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A Review on Pasting Fibers and their Thermo-Chemical Characteristics for Lead-Acid Energy Storage Devices

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Abstract: ***Tremendous efforts have been devoted to the development of electrode materials, electrolytes and separators for Lead Acid energy-storage devices to address the fundamental needs of emerging technologies ranging from vehicle starter batteries, mobile industrial applications (e.g. forklifts and other automated guided vehicles) to stationary power storage (e.g. uninterruptable power supply). However, binders, as an important component of energy-storage devices, are yet to receive similar attention. Binders should have good thermal, physical and chemical stability. They should be efficient, economic and environmental friendly. Polyester has been the dominant binder in the lead acid battery industry. To understand the binding mechanism in electrode assembly of energy-storage devices (Lead Acid Batteries) state-of-the-art structural characterizations were carried out with SEM and XRD for binder research studies. The molecular vibrations studies to find the bond interactions within electroactive materials were studied with FT-IR analysis and the thermal behavior of binders was predicted with DSC. Polymeric binders will play crucial roles in future high-performance energy-storage devices.***

Keywords: LAB, PE Binder, PAN Binder, HS Binder, SEM, FT-IR, DSC, ICP-OES

1. Introduction

Batteries are electrochemical devices, which stores chemical energy and renovate it into electrical energy. A battery is a multicomponent device, in general encompasses a cathode, an anode, electrolyte and the respective interfaces between the components. Upon discharge, cations are removed from the anode, transported thru the electrolyte and interpolated into the cathode. Improving electrochemical energy storage is one of the major issues of our time. The search for new battery materials together with the drive to improve performance and lower cost of existing and new batteries is not without its challenges. Achievement in these difficulties is absolutely based on first thoughtful the fundamental chemistries of the materials and the relations between the components involved. In 2018, Lead Acid Battery (LAB) provided approximately 72% of the world rechargeable battery capacity (in GWh). Approximately 65% of global demand for LAB's is currently driven by automotive applications, with nearly every vehicle on the road currently requiring a LAB for starter, light and ignition (SLI) functions. Compared to today, global lead-acid battery demand is expected to grow by a factor of ~1.1 to reach ~490 GWh in 2030. [1]

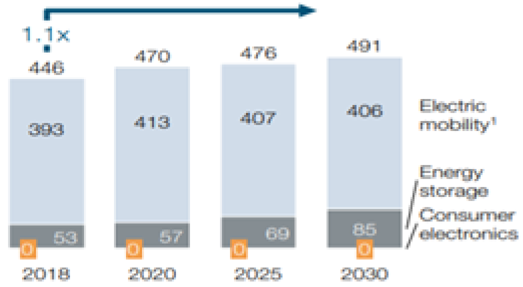


Figure 1: Global demand for LAB

Batteries are fabricated of electrochemical cells with negative and positive electrodes along with an electronically insulating (but ionically conductive) separators and electrolytes that are present both thru the electrodes and in the separator. Each electrode is a multi-component system consisting of electrode active materials, conductive agent, polymer binder and current collector.

The microstructures of electrodes play a vital part in governing the charge transport in electrode composites. Attaining uniform and stable microstructures for battery electrodes with help of binder materials is an important task in battery research. [2]

In particular, polymer binder is the key component for the control of the electrode interfaces, which include the conductive agent/active materials interface, the conductive agent/current collector interface, and the initial active materials/electrolyte interface. In addition, the polymer binder also plays a pivotal role in controlling the porous structures and conductive network around the active materials. The configuration, uniformity and stability of these microstructures significantly affect the transport of charges (ions and electrons) in the whole electrode, and thus, the performance and performance stability of the final energy storage devices. Therefore, development of new binder systems with ability of controlling the interfaces in the microstructures is in critical need for performance enhancement of battery electrodes.

Polymer binders with various functional groups contributing to strong adhesion with either electrode particles or conductive agents. They holds critical components of energy-storage devices, such as electrode material, conductive additive, and current collector.
Focusing increasingly on the binder chemistry and its interaction with the active material rather than solely

considering rather basic characteristics like stiffness or flexibility. In this paper, the primary mechanism of binding and the thermal and chemical behavior of binders in LAB were studied to achieve the potential benefits of highly functional binding agents.

1.1 Characteristics of Binders

- Performances as both a diffusing agent and a thickener to allow a homogeneous circulation of critical components;
- Bonds particles together with a current collector via certain mechanical, intermolecular, or chemical forces to maintain mechanical integrity
- Preserves electronic contact upon cycling for electrons to passageway near or through polymer chains
- Transforms the wettability and smooths mass transport
- Clutch electrode active material micron sized powder particles organized to form a porous structure.

1.2 Types of Binders

The most import classification binders were explained as below. [3]

1.2.1 Natural Binders

These are available naturally from organic sources such as plants and animals.
Ex: Carboxyl Methyl Cellulose (CMC), Gum Arabic (GA), Xanthan Gum (XG).

They contains multiple components, such as polysaccharide, glycoprotein, and/or other functional components. The multiple components might form a synergetic effect to reinforce binding strength; therefore, provides excellent mechanical and electrochemical performance.

Advantages of Natural Binders:

- Sustainable
- Abundant
- Low cost
- Eco-friendly
- Simply soluble in water

1.2.2 Synthetic Binders

These are manufactured thru modern chemical industry. Ex: Poly vinylidene fluoride(PVDF), Polyacrylonitrile (PAN), Polyester(PE) Poly acrylic acid (PAA), Styrene butadiene rubber (SBR), Poly amide imide (PAI), Poly vinyl alcohol (PVA), Poly ethylenimine (PEI), Polyimide binder (PI), and Poly tert-butyl acrylate-co-triethoxyvinylsilane (TBA-TEVS).

Advantages of Synthetic Binders:

- Composition and structure of the binders can be strictly controlled and fixed
- Positive for uniform and large-scale production
- Structures can be specially designed

1.2.3 Reactive Binders

In reactive binding processes, binder precursors carry out a polymerization reaction to form a polymer and simultaneously creates strong binding forces between active materials and current collectors. Before the binding process, the precursors are blended with electroactive materials to ensure sufficient mixing and wetting.
Ex: PAA-BP, PVA−PEI

1.2.4 Nonreactive Binders

These are used directly without further chemical reaction. Binders are first dissolved in solvent and then forms the binding forces among the electrode active materials after drying, i.e., the hardening process.
Ex: PVDF and PAA

1.3 Criteria for selection of a Binder

a) Confirming suitable cohesion between the active material particles and the additional electrode components as, Ex: Conductive agent.
b) Guaranteeing strong adhesion of the electrode coating to the current collector.
c) Facile electrode processing.
d) Insolubility in the electrolyte and low electrolyte swelling.
e) High chemical, thermal, and electrochemical stability, while not detrimentally affecting the electron and ion transport in the electrode composite.
f) Providing low additional cost, ideally being also environmentally friendly.[4]

1.4 Binding Mechanism

An effective binding process can be divided into two steps:
i. The diffusion step and
ii. The hardening step.
a) In the first step, the binder moistures the substrate surface and enters into the pores of electrode material particles, as shown in Figure 2a.
b) In the second step, the binders are hardened via different reaction mechanisms which leads to the mechanical interlocking effect (Figure 2b) and interfacial forces (Figure 2c)
c) The mechanical strength of the binded composite also depends on
    - The mechanical strength of the binder and electrode materials
    - The intrinsic polymer properties like electric and ionic conductivity, porosity and mechanical properties.

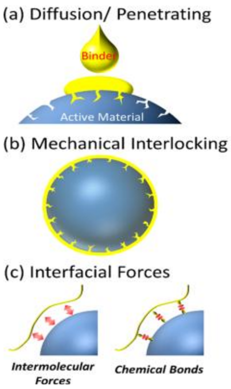


Figure 2: Binding Mechanism

2. Experimental

2.1 Investigated Binders

The following binders were investigated: Polyester Binder (PE Binder), Poly acrylonitrile binder (PAN Binder) and High Strength PE Binder (HS Binder).

2.1.1 Polyester Binders

Polymers chemically composed these long-chains of at least 85% by weight of an ester and a dihydric alcohol and a terephthalic acid.

Characteristics of PE Binders:

- Extremely strong.
- Durable & resistant to most chemicals,
- Resistant to stretching and shrinking, abrasion resistant.
- Hydrophobic in nature

2.1.2 Acrylic Binders (PAN)

These are the third largest class of synthetic fiber after polyester and nylons

Characteristics of PAN Binders:

- Soft, light weight, durable strong
- High abrasion resistance, good aesthetics-high luster
- Good wicking action
- Non-toxic

It is very resistant to deterioration from sunlight exposure

2.1.3 High Strength PE Binder

These are polyester binders composed of ester and alcoholic functional groups.

Characteristics of HS Binders:

- High dispersion
- High surface area
- Less Plate Vibration Loss

2.2 ICP-OES Analysis

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is a technique which usages plasma as a source and relies on optical emission for analysis. It is used to determine elemental constituents in materials. [5]

2.3 Differential Scanning Calorimetry

DSC is a thermoanalytical technique during which the temperature of a sample and reference material is increased at a constant rate. The heat flow required increasing the temperature of the sample and the reference material at a constant rate is measured.

A DSC analyzer measures the energy changes that occur, as a sample is heated, cooled or held isothermally, together with the temperature at which these changes occur. Heat-flux (sample and reference pans are in an identical furnace block) Principally, sample and reference are maintained at the same temperature, while any transition occurred in the sample needs an energy supply, which is recorded by the DSC as a rate dQ/dt against a temperature or a time. Often the glass transition temperature (T_g) and the change in heat capacity are reported.[6]

2.4 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a technique that provides high-resolution electronic images of the surface of different materials by scanning with an electron beam. It is a surface imaging method in which the incident electron beam scans across the sample surface and interacts with the sample to generate backscattered and secondary electrons, which will be used to create an image of the sample that offers a clear, high-resolution images of the size and surface. The dried specimens are coated with a conducting material usually platinum or gold to make the surface conducting and cause it emit more secondary electrons.

2.5 X-Ray Diffraction Analysis

The scattering of X-rays from atoms produces a diffraction pattern, which contains information about the atomic arrangement within the crystal. X-rays show wave nature with wavelength ranging from about 10 to 10^{-3} nm. Polymer specimens may be non-crystalline or polycrystalline. The amorphous specimens does not have long-range atomic order and therefore produces only broad scattering peaks. Polymers are not highly absorbing to x-rays.

2.6 FT-IR Spectroscopy Analysis

IR spectroscopy is an absorption technique made possible because molecular vibration modes absorb specific frequencies of the electromagnetic spectrum at varying intensities. However, a change in electric dipole moment must occur during the vibration. During IR spectroscopy, electromagnetic radiation is either transmitted through the sample or reflected off the surface. The absorption bands in the 4000 – 1500 cm^{-1} region help in the identification of functional groups; this region therefore is also termed the functional group region of the IR spectrum (Most useful information obtained in this region). The lower energy portion of the mid-IR region (1500 – 400 cm^{-1}) usually contains a very complicated set of peaks arising due to complex vibrations involving several atoms.

This is possible because different functional groups vibrate at different frequencies allowing their identification. The frequency of vibration, however, depends on additional factors such as delocalization of electrons, H-bonding, and substitutions at the nearby groups. [7]

The Binders are mixed with a small quantity of KBr salt and pressed to form pellet of 10 mm through which the passing infrared beam.

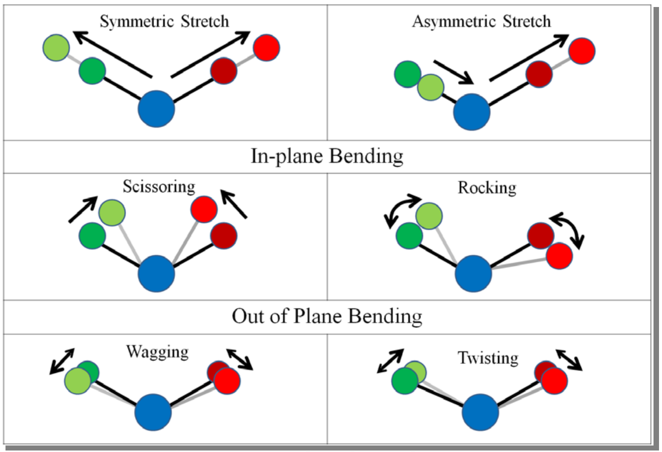


Figure 3: Molecular Vibrations

3. Results and Discussion

3.1 Wet Lab Analysis

In general, the physical parameters were measured and given as below

Table 1: Physical Parameters

S. No	*Parameter*	*Unit*	*PE Binder*	*PAN Binder*	*HS Binder*
01	Color		White	Pale Yellow	White

3.2. ICP-OES Analysis

For the quantification of elemental composition, the binders were refluxed with Sulphuric acid under slow boiling conditions over a period of 24 hours along with a blank sample under the same conditions. Tests were performed using ICP-OES (**Make: Agilent 5110, United States**). Most of the elements were in trace levels as shown in Table 2. The binders are of no impurities. If the undesired elemental composition is high, then the performance of the battery will be impacted.

Table 2: Elemental Composition Traceability

S.No	*Element*	*Unit*	*PE Binder*	*PAN Binder*	*HS Binder*
01	Copper	%	0.000025	0.000025	0.000025
02	Manganese		0.0010	Trace	Trace
03	Iron		0.00062	Trace	Trace
04	Silver		Trace	0.000025	Trace
05	Aluminum		Trace	Trace	Trace
06	Arsenic		Trace	Trace	Trace
07	Calcium		0.0053	0.00547	0.00265
08	Cadmium		Trace	Trace	Trace
09	Cobalt		0.00075	Trace	0.000025
10	Chromium		Trace	Trace	Trace
11	Magnesium		0.00137	0.0015	0.0021
12	Nickel		0.0010	Trace	Trace
13	Zinc		0.00212	Trace	0.00202

3.3. Differential Scanning Calorimetry

Tests were performed using DSC 214 Polyma (**Make: NETZSCH, Germany**).All the experiments were carried out in Nitrogen atmospheres at a gas flow rate of 40 ml/min, and at a constant heating rate of 10 K/min. Amorphous polymers exhibit a glass transition temperature and semi-crystalline polymers may possess the glass transition temperature, a crystallization temperature, a melting temperature with various crystallization and melting enthalpies. [8].

The DSC analysis of binders were given below with DSC plot at 10 K/min heating rate and the results were given in Table 3 & 4.

The test was done as per:

ASTM D 3418: 2015 - Standard Test Method for Transition Temperatures and Enthalpies of Fusion and Crystallization of Polymers by Differential Scanning Calorimetry.

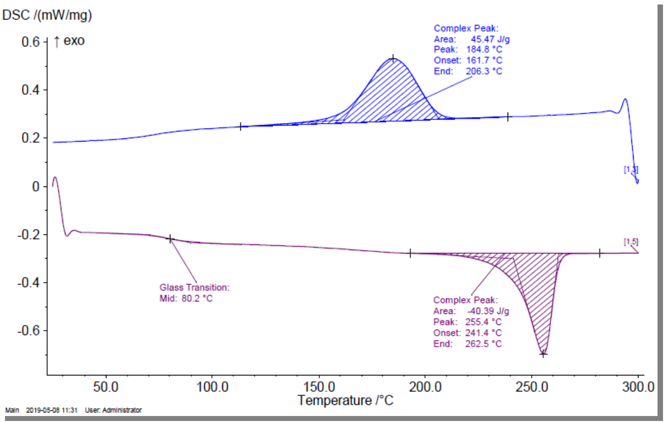


Figure 4: DSC of PE Binder

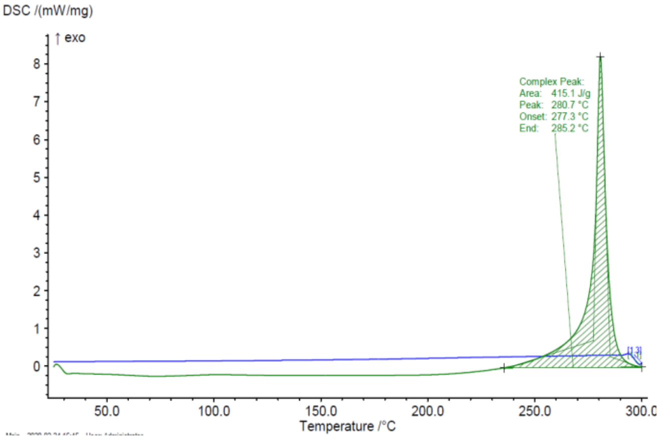


Figure 5: DSC of PAN Binder

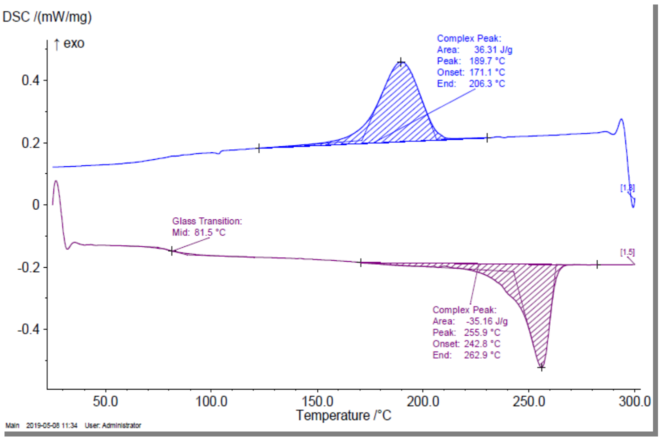


Figure 6: DSC of High Strength PE Binder

Most of the polymer binders with higher glass transition temperature will have both higher melting and decomposition temperatures.

Table 3: "As Received" DSC Characterization of Samples

S. No	*Sample*	*PE Binder*	*PAN Binder*	*HS Binder*
1	Glass transition temperature-Mid(^oC)	80.2	-	81.5
2	Melting Extrapolated Onset Temperature (^oC)	241.4	277.3	242.8
3	Melt Peak Temperature(^oC)	255.4	280.7	255.9
4	Melting Extrapolated End Temperature (^oC)	262.5	285.2	262.9
5	Melting Enthalpy/Area (J/g)	-40.39	415.1	-35.16

Table 4: DSC Characterization of Samples after a Common Thermal History

S. No	*Sample*	*PE Binder*	*HS Binder*
1	Crystallization Extrapolated Onset Temperature (^oC)	161.7	171.1
2	Crystallization Peak Temperature (^oC)	184.8	189.7
3	Crystallization Extrapolated End Temperature(^oC)	206.3	206.3
4	Crystallization Enthalpy/Area(J/g)	45.47	36.31

From Figures 4, 5 & 6, the thermal behavior of PE binder and HS binder was similar, whereas the PAN binder was decomposed completely before the cooling was started. The same behavior of each binder was observed in similar to PET & ETFE. [9]

3.4 Scanning Electron Microscopy Analysis

The surface morphology was studied using **SEM: JSM – 6010 Plus (Make: JEOL – JAPAN).** The sample surfaces were coated with platinum before doing the analysis. The surface morphologies of the binders were studied. [10]

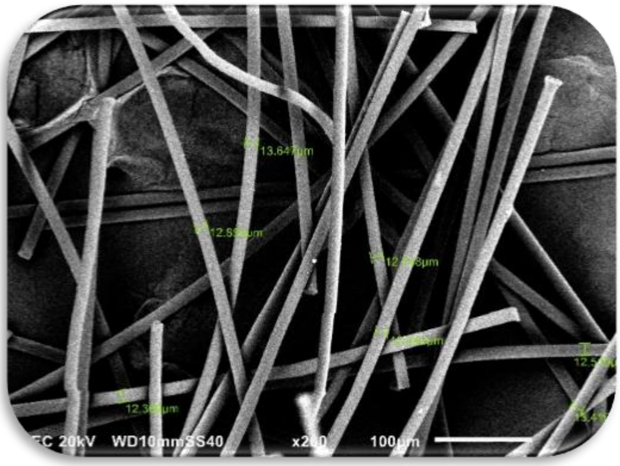


Figure 7: SEM Image of PE Binder

The morphology of binders was studied and observed the variation in fiber diameters.

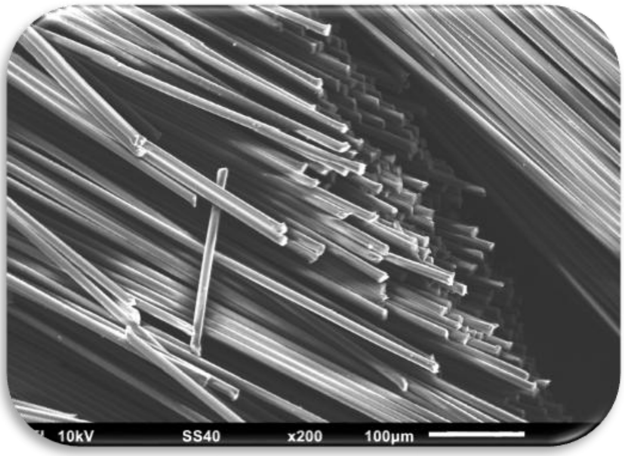


Figure 8: SEM Image of PAN Binder

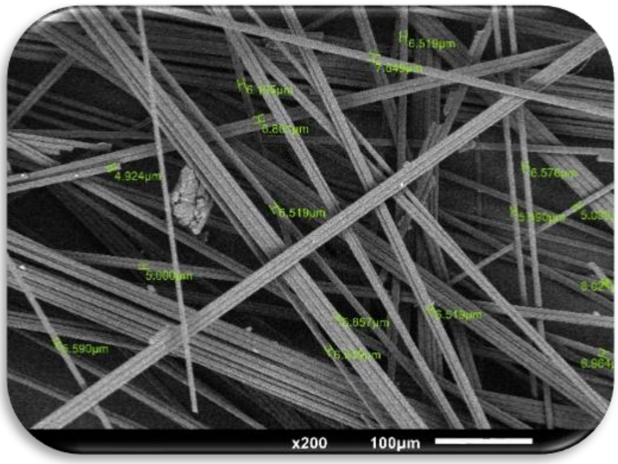


Figure 9: SEM Image of HS Binder

3.5 X-Ray Diffraction Analysis

X-rays are high-energy electromagnetic radiation and causes transitions in the internal electrons of the molecules.**XRD: Ultima IV (Make: Rigaku, JAPAN)** is used to find the crystallinity of polymers and their orientation. Polymers are never 100% crystalline. The PE & HS binders exhibited amorphous nature with multiple broad peaks whereas PAN binder exhibited semi-crystalline nature with a narrow peak as shown in Figure 10. [10]

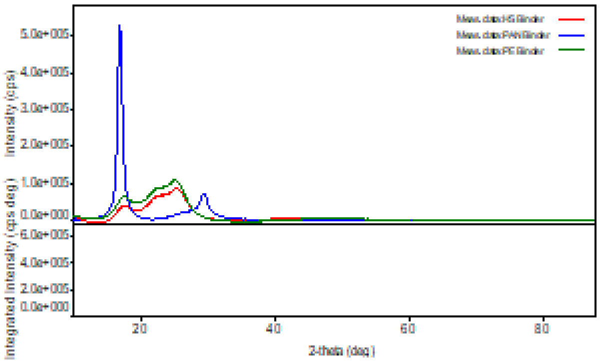


Figure 10: XRD Analysis of Binders

3.6 FT-IR Spectroscopy Analysis

The primary goal of this study was to investigate whether

Fourier transform infrared spectroscopy (FTIR) or melting point analysis provides higher discrimination of binders when used for comparative purposes. In infrared spectroscopy, a sample is irradiated with infrared light and the substance-dependent absorbance used to obtain molecular information about the examined sample. The result is an IR spectrum that allows a clear identification of the substance, just like a fingerprint. [11]

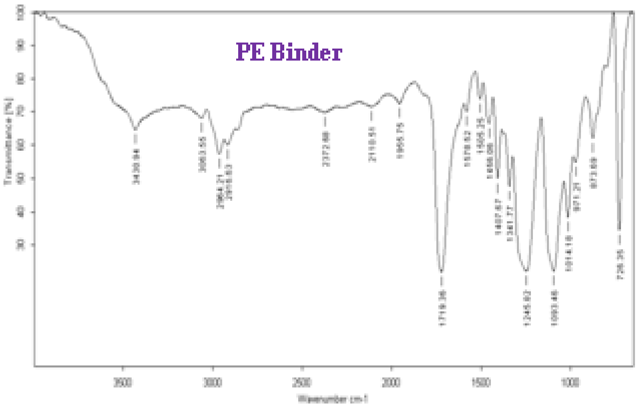


Figure 11: FT-IR analysis of PE Binder

Table 5: PE Binder

S. No	*Frequency (cm^{-1})*	*Bond*	*Functional Groups*
1	3430.94	C=O/N-H	Amine or Amide
2	3063.55	C-H	Alkenes
3	2964.21	C-H	Alkanes
4	2916.63		
5	2372.68	C=O-OH	Carboxylic Acid
6	2110.51	-N=C=S	Isothio Cyanates
7	1955.75	C=C	Aromatic Group
8	1719.36	C=O	Carboxylic acid/ Aliphatic Ketone
9	1578.52	N-H	Amino salts
10	1505.25		Amines
11	1456.06	C=O	Esters/Ketones/Aldehyde(For Ring)
12	1407.67	P-CH_3	Phosphines
13	1341.77		
14	1245.82	C-O	Carboxylic acid/Ether
15	1093.46		Ether
16	1014.18	C-X	Fluoride
17	971.21	C-H	Alkenes(out of plane bend)
18	873.69	C-H	Aromatics
19	726.35	C-X	Chloride

The FTIR studies for binders was done with a scanning range of 4000 - 500 cm^{-1} .Most of the bonds are stretched and bended with strong, medium and weak intensities. The common molecular vibrations among PE, PAN and HS binders are alkanes, alkenes, carboxylic acid, ketone, aldehyde, ester and aromatics. There is a similarity in PE and HS binders in which the frequency of molecular vibrations are very near to each other. [12]

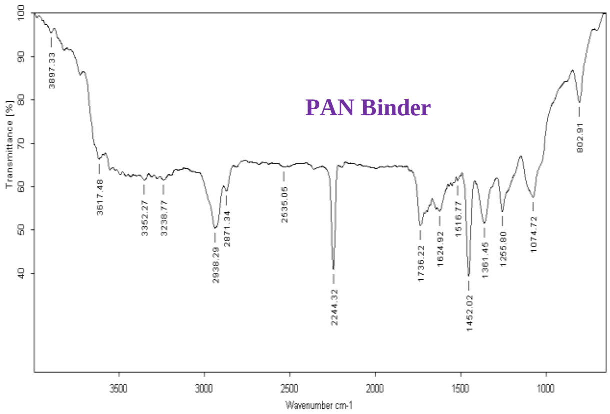
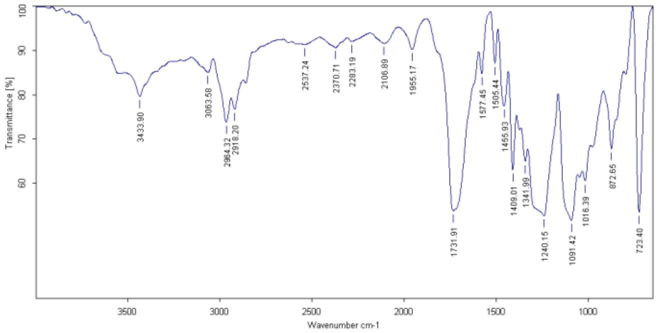


Figure 12: FT-IR analysis of PAN Binders

Table 6: PAN Binder

S. No	*Frequency (cm^{-1})*	*Bond*	*Functional Groups*
1	3897.33	C=C / C≡C	sp^2/sp hybridization
2	3617.48		
3	3352.27	N-H	Sulfonamides/Amines
4	3238.77		
5	2938.29	C-C	Alkanes
6	2871.34		
7	2535.05	O-H	Carboxylic Acid
8	2244.32	C≡N	Nitrile
9	1736.22	C=O	Ester
10	1624.92	C=O	1^0 Amine/Ester/Ketone
11	1515.77	N-H	Amine salts/2^0 Amines
12	1452.02	C=O	Esters/Ketones/Aldehyde(For Ring)
13	1361.45	-NO_2	Aliphatic Nitro compounds
14	1255.80	C-O-H	Alcohols and Phenols
15	1074.72	PH_2	Phosphines
16	802.91		



HS Binder

Figure 13: FT-IR analysis of HS Binders

Table 7: HS Binder

S. No	*Frequency (cm^{-1})*	*Bond*	*Functional Groups*
1	3433.90	N-H	Amine or Amide
2	3063.58	C-H	Alkenes
3	2964.32	C-H	Alkanes
4	2918.20		
5	2537.24	O-H	Carboxylic Acid
6	2370.71	C=O-OH	Carboxylic Acid
7	2283.19	P-H	Phosphines
8	2106.89	-N=C=S	Isothio Cyanates
9	1955.17	C=C	Aromatic Group

10	1731.91	C=O	Ester
11	1577.45	N-H	Amino salts
12	1505.44		Amines
13	1455.93	C=O	Esters/Ketones/Aldehyde(For Ring)
14	1409.01	P-CH_3	Phosphines
15	1341.99		
16	1240.15	C-O	Carboxylic acid/Ether
17	1091.42		Ether
18	1016.39	C-X	Fluoride
19	872.65	= C - H	Aromatics
20	723.40	C-X	Chloride

4. Conclusion

The thermal properties of polymeric binders are influenced by their origin, purity, composition, heat & mechanical treatment, and aging. The identification can generally be carried out mainly based on characteristic caloric effects of the type glass transition, crystallization or melting and because of mass changes, which reflect the temperature-dependent decomposition of a sample. Focusing increasingly on the binder chemistry and its interaction with the active material.

In fact, the interplay of covalent and non-covalent interactions, including inter alia the self-healing properties of hydrogen bonds, between the binder and the particle surface appears to be the key factor to achieve long-term stable cycling. Binding mechanisms between binders and active materials are mainly based on mechanical interlocking and interfacial binding forces consisting of intermolecular forces and chemical bonds.

5. Acknowledgement

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References

[1] Source: World Economic Forum, Global Battery Alliance; McKinsey analysis,2018
[2] A. Bonnaccorsi, "On the Relationship between Firm Size and Export Intensity," Journal of International Business Studies, XXIII (4), pp. 605-635, 1992. (journal style)
[3] Exploring Chemical, Mechanical, and Electrical Functionalities of Binders for Advanced Energy-Storage Devices, Hao Chen,†,§ Min Ling, Chemical Reviews
[4] A Polymer-Alloy Binder for Structures-Properties Control of Battery Electrodes, Min Zheng, Yu Wang⁎, Jacqueline Reeve, Hamid Souzandeh, Wei-Hong Zhong, Energy Storage Materials 14 (2018) 149–158.
[5] Concepts, Instrumentation and Techniques in Inductively Coupled Plasma Optical Emission Spectrometry Charles B. Boss and Kenneth J. Fredeen
[6] Thermal Analysis of Phase Transitions and Crystallization in Polymeric Fibers W. Steinmann, S. Walter, M. Beckers, G. Seide and T. Gries
[7] Interpretation of Infrared Spectra, A Practical Approach, John Coates
[8] Thermal Characterization of Polymeric Materials, EDITH A. TURI
[9] Identification of polymers by means of DSC, TG, STA and computer-assisted database search Alexander Schindler & Martin Doedt
[10] Studying cellulose fiber structure by SEM, XRD, NMR and acid hydrolysis Haibo Zhao, Ja Hun Kwak
[11] The thermal degradation of PET and analogous Polyesters measured by the Thermal Analysis-Fourier Infrared Spectroscopy, B.J.Holland & J.N.Hay
[12] FTIR and SEM analysis of polyester- and epoxy-based composites manufactured by VARTM process, Volkan Cecen & Yoldas Seki