An Overview of Thermal Behavior of Polymers: Lead Acid Battery Applications

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Abstract — Thermal analysis is the analysis of a change in a property of a material, which is related to the temperature difference. Polymer samples are typically in solid form and undergo various thermal transitions upon heating, including melting, phase transition, sublimation, and decomposition. The purpose of this study is to demonstrate how thermal techniques such as DSC and TGA may be used to evaluate polymer thermal stability through the examination of polymer characteristics such as glass transition temperatures, melting points, and mass changes. Different polymers have been investigated and used in lead-acid batteries for various applications based on their mechanical and thermal characteristics. Few lead-acid battery-related polymers like Polypropylene (PP), Polyethylene (PE) Separator, Polyethylene Terephthalate (PET), Polyvinyl Chloride (PVC) and Acrylonitrile butadiene styrene (ABS) were studied and explained.

Keywords — ABS, Differential Scanning Calorimetry (DSC), PET, PPCP, PVC, Thermogravimetry Analysis (TGA), etc.

I. INTRODUCTION

Polymers are either inorganic or organic macromolecules and have a higher molecular weight, which are composed of longer molecule chains that are either entirely disordered (amorphous in nature) or partially disordered (semi-crystalline in nature). As the temperature increases, the ordered polymers will start melting, whereas the amorphous polymers will exhibit only glass transition temperatures [1].

Depending on the nature of the bonds between the polymer chains, polymers are classified into three groups: thermoplastics, thermosets, and elastomers. In thermoplastics, there will be no covalent bonding between the polymer's chains. These polymers are either ordered or disordered in nature. The chemical nature of thermoplastics won't be impacted with repeated heating's and cooling's, and the process is reversible as long as there is no thermal damage to the material during heating. Examples of Thermoplastics are Polyethylene and Polypropylene etc.

In thermosets, the polymer chains undergo dense cross-linking during heating. When fully cured, these polymers are neither deformable nor melt-able. Thermosets have only glass transition temperatures and decompose at higher temperatures. Examples of Thermosets are Epoxy Resins and Polyurethane etc.

Fig. 1. Classification of Polymers.

In elastomers, the polymers chains have low density cross-linking. At low temperatures, they will lose elasticity and freezes as hard as glass. Likewise, thermosets, elastomers exhibit only glass transition temperatures and do not melt. Examples of Elastomers are Natural Rubber and Ethylene Propylene Diene Rubber etc.

The glass transition occurs when amorphous polymers or amorphous domains of semi-crystalline thermoplastics change from a glassy or energy-elastic state to a rubbery or entropy-elastic state. The temperature at which the glass transition occurs is dependent on the processing induced morphology (e.g., orientation, crystallization, cross-linking, internal stress). Amorphous thermoplastics undergo major, usually step-like changes in their properties during the glass transition. Semi-crystalline thermoplastics are less affected by these changes since the crystalline phase is still unmelted and crystallinity, which is the proportion of the crystalline phase, plays a role. The crystallinity of a polymer is influenced by its chemical structure, cooling conditions during processing, and any thermal post-treatment. The more crystalline the molded part, the more rigid and robust it is and the more brittle [2], [3].

Thermal analysis is one of the oldest analytical techniques used for determining the material properties and phase transitions and characterizing polymers. Identification of materials, especially those used in the field of polymers, is of critical importance, especially when it comes to raw material quality control and failure analysis. Classical thermal analysis techniques such as differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) are also commonly utilized to analyze polymers. Energy effects observed in the DSC signal, e.g., the glass transition, crystallization and melting, and the pyrolytic decomposition and the combustion of the polymer samples can be studied using TGA [4].

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Simultaneous thermal analysis (STA) refers to applying two or more techniques to the same sample at the same time, which signifies the simultaneous measurement of DSC and TGA. The STA technique has essential advantages over simply combining measurements performed in different instruments on different samples of the same type. In addition to the higher efficiency, we can directly compare the signals from the DSC and TGA measurements without having to discuss possible differences in sample composition, sample preparations, or measurement conditions.

DSC, one of the most effective analytical methods, is used to investigate material thermal characteristics and phase changes. It measures the heat flow difference between the reference crucible and sample during the heating or cooling conditions in a specified atmosphere. The critical parameters like Glass transition temperatures, Melting temperatures, Heat of reaction (Transition / Reaction Enthalpy), Specific Heat Capacity, Fraction of crystallinity of a polymer etc., can be studied through DSC [5], [6].

Basic Equations of DSC & TGA:

Enthalpy:

$$dQ/dt = m * C_p * [dT/dt]$$

Mass Loss / Gain:

$$\alpha = \frac{m_o - m_i}{m_o}$$

where, m = mass of sample, g;

T = Temperature, K;

t = Time, min;

C_p = Thermal capacity, J/(g×K);

Q = Heat of the process (reaction);

α = Mass loss/ Gain.

TGA measures the mass change and transformation energetics of a sample with respect to time or temperature in an inert or reactive atmosphere. Key studies like compositional analysis, thermal and oxidative stabilities, decomposition analysis of materials can be studied through TGA. This technique can be used to estimate the mass changes happened during oxidation, dehydration, adsorption, desorption, and decomposition processes.

II. MATERIALS & EXPERIMENTATION

Polymers have wide applications in different fields due to their versatile and unique physical, chemical, and thermal properties. Materials like PPCP, PE Separator, PET, PVC, and ABS have been used in Lead Acid battery for various applications and were described in detail [7], [8].

A. Polypropylene Copolymer

Polypropylene is a thermoplastic polymer in the polyolefin family. Polypropylene is an economical polymer with unique physical, mechanical, thermal, and electrical properties not found in any other thermoplastic. It has a lower impact strength but a higher operating temperature and tensile strength than low or high-density polyethylene. Polypropylene provides excellent chemical resistance to organic solvents, corrosive environments, and electrolytic attacks. In general,

it is light in weight, strain resistant and has a low moisture absorption rate. It is available in two basic types as either homopolymer or copolymer material. Although similar in many characteristics, each type exhibits distinct differences in both appearance and performance.

Polypropylene Homopolymer (PPHP) is the most widely utilized. It offers a high strength-to-weight ratio and is stiffer and stronger than copolymer; combined with good chemical resistance and weldability, this material can be used in many corrosion-resistant structures.

Polypropylene Copolymer (PPCP) is slightly softer and more malleable than the homopolymer but has higher impact strength and durability. It is also more resistant to stress cracks and is tougher at lower temperatures. PPCP is very versatile and low-cost material. Its lower rigidity is ideal for use in automotive tanks to prevent cracking from road vibration and can also be used for applications that require good chemical resistance

Fig. 2. Chemical Structure of PP.

The polypropylene copolymer has the ideal properties that make it the best material for a battery cover and container. Polypropylene containers moulded with thin partitions and thin walls which increases the acid volume thereby makes possible higher capacities for given sizes or new compact battery designs [9].

B. Polyethylene

Polyethylene (PE) is a semi-crystalline thermoplastic polymer and belongs to the Polyolefin family, synthesized from ethylene's polymerization. Due to its molecular weight and density, there are different grades of PE like Low density (LDPE), Linear Low density (LLDPE), High density (HDPE) and Ultra High Molecular Weight (UHMWPE).

LDPE is a low density polymer which consists of extensively branched polymer chains. LLDPE is conventionally different from LDPE, which has only short branching and significantly different rheological properties. HDPE has relatively few branching structures and hence, have a high density. Polyethylene of ultra-high molecular weight (UHMWPE) has very long molecular chains with a very high molecular weight.

Fig. 3. Chemical Structure of PE.

In general, Polyethylene exhibits high chemical resistance, better stability, very low water absorption and good electrical resistance. Polyethylene based separators (PE Separators) are broadly used in lead acid batteries as battery separators to avoid the contact between Positive and Negative electrodes. These are composed of Polyethylene, Silica, Oil, and other

pigments for the required properties. The separator should be porous and resistant to acid [10].

C. PET

Polyethylene terephthalate (PET) is a semi-crystalline polymer with a hydrophobic characteristic. The basic building blocks of PET are ethylene glycol and terephthalic acid, which are combined to form a polymer chain. Its glass transition temperatures range from 70 to 85 °C, and melting temperatures range from 245 to 260 °C.

PET has good abrasion resistance, good acid resistance, high stability, and stiffness. For beverages bottles and packing application, PET in amorphous nature will be used due to its high transparency and breaking resistance.

Fig. 4. Chemical Structure of PET.

Polyester, the world's synthetic fiber is synthesizing from PET, when can be used for fiber or fabric applications. PET is electrically and chemically stable with these advantages; the Polyester fibers are widely used as binders for the lead acid active materials, which improves the adhesion of the electrode's active material [11].

D. PVC

Polyvinyl Chloride (PVC) is an amorphous thermoplastic polymer and the most widely produced synthetic plastic polymer due to its versatile nature. It does not have true melting temperatures and has only a glass transition temperature. PVC is available in two grades based on with and without plasticizer, i.e., namely, Plasticized PVC and Unplasticized PVC.

PVC generally exhibits good chemical resistance, good electrical insulation and low water absorption. It has a wide application in the fields of electrical cable construction for insulation, sheathing and bedding. Synthetic PVC is resistant to various chemicals, including oils, acids, and alkalis, and is tough, durable, and resistant to abrasion.

Fig. 5. Chemical Structure of PVC.

Due to its electrical insulation properties, PVC sheets/shims are used in lead acid batteries to avoid the electrical shorts between the groups [12].

E. Acrylonitrile Butadiene Styrene

Acrylonitrile Butadiene Styrene (ABS) is an amorphous thermoplastic polymer, which is a terpolymer with acrylonitrile, 1, 3-butadiene and styrene. The proportions of individual components may vary from 15 to 35% acrylonitrile, 5 to 30% butadiene and 40 to 60% styrene. It does not have a true melting point, and its glass transition

temperature is approximately 95 to 125 °C.

The mechanical and chemical properties of ABS depend on the individual components proportion and the method of manufacturing. ABS is a heat-resistant and low water absorption polymer with good mechanical properties like stiffness and impact strength. It remains hard, rigid, and tough even at low temperatures. It is also available in different grades like fire-resistant, heat-resistant, etc.

ABS material is suitable for containers and covers material for battery application with these versatile properties. The ABS container and covers either coupled with heat sealing or hot melt adhesives [13].

Fig. 6. Chemical Structure of ABS.

F. Experimentation

The DSC and TGA analysis measurements were executed using the NETZSCH DSC 214 Polyma and the NETZSCH STA 449 F3 Jupiter® and pure nitrogen as the purge gas. For thermal analysis, the selection of temperature range plays a critical role and polymer samples of masses in the range of 8 to 12 mg were prepared with the help of Sample cutter for a better thermal contact between crucible and sample and sample analyzed conditions were tabulated in Table I.

For DSC analysis, the polymer samples were heated from an initial temperature of 25 °C to above its melting temperature to erase the previous thermal history with a heating rate of 10 K/min and kept isothermal for 5 mins, then cooled down with a rate of 10 K/min to initial temperature of 25 °C and then heated again with a heating rate of 10 K/min to above the melting temperature. The first heating will assess the material properties in moulded or previous processed conditions whereas the second heating will assess the inherent material properties. For better understanding, the second heating curve results were taken into consideration.

For TGA analysis, the polymeric samples were heated from room temperatures to 600 °C with a heating rate of 10 K/min, in which the samples were kept isothermal at room temperatures for 5 mins and then heated to 600 °C. In this paper, TGA analysis was performed, and the results were shown in two ways i.e., TG curve – mass loss curve w.r.t temperature and DTG curve – derivative mass loss curve w.r.t temperatures.

TABLE I. SAMPLE ANALYSIS CONDITIONS

S. No	Parameter	DSC	TGA
1	Model	DSC 214 Polyma	STA 449 F3 Jupiter®
2	Make	NETZSCH, Germany	NETZSCH, Germany
3	Heating Rate	10 K/min	10 K/min
4	Atmosphere	Nitrogen	Nitrogen
5	Purge Gas Flow rate	40 ml/min	50 ml/min
6	Protective Gas Flow rate	20 ml/min	20 ml/min

III. RESULTS & DISCUSSIONS

Under applied heating conditions, the polymeric sample will undergo changes in physical and chemical properties, which affects the chemical composition of the polymer and the physical parameters like the color of polymer, chain length, molecular weight and its distribution, crystallinity, chain flexibility, cross linking and branching [14]. The cumulative outcome of DSC analysis tabulated as given in Table II & Table III.

A. PPCP

From the DSC analysis as shown in Fig. 7(a), observed that the cold crystallization at 119.6 °C, and melting at 167.6 °C. Under an inert nitrogen atmosphere, as shown in Fig. 7(b), the TGA of PPCP shows a single step of thermal degradation around 446.6 °C which ranges from 350 °C to 500 °C. During the heating process, pyrolysis takes place due to similar chemical bonds which results in major mass loss. Thermal degradation of PPCP causes chain breaking and then reduced chain length reduces the molecular weight, which influences the mechanical properties leading to highly reduced ductility and embrittlement [15]-[17].

Fig. 7(a). DSC Analysis of PPCP.

Fig. 7(b). TGA/DTG Analysis of PPCP.

B. PE Separator

Under inert nitrogen atmosphere, TGA of PE Separator shows a multi-step of thermal degradation with different mass losses due to other materials like oil and silica. From the DSC analysis as shown in Fig. 8(a), observed that the cold crystallization was at 107.4 °C, and melting at 127.7 °C. The decomposition temperature of PE is around 473.1 °C which ranges from 400 °C to 500 °C, as shown in the Fig. 8(b) DTG curve [16]-[19].

Fig. 8(a). DSC Analysis of PE Separator.

Fig. 8(b). TGA/DTG Analysis of PE Separator.

C. PET

From Fig. 9(a) & Fig. 9(b) i.e., the DSC and TGA curves, it is evident that PET is semi-crystalline in nature and has the glass transition temperature. TGA of PET shows a single step thermal degradation, in which the observed decomposition temperature of PET is around 434.3 °C which ranges from 350 °C to 500 °C, as shown in the DTG curve. From the DSC analysis, observed that the cold crystallization was at 177.3 °C, and melting at 254.9 °C. This maximum mass loss is due to thermal degradation of the polymer backbone, i.e., chain scission of the ester bonds. [19]-[21].

Fig. 9(a). DSC Analysis of PET.

Fig. 9(b). TGA/DTG Analysis of PET.

TABLE II: "AS RECEIVED" DSC CHARACTERIZATION OF SAMPLES

S. No	Parameter	UOM	PPCP	PE	PET	PVC	ABS
1	Glass transition temperature-Mid	°C			81.4	63.6	104.8
2	Extrapolated Onset Temperature	°C	160.9	114.2	238.8		
3	Melt Peak Temperature	°C	167.6	127.7	254.9		
4	Extrapolated End Temperature	°C	173	134.2	262.5		
5	Enthalpy/Area	J/g	92.59	42.96	46.55		

TABLE III: DSC CHARACTERIZATION OF SAMPLES AFTER A COMMON THERMAL HISTORY

S. No	Parameter	UOM	PPCP	PE	PET	PVC	ABS
1	Crystallization Extrapolated Onset Temperature	°C	114.1	96.2	146.7		
2	Crystallization Peak Temperature	°C	119.6	107.4	177.3		
3	Crystallization Extrapolated End Temperature	°C	124.7	122.8	196.7		
4	Crystallization Enthalpy/Area	J/g	97.73	42.47	36.86		

D. PVC

PVC has a glass transition temperature of 63.6 °C, as shown in the Fig. 10(a) DSC curve. It has a two-step thermal degradation process with two decomposition temperatures of 297.3 °C & 438.2 °C, as shown in the Fig. 10(b) DTG curve. In general, Dehydrochlorination of PVC is a free radical reaction. The first mass loss step ranging from 230-360 °C, is considered the most important step because in this stage C-Cl bond in the PVC, which has less energy than the C-C bond, dissociates first, resulting in the volatilization of hydrogen chloride molecule. The next mass loss step ranging from 360-500 °C, corresponds to the thermal cracking of the carbon chain leading to the formation of alkane and alkene compounds [19], [22], [23].

Fig. 10(a). DSC Analysis of PVC.

Fig. 10(b). TGA/DTG Analysis of PVC.

E. ABS

Fig. 11(a) & Fig. 11(b) shows the DSC and TGA analysis results for ABS polymer at a constant heating rate. As earlier said, ABS is an amorphous polymer that does 'not have a true melting point and observed the glass transition temperature of 104.8 °C. ABS decomposes in a single step thermal reaction mechanism and major mass loss ranging from 340 °C to 510 °C and decomposes at 420.4 °C as per the DTG curve. ABS is thermo-oxidative degradation, which begins at 340 °C with the evolution of butadiene monomer. With increasing temperatures, styrene becomes more important, and at 420.4 °C the intensities of the C-H bonds in butadiene and styrene will become equal. Aliphatic and aromatic C-H bonds will be broken with increased temperatures. The evolution of acrylonitrile begins at about 400 °C and ceases by 510 °C [24], [25].

Fig. 11(a). DSC Analysis of ABS.

Fig. 11(b). TGA/DTG Analysis of ABS.

IV. CONCLUSION

In Summary, DSC and TGA are efficient analytical tools to assess the thermal behavior of basic raw materials, sub-products, and active materials for lead-acid batteries. These thermal methods provide new information about the changes in phase composition and physical properties of the active materials and other Raw materials. This analytical data can throw light on the processes during battery production and operation, which will be more helpful in the decision making of raw material selection, process parameters optimization, trouble shooting, grade variations, new material validations, new polymer formulations and vendor validations etc. Some of the useful areas in which these techniques play a predominant role in a better poly grade selection for battery container and cover, identification of root causes for heat seal rejections, polymer cover variations, polymer based separator quantification and polymer crystallinity etc.

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