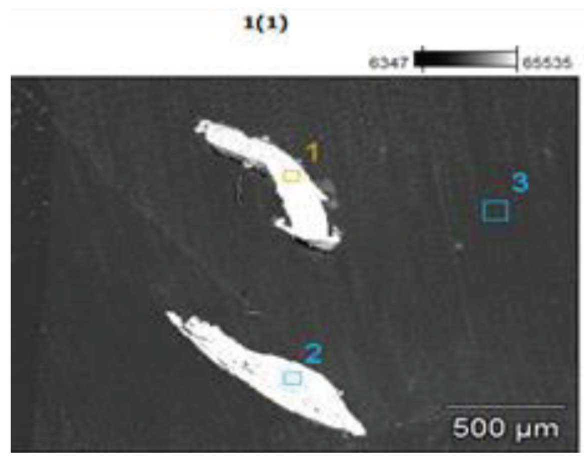

Figure 3: SEM (scanning electron microscope) image of the foreign inclusion.

Then, as the first step for the sample in Figure **2**, the black dots have been inspected using an optical microscope. The next step, SEM / EDS has been carried out for elemental analysis. To identify the inclusion, the normal and the sample in Figure **2** are compared together with each other. The test results have shown that both are organic matter consisting of C and O. The part without foreign substances have been found to be composed of C 44.10wt.%, O 55.49 wt.% while the part with dots composed of C 47.6 wt.%, O 52.4 wt.%. The results are summarized in Figure **4**. Although these results cannot suggest something clear, what is sure from them is the part with dots have more carbon atoms. It is suspected that the added carbon in the dotted sample is from degradation of carbons in the backbone of PET (polyetherterephthalate).

2.4. FTIR

To further identify the cause of the dots, FTIR (Fourier transform infrared) spectroscopy has been

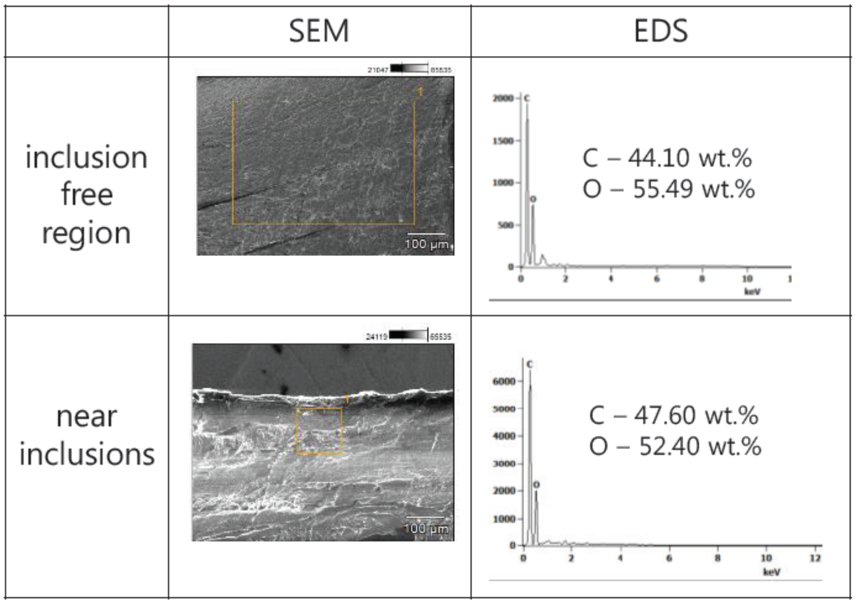

Figure 4: IR spectrum according to existence of inclusions.

chosen [4]. The alterations in the polymer under test by chemical reactions such as oxidation and hydrolysis is of great importance. Many important polymer characteristics such as molecular weight and conformation can be identified by IR spectroscopy [9-11]. As the infrared bands of polymers in chain are wide and the intensity is quite low, it is not easy to catch such an alterations. Therefore, well prepared elimination procedure to extract the IR bands solely from the alterations should be engaged. Moreover, to analyze the dots, we have to focus on the small area with dots. Since this is not facilitated in the conventional FTIR, the micro-IR has been selected. It is the most used method for analyzing the foreign material of micrometer size because it can analyze the spot of the desired part. As a result of the analysis, there have been slight differences in the spectrum between the part with and without the dots. From the spectra obtained in this work, both materials have been found to be PET. As shown in Figure **5**, the peak points are almost the same and the difference can be hardly described. However, differences between those two will provide useful information regarding the dots. Interpretation of the differences can be found elsewhere [5].

Two analyzes revealed that the foreign material was an organic material consisting of C and O, that the amount of carbon increased compared to the part without the foreign material, and that it was a polyester polymer. Therefore, it could be assumed that the resin was carbonized, and if it was completely carbonized, it should be inorganic, but came out as organic matter.

2.4. XRF

One can easily make a conjecture that the foreign material might be a kind of stainless steel based on the SEM/EDS results. However to make it clearer, an additional step is in need. For metallic materials, XRF (x-ray fluorescence) can be powerful tool for elemental analysis. In this device, secondary x-ray emission excited by the primary x-ray emission is measured. Each material generates the secondary x-ray that is specific to it. The reliability and viability of this device has caused rather recent manufactures of handheld XRF. The sample shown in Figure **1** has been identified as stainless steel 416 by an XRF device (Olympus Vanta).

2.5. Thermal Analysis

Thermal characteristics can change along with the chemical variation of the polymer under test. The thermal tests such as DSC (differential scanning calorimetry) and TGA (thermos gravimetric analysis) do not require large amount of specimen. Especially, DSC has been widely used in analysis of the injection molded thermoplastics [12, 13]. Thus, these methods is especially beneficial when the target is difficult to be pointed out and the amount is not enough.

Let us conduct the thermal analyses with yellowed specimen from injection molding process. Yellowing is one of the representative symptoms of defective injection products. To test the yellowing effects, injection molding process has been conducted for different residence times in the injection barrel while

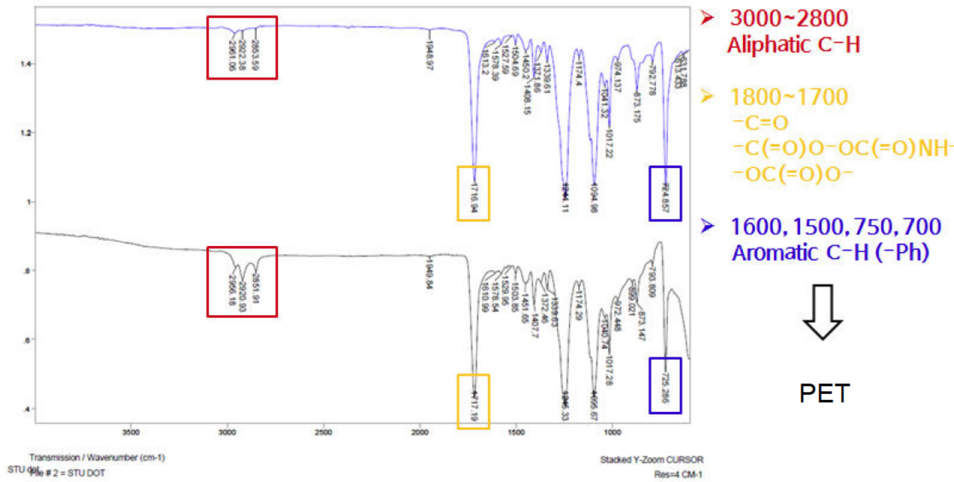

Figure 5: Micro-IR results of the specimen: the upper is for the sample with dots and the lower is for the normal sample.

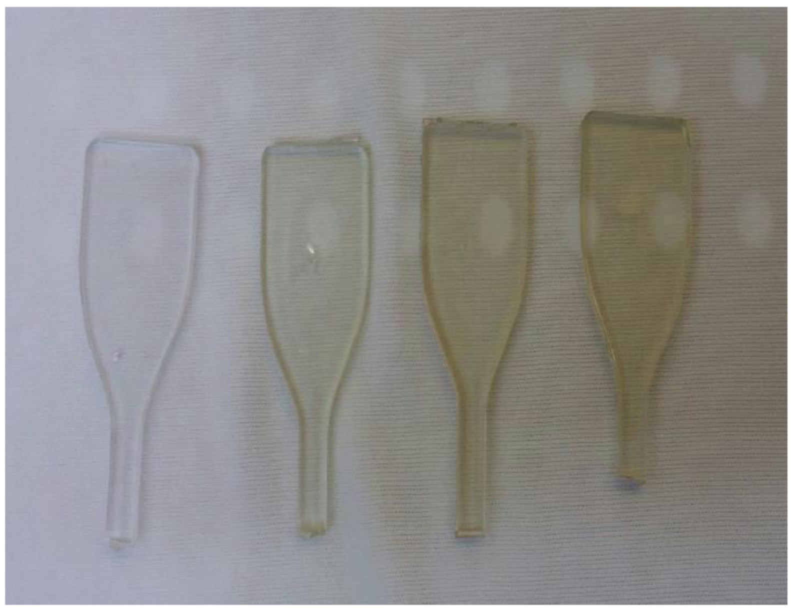

Figure 6: Degraded specimen according to the residence times (from left, 0 min (normal), 60, min, 90 min, 120 min).

keeping the other conditions constant. Injection temperature have been fixed at 260 ℃ and the resin was the injection molding grade PET. The resident times were 0 min (instant), 60 min, 90 min and 120 mins. The yellowing in this case is attributed to thermal degradation of the polymer.

The molded specimen are shown in Figure **6**. As the resident time increases, the specimen becomes more yellow. To fulfill the DSC test, circular specimens with 5 mm in diameter have been prepared to fit them into DSC pan. In addition, all the samples have been weighed 0.025g. DSC is a device that collects property change information about thermal deformation and temperature change by changing temperature with time. It can get information such as glass transition temperature, recrystallization temperature and melting temperature. In this analysis, the analysis has been carried out by changing the temperature by 10 ℃ per minute up to 300 ℃.

Figure **7** shows the DSC test results for 0 and 120 min. The peaks of the specimen are similar for the both curves shown. If other materials have been introduced, the peak would be different from the normal PET peaks. Thus, there would not be any inclusion in the yellowed sample. In addition, the glass transition temperature, recrystallization temperature and the melting temperature can be obtained from DSC peak. It cannot be mentioned that these temperature are changed due to the residence time as they are similar for both the test results. What is most noticeable here is the base slope shown in the figures. It can be concluded that the degradation showing yellow color

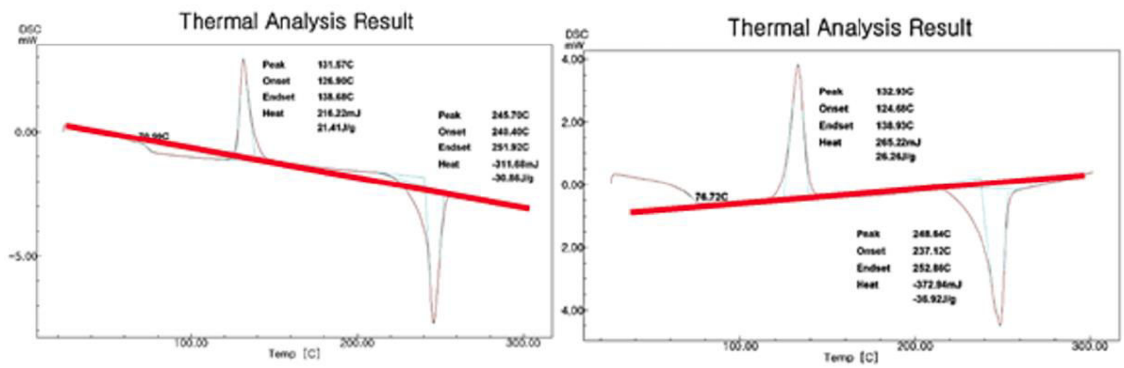

Figure 7: DSC results of normal and degraded specimens: the left graph is for 0 min and the right graph is for 120 min.

causes the reversal of slope of base lines in DSC tests. The overall tilt of the DSC graph indicates the degree of degradation. Normal specimens generally have an overall decrease in slope, whereas deteriorated specimens tend to increase because deterioration has already occurred and heat is generated by decomposition due to degradation.

3. PROTOCOLS AND DISCUSSIONS

As a result of all the test conducted in this test, it has been proved that the following analysis has to be able to supplement the limitations of the preceding analysis. In addition, it has been found that the amount of foreign material or degree of anomaly have great impact on the analysis. Therefore, as in the first case, if there is a very small amount of foreign material and if it is a metallic material, the foreign material can be easily identified even in the polymer processing environment.

Information on the material constituting the main equipment of the injection molding machine can also help. The injection molding is conducted in a harsh environment especially inside. Because of high internal pressure, metal chipping or abrasion can happen inside the machine during the process. These can be source of the foreign material but XRF examination will be able to identify immediately where it is from. The foreign materials can intrude into the feeding line while handling and drying.

On observation of foreign objects and defects, it is necessary to prepare specimens for the corresponding test before proceeding with the analysis. Specimen fabrication is the most difficult task of the analysis process. It is difficult to find a laboratory or an agency where the specimen can be prepared. Therefore, as aforementioned here, in the course of the identification analysis, the specimens should be prepared in-house. Moreover, companies or institutions have more information on the processing environment where any third parties would not be able to access or understand easily. If an in-house worker who knows both the working environment and the process is to conduct the analysis directly, the identification will be easier and more efficient. Thus, the optimal protocol will help those in-house engineers who might not be well versed in analyses for material identification. Recently, ocean plastics have become a social as well as an environmental issue. To identify the plastics in ocean creatures, the procedure has been established [14]. A study more similar to the current study can be found in [15], where Strömberg and Karlsson investigated the test protocol for the degradation of the recycled polymer. Here, also a well-defined procedure is necessary. To aid them identify the inclusion or the unwanted material, this work provides simple protocol in this work.

Once the anomaly is detected with naked eyes or by other way, it should be identified systematically. Let us describe the system this study intends to suggest. Initially, it should be inspected by the optical microscopy to visualize its shape in the enlarged image. In this phase, if further investigation is required, SEM/EDS should be adopted after surfacing the anomalies. If the amount of material is enough, check the material is organic or inorganic. If it is organic, move on with FTIR and DSC. Otherwise, XRD or XRF should be engaged in the analyses. For small micro-anomalies, micro-IR will help the identification. These are schematically shown in Figure **8**. Thanks to established protocols, non-experts in polymer forensics will be able to identify the existing and possible anomalies.

4. CONCLUSIONS

The inclusion of foreign or unwanted materials is one of the serious as well as difficult problems. When they are visible on the part, an aesthetically

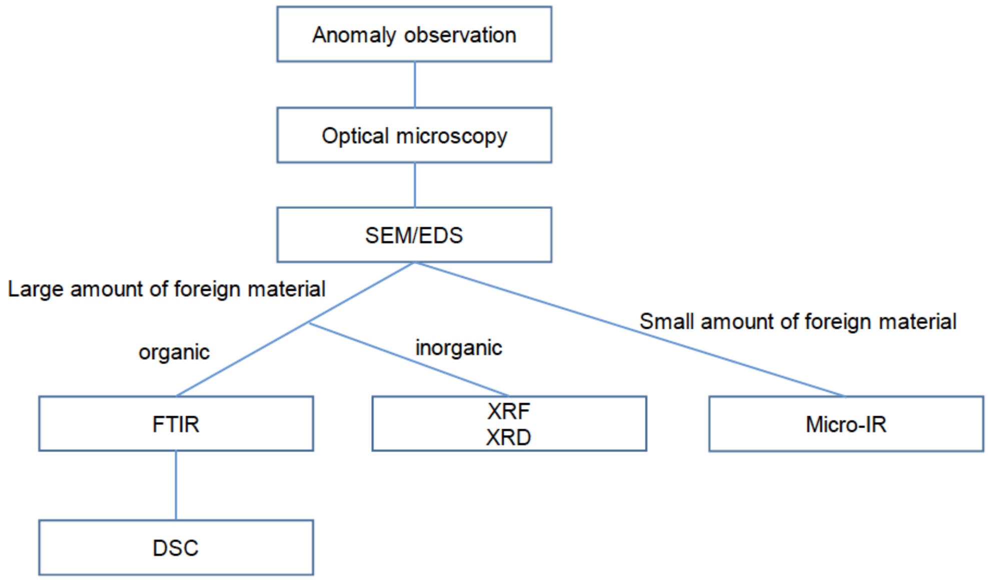

Figure 8: Designed protocol.

unacceptable part can be attained. In addition, this would be sign for premature mechanical failure. To conduct the identification, material composition is needed to be acquired. This work has assumed these are from polymer processing, especially injection molding since processing is the greatest source for such anomalies. The key here is efficient analysis with minimal time and cost to minimize down time. However, finding an agency or service organization that meets these requirements is very rare or impossible. In many cases, you need to deal with inclusion yourself alone. Thus, a formal procedure is required to solve this problem.

In this work, injection molded specimens with two different kinds of inclusions are considered. By microtoming the inclusions have been exposed to the surface and then they have been analyzed by XRD, XRF, FTIR and DSC. This is especially important when it comes to legal liability of the issues. Therefore, based on the results, this study have proposed a simple protocol for identifying visually observable foreign or unwanted substances. It starts with optical microscopy followed by SEM/EDS. Based on the result and amount of the inclusions, the procedure move onto conventional FTIR or micro-IR test. The XRF can be of aid especially when the inclusion is inorganic.

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