STRUCTURE-PROPERTY RELATIONSHIP OF ABSORPTIVE GLASS MAT (AGM) SEPARATORS

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by

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Dedicated to my loving family

CERTIFICATE

This is to certify that the thesis entitled **"Structure-Property Relationship of Absorptive Glass Mat (AGM) Separators"** being submitted by **Mr. Kameswara Rao P.V.,** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** in the Department of Textile Technology, is a record of bonafide research work carried out by him. Mr. Kameswara Rao P.V. has worked under my guidance and supervision and fulfilled all the requirements for the submission of the thesis.

The results contained in this thesis have not been submitted, in part or full, to any other university or Institute for the award of any degree or diploma.

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Abstract

Valve regulated lead acid (VRLA) batteries, a common variant of traditional lead-acid batteries, have evolved as one of the major constituents serving the worldwide battery market share with ever-increasing list of applications. To meet such a host of requirements for these applications, it becomes imperative to unravel the design aspects of key constituents of VRLA batteries. Absorptive glass mat (AGM) separator is the most important technical component in VRLA batteries with a view to fulfil the multi-functional requirements of separation of electrodes, retaining the electrolyte reliably, good contact force with the electrode plates and provide assistance in oxygen recombination cycle. In order to selectively design and tailor an AGM separator, the intricate three-dimensional (3D) structure needs to be unravelled and analytically related with the key set of properties that fulfil the demands of these multi-functional requirements. In this research work, a toolkit of analytical models of compression-recovery, pore size distribution (PSD) and electrolyte uptake expressed via wicking characteristics of AGM separators has been presented. The exploratory research work pertaining to the development of two-dimensional (2D) analytical models of compression-recovery and PSD of AGM separators pinpointed certain demerits, which motivated us to develop a series of 3D analytical models. Accordingly, a toolkit of 3D analytical models of key set of properties of AGM separators was proposed. 3D fibre orientation distribution (FOD) was a pre-requisite for the successful validation of these analytical models. With the aid of X-ray micro–computed tomography (micro CT) analysis, the 3D FOD of AGM separators was successfully obtained. A range of AGM separators by varying FOD, fibre diameter and mass per unit area were developed in order to validate the 3D analytical models.

The novelty of the research work can be highlighted in terms of development of 3D analytical models incorporating certain key aspects, which have never been attempted in the literature. Particularly, the 3D analytical model of compression-recovery characteristics included the fibre slippage criterion and internal friction losses. Similarly, the effect of gravity component was included in the analytical model of wicking characteristics of AGM separators, which was neglected in the classic Lucas-Washburn's model. Further, the ‘robust’ analytical model of PSD of AGM separators has been presented and assessed via the commonly used

experimental set-up that usually applies high level of compressive stresses. Most importantly, this research work uses, for the first time, 3D data of fibre orientation from micro CT analysis, as a key input parameter for the experimental validation of the developed analytical models. Generally, a satisfactory agreement was observed between the theoretical and experimental results. Such an agreement bolstered the confidence to simulate the realistic charge-discharge modes of the battery by applying the cyclic loading conditions. A threshold criteria describing the invariant behaviour of PSD and wicking characteristics in terms of maximum permissible limit of key structural parameters during charge-discharge mode of the battery has also been presented.

To ensure the practical utility of toolkit of 3D analytical models, an '*ideal*' AGM separator was proposed that concomitantly matched with the guidelines provided in the literature. The hypothesised AGM can be engineered with gradient structure that possessed variation in densities towards the positive and negative plates of the battery. The improvement in the structural characteristics as assessed by the developed analytical models can potentially enhance the life-cycle of the battery.

शोध प्रबंध सार

वाल्व विनियमित लेड-अम्ल (वीआरएलए) बैटरी, पारम्परिक लेड - अम्ल बैटरी का आम संस्करण है जो दुनिया के बैटरी बाजार में तेजी से वृद्धि करने वाले एक प्रमुख घटक के रूप में उभर कर आया है । इन अनुप्रयोगों के घटको की आवश्यकता पूरी करने के लिए वीआरएलए बैटरी के प्रमुख घटको के डिज़ाइन के पहलुओं को समझना आवश्यक हो जाता है। इलेक्ट्रोड के अलगाव की बहु-कार्यात्मक आवश्यकताओं को पूरा करने के लिए एक दृष्टिकोण युक्त अवशोषक ग्लास चटाई (एजीएम) विभाजक वीआरएलए बैटरी के प्रमुख तकनिकी घटक हैं जो इलेक्ट्रोलाइट विश्वसनीय रूप बनाये रखते हु ए इलेक्ट्रोड प्लेट्स के साथ अच्छा संपर्क बल और ऑक्सीजन पुनर्मूल्यांकन चक्र में सहायता प्रदान करते हैं | एजीएम विभाजक के चुनिंदा डिजाइन एवं सीलने के क्रम में एक जटिल त्रिविमीय संरचना को सुझाने की आवश्यकता है तथा जो इनके बहु-कार्यात्मक आवश्यकताओं की मांगों को पूरा करते हैं उन गुणों के प्रमुख समूह को विश्लेषित करने की आवश्यकता है । इस शोध कार्य में संपीड़न-वसूली के विश्लेषणात्मक मॉडल का एक टूलकिट, छिद्र आकर वितरण (पी एस डी) एवं एजीएम विभाजक के इलेक्ट्रोलाइट अपटेक को विकिंग विशेषताओं के माध्यम से प्रस्तुत किया गया है | यह अन्वेषण शोध कार्य संपीडन - वसूली तथा एजीएम के पी एस डी के कुछ निश्चित दोष के द्वि-आयामी (2 डी) विश्लेषणात्मक मॉडल के विकास से संबंधित है जिसने हमें 3 डी विश्लेषणात्मक मॉडल की एक श्रृंखला विकसित करने के लिए प्रेरित किया | तदनुसार, एजीएम विभाजक के गुणों के प्रमुख सेट के 3 डी विश्लेषणात्मक मॉडल का टूलकिट प्रस्तावित किया गया था | इन विश्लेषणात्मक मॉडल के सफल सत्यापन के लिए 3 डी फाइबर अभिविन्यास वितरण (एफओडी) एक पूर्व-आवश्यकता थी । एक्स-रे माइक्रो-संगणित टोमोग्राफी (माइक्रो सीटी) विश्लेषण की सहायता से, एजीएम विभाजकों का त्रिविम एफओडी सफलतापूर्वक प्राप्त किया गया था। 3-डी विश्लेषणात्मक मॉडल को प्रमाणित करने के लिए विभिन्न एफओडी, फाइबर व्यास और द्रव्यमान प्रति इकाई क्षेत्र द्वारा एजीएम विभाजक की एक श्रृंखला विकसित की गई थी।

इस शोध कार्य की नवीनता पर कुछ महत्वपूर्ण पहलुओं को शामिल करने वाले 3 डी विश्लेषणात्मक मॉडल के विकास रूप में प्रकाश डाला जा सकता है जिसे किसी भी अन्य साहित्य में प्रकाशित नहीं किया गया है । इसमें विशेष रूप से, संपीड़न पुनर्प्राप्ति विशेषताओं के 3 डी विश्लेषणात्मक मॉडल में फाइबर स्लीपेज मानदंड और आंतरिक घर्षण नुकसान शामिल हैं। इसी प्रकार, इस विश्लेषणात्मक मॉडल में एजीएम विभाजक के विकिंग लक्षण पर गुरुत्व का भी प्रभाव शामिल किया गया है जिसे प्रतिष्ठित लुकस-वॉशबर्न के मॉडल में उपेक्षित किया गया था | इसके अलावा, एजीएम विभाजक के पी एस डी के 'मजबूत' विश्लेषणात्मक मॉडल को आम तौर पर प्रयुक्त प्रयोगात्मक सेट-अप के माध्यम से प्रस्तुत और मूल्यांकन किया गया है जो आमतौर पर संपीड़न तनाव के उच्च स्तर पर लागू होता है । सबसे महत्वपूर्ण बात यह है कि, इस शोध कार्य में पहली बार विकसित विश्लेषणात्मक मॉडल के प्रयोगात्मक सत्यापन के लिए एक महत्वपूर्ण निवेश प्राचल के रूप में माइक्रो सीटी विश्लेषण से फाइबर अभिविन्यास का 3 डी डेटा उपयोग किया गया है । आम तौर पर, सैद्धांतिक और प्रयोगात्मक परिणामों के बीच एक संतोषजनक समझौता देखा गया था ।इस तरह के एक समझौते ने चक्रीय लदान स्थितियों को लागू करके बैटरी के यथार्थवादी आवेशन- अनावेशन मोड को अनुकरण करने के लिए आत्मविश्वास बढ़ाया है। एक देहली मानदंड जो पी एस डी के अपरिवर्तनीय व्यव्हार को परिभाषित करता है तथा बैटरी के आवेशन- अनावेशन मोड के दौरान प्रमुख संरचनात्मक मानकों की अधिकतम अनुमत सीमा के संदर्भ में विशेषताओं को विकृत करना भी प्रस्तुत किया गया है।

3 डी विश्लेषणात्मक मॉडल के टूलकिट की व्यावहारिक उपयोगिता सुनिश्चित करने के लिए, एक 'आदर्श' एजीएम विभाजक प्रस्तावित किया गया था जो साहित्य में दिए गए दिशानिर्देशों के साथ मेलजोल खता है ।परिकलित एजीएम को ढाल संरचना के साथ इंजीनियर किया जा सकता है जिसमें बैटरी की सकारात्मक और नकारात्मक प्लेटों की दिशा में घनत्व में भिन्नता है । विकसित विश्लेषणात्मक मॉडल द्वारा मूल्यांकन की गई संरचनात्मक विशेषताओं में सुधार संभावित रूप से बैटरी के जीवन चक्र को बढ़ा सकता है ।

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Nomenclature

φ, ς	In-plane fibre orientation angle
θ, γ	Out-of-plane fibre orientation angle
θ'	Updated out-of-plane fibre orientation angle
θ_c	Critical out-of-plane orientation angle
ϑ	Angle between the test direction and the direction of the liquid flow
ϕ	Contact angle of wetting liquid
Θ	Out-of-plane orientation angle of imaginary secant plane
Φ	In-plane orientation angle of imaginary secant plane
Ψ	Dynamic viscosity of electrolyte
ξ	Porosity of AGM
η	Beam constant
λ	Fibre length
α	Angle formed between the directions, (θ, φ) and (Θ, Φ)
β	Angle between axis of fibre and direction of electrolyte flow
σ	Surface tension of electrolyte
ρ	Density of electrolyte
ρ_{AGM}	Bulk density of AGM separator
ρ_f	Density of fibre
Γ	Angle made by porous medium with liquid level
τ	Function specifying mean cross effect of $J(\theta,\varphi)K(\theta,\varphi)$
$\bar{\delta}_{jj}$	Statistical mean of the deformation of all the fibre segments in the direction *j*

$\Delta\varepsilon$	True strain experienced by the fibres in the mesodomain
$\Omega(\varphi)$	2D fibre orientation density function (2D)
$\Omega(\theta, \varphi)$	3D fibre orientation distribution function (3D)
$\Omega(\theta', \varphi)$	Fibre orientation distribution function with updated out-of-plane fibre orientation angle
χ	Angle formed between the axes of fibres having orientations (θ, φ) and (γ, ς)
μ	Coefficient of friction between the fibres
$\Delta P_{Wf\bar{b}}$	Pressure losses due to the internal friction accounting for the withdrawal forces
ΔP_s	Pressure loss due to fibre slippage
$\Delta P_{s(i)}$	Pressure loss due to fibre slippage at *i*th iteration during recovery
v_{jk}	Poisson's ratio of AGM in the direction, *k*, as a result of tensile load applied in *j* direction
$\upsilon(\Theta, \Phi)$	Total number of intersections of fibres on a unit area of the plane
ω_F	Specific length representing the total length of lines per unit area
ω_{2D}	2D coverage parameter
ω_{3D}	3D coverage parameter
a_c	Cross-sectional area of capillary
θ_f, φ_f	Out-of-plane and in-plane orientation angles of direction of electrolyte flow
A	Cross sectional area of AGM

B	Bending modulus of the fibre
$\overline{b}$	Mean distance between two consecutive fibre-fibre contacts
$\overline{b}^{c}$	Mean distance between two consecutive non-slipping fibre-fibre contacts
$\overline{b}_{j}$	Distance between the centres of two successive contacts
C_1	Parameter based on fibre arrangement
C_j	Mean force experienced by the fibre–fibre contact
C_{jn}, C_{jp}	Normal and tangential components of C_j, respectively
C_{nsj}, C_{sj}	Mean forces per non-slipping and slipping contact points
c	Fitting parameter
D_h	Hydraulic diameter of AGM
D	Capillary diameter
d	Fibre diameter
d_p	Pore diameter
E_f	Young's modulus of fibre
$\lfloor F_f(d_p)\rfloor_{2D}$	Cumulative probability of a particle with diameter d_p, passing through the planes of AGM in 2D
$\lfloor F_f(d_p)\rfloor_{3D}$	Cumulative probability of a particle with diameter d_p, passing through the planes of AGM in 3D
f_s	Fraction of slipping contact points within the mesodomain
g	Acceleration due to gravity
$G(d_p)$	Cumulative probability of an inscribed circle formed between the polygons of a diameter that is equal to or less than d_p
h	Distance covered by the electrolyte within the capillary
h_0	Initial wicking height
h_1	Wicking height at time t
$\dot{h}_c$	Wicking rate
h_c	Wicking height
h_{max}	Maximum obtainable wicking height
h_{FD}	Wicking height based upon Fries and Dryer model
$\dot{h}_{FD}(t)$	Wicking rate based upon Fries and Dryer model
h_{LW}	Wicking height based upon Lucas-Washburn model
$\dot{h}_{LW}$	Wicking rate based upon Lucas-Washburn model
I_f	Area moment of inertia of fibre
'*i-1*', '*i*'	indices referring to the preceding and current structural level being analyzed, respectively
I_{2D}, I_{3D}	2D and 3D overall orientation parameter of the fibre alignment in the AGM
I_{3D}^{c}	3D overall orientation parameter of the non-slipping fibre segments in the AGM
K	Permeability of the porous medium
$K(\vartheta)$	Directional anisotropy in permeability of AGM
K_{j2D}, K_{j3D}	2D and 3D directional parameter representing the projection of $\overline{b}$ on j direction
K_{j3D}^{c}	Directional parameter representing the projection of $\overline{b}^{c}$ on j direction
K_{k3D}^{c}	Directional parameter representing the projection of $\overline{b}$ on k direction

k_4, k_5	Fitting parameter
L	Total length of a fibre in a defined volume *V* of AGM separator
L_a	Length of AGM separator sample
M	Mass of AGM separator
M_{jj}	Geometric coefficient representing combined effects of projection of force, and deflection for all possible alignment of fibres in the direction of compressive stress (*j*)
M_{jj}^{c}	Geometric coefficient of non-slip contacts representing combined effects of projection of force, and deflection for all possible alignment of fibres in the direction of compressive stress (*j*)
M_{jk}	Geometric coefficient representing combined effects of projection of force, and deflection for all possible alignment of fibres present in the direction (*k*) as a result of compressive stress (*j*)
m	Mass of fibres
m_{AGM}	Areal density of AGM separator
N	Number of planes in an AGM separator
N_{cc}	Number of cylindrical capillaries possessing hydraulic diameter (D_h)
N_{cd}	Number of charge-discharge cycles
n_b	Number of non-slipping fibre–fibre contacts inside mesodomain of unit area of cross-section
n_{dV}	Number of fibre–fibre contacts inside mesodomain of unit area of cross-section

n_l	Number of fibre–fibre contacts per unit length of fibre
n_s	Number of slipping fibre–fibre contacts inside mesodomain of unit area of cross-section
n_V	Number of fibre–fibre contacts per unit area
P	Compressive stress or pressure applied
P_b	Pressure expended to bend the fibres
P_r	Remnant pressure exerted by AGM separator during recovery stage
P_s	Pressure loss due to fibre slippage
$P_{r(i-1)}$, $P_{r(i)}$	Remnant pressure exerted by AGM during recovery stage at i-1th and i^{th} iterations, respectively
$P_{b(i-1)}$	Pressure stored in the form of fibre bending by AGM separator during recovery stage at $i-1$ th iteration
$P_{W\bar{fb}(i)}$	Pressure losses due to the internal friction accounting for the withdrawal forces
$P_{W\bar{fb}(0)}$	Pressure losses due to the internal friction accounting for the withdrawal forces at initial state
$Q(d_p)$	Probability of a particle with a diameter d_p passing through a pore channel across the thickness of nonwoven.
r	Step number in algorithm calculating recovery of AGM separator
R	Capillary or pore radius
S	Semi-empirical constant in van Wyk's equation
S_0	Surface area of the channel per unit volume
s	Aspect ratio of glass fibres

t	Time
T	Thickness of AGM seperator
T_0	Initial thickness of AGM separator
T_{10}	Thickness of AGM measured under 10 kPa pressure
$T_{(i-1)}$, $T_{(i)}$	AGM thickness at preceding (i.e. i-1th iteration) and current (i.e. i^{th} iteration) structural level being analyzed.

V	Volume of fibrous assembly
V_o	Initial volume of fibrous assembly
V_f	Fibre volume fraction of AGM
V_{f0}	Initial fibre volume fraction of AGM
V_{f10}	Fibre volume fraction of AGM calculated from thickness measured under 10 kPa pressure
V_{fm}	Maximum permissible fibre volume fraction of AGM
Wf_0	Mean withdrawal force per unit fibre length
W	Lambert function

List of acronyms

Symbol	Detail
2D	Two-dimensional
3D	Three-dimensional
AGM	Absorbent glass mat
AJS	Acid jellifying separator
CD	Cross-machine direction
CFD	Computational fluid dynamics
CTAn	CT analyser
FOD	Fibre orientation distribution
FVF	Fibre volume fraction
MD	Machine direction
PSD	Pore size distribution
SD	Standard deviation
SEM	Scanning electron microscopy
SSA	Specific surface area
VRLA	Valve regulated lead acid
X-ray micro CT	X-ray micro computed tomography