

Chapter 2

Materials and Experimental Procedures

Abstract

This chapter deals with the materials used, procedure for preparing composites and the methods used for the characterisation of fibres and the composites under specific conditions.

2.1 Materials

2.1.1 Pineapple leaf fibre (PALF)

Pineapple leaf fibres were provided by South India Textile Research Association (SITRA), Coimbatore, India. They were extracted from the leaves of the plant *Ananus cosomus* belonging to Bromeliaceae family. Neatly separated PALF cut at a uniform length of 30 mm was used for the study. The chemical constituents of PALF are cellulose (70-82 %), lignin (12.7 %), ash (1.1 %) and moisture content (10-11 %). The important properties are given in Table 2.1.

2.1.2 Glass fibre (GF)

Woven E-Glass fibres were supplied by Ceat Ltd, Hyderabad, India. The properties of glass fibre are given in Table 2.1.

Table 2.1 Properties of PALF and GF

Properties	PALF	GF
Tensile strength (MPa)	413-510	2500
Tensile modulus (GPa)	6.2-7	70
Elongation at break (%)	1.6	2.5
Density (g cm ⁻³)	1.526	2.54
Diameter (micrometer)	30-60	15
Microfibrillar angle (°)	14	-

2.1.3 Polyester resin

Unsaturated polyester resin HSR 8131 obtained from M/S Bakelite Hylam, Hyderabad, India was used. This was synthesised from maleic anhydride, phthalic anhydride and propylene glycol. The important characteristics of the polyester resin are given in Table 2.2.

Table 2.2 Typical properties of polyester (PER) resin

Appearance	A clear pale yellow liquid
Viscosity at 25 ^o C (cP) Brookefield viscometer	650
Specific gravity at 25 ^o C	1.11
Typical properties of cured unreinforced resin (specimen cured for 24 h at room temperature followed by post curing at 50 ^o C for 24 h)	
Tensile strength (MPa)	23
Young's modulus (MPa)	970
Elongation at break (%)	1.6
Flexural strength (MPa)	50
Impact strength (J/m)	11

2.1.4 Chemicals

Methyl triethoxy silane, vinyl tri (2-methoxy ethoxy) silane and γ - methacryloxy propyl trimethoxy silane were obtained from Sigma-Aldrich, India. Sodium hydroxide, glacial acetic acid, and polystyrene

maleic anhydride (PSMA) were of commercial grade. The structures of PSMA and various silanes used are given in Fig. 2.1. Methyl ethyl ketone peroxide (MEKP) and cobalt naphthenate used were also of commercial grade supplied by Sharon Enterprises, Cochin, India.

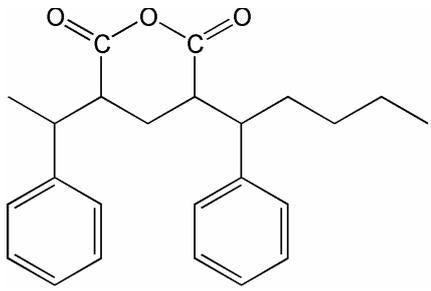
Chemical description	Chemical structures
Methyl triethoxy silane	$\begin{array}{c} \text{OC}_2\text{H}_5 \\ \\ \text{H}_3\text{C}-\text{Si}-\text{OC}_2\text{H}_5 \\ \\ \text{OC}_2\text{H}_5 \end{array}$
Vinyl tri (2-methoxy ethoxy) silane	$\begin{array}{c} \text{OCH}_2-\text{CH}_2-\text{OCH}_3 \\ \\ \text{H}_2\text{C}=\text{C}-\text{Si}-\text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$
γ - methacryloxy propyl trimethoxy silane	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{C}=\text{C}-\text{COO}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3 \end{array}$
Polystyrene maleic anhydride (PSMA)	

Fig. 2.1 The chemical structures and descriptions of silane coupling agents and PSMA

2.2 Chemical modification of fibre surface

2.2.1 Silane treatment

0.3 and 0.6 % of the respective silanes were mixed with an ethanol/water (6:4) mixture and allowed to stand for 1 hour. The pH of the solution was maintained 4 by the addition of acetic acid. The chopped PALFs were dipped in this solution for one and half hours. The solvent was drained out and the fibre was dried in air followed by drying at 60^oC for 1 hour.

2.2.2 Polystyrene maleic anhydride (PSMA) treatment

A fixed amount of the cut fibre was kept in 5 % solution of polystyrene maleic anhydride (PSMA) in toluene and refluxed for half an hour. The fibre was then dried at 60^oC in an oven for 1 hour.

2.2.3 Sodium hydroxide treatment

Chopped PALF was treated with 2 % solution of NaOH for 2 hours. The fibres were then washed with very dilute acid to remove alkali. Washing was continued till the fibres were free of alkali. The washed fibres were then dried in an oven at 60^oC for 2 hours.

2.2.4 Potassium permanganate (KMnO₄) treatment

The fibres were soaked in 0.03 % KMnO₄ in acetone solution for half an hour. The fibres were then dried in an air oven at 60^oC for 1 hour.

2.3 Solvatochromic measurements

The dyes used for the solvatochromic measurements are cis-dicyano-bis (1,10-phenanthroline)-iron [Fe(phen)₂(CN)₂] (**1**) which can be used as an indicator to quantify surface acidity α , Michler's ketone (4,4'-bis(N,N-dimethyl amineo benzophenone); (**2**) which allows one to estimate

surface's dipolarity/polarisability, π^* , and the indicator 3-(4-amino-3-methyl phenyl)-7-phenyl-2,6 dihydrofurano[2',3':4,5] benzofuran-2,6-dione (ABF; **3**) which is sensitive for surface basicity, β .

The probe dye indicator **1** was prepared according to Schilt [1]. Dye **2** was purchased from Merck (Darmstadt), recrystallised twice from ethanol, and carefully dried before use. Dye **3** was kindly provided by BASF Aktiengesellschaft, Manchester, England. The formulae of the probe dyes are given in Fig. 2.2. The solvents used for solvatochromic measurements are 1, 2 dichloroethane (DCE) and cyclohexane which were dried over calcium hydride (CaH_2) and freshly distilled before use.

PALF was soaked in 20 ml of the respective solvent. Stock solutions of the probe dyes of specified concentration were prepared. In the case of dye **1**, a concentration of 2×10^{-3} mol/L in 1, 2 dichloroethane (DCE), and for the dyes **2** and **3**, a concentration of 1×10^{-3} mol/L in cyclohexane were used. The fibres soaked in the probe dyes were kept vibrating overnight. Then the solvent was decanted off, the PALF was washed with the respective solvent to remove any adhering dye particles. The samples were dried in vacuum at room temperature for 24 h. The dried samples were used for UV/Vis measurements.

The equipment employed was a UV/Vis spectrometer MCS 400 with glass fibre optics (ZEISS GmbH, Germany). UV/Vis spectra of fibres were recorded by a special reflectance technique. The fibres were placed between two quartz plates. The sensor head for measuring reflectance spectra was located under one of these quartz plates and the UV/Vis spectrum of the adsorbed dye was monitored. The absorption maxima were detected with a software program. The following multiple

correlation equations are used in this article to separate the polarity parameters from the unit of measurement of each λ_{\max} indicator [2].

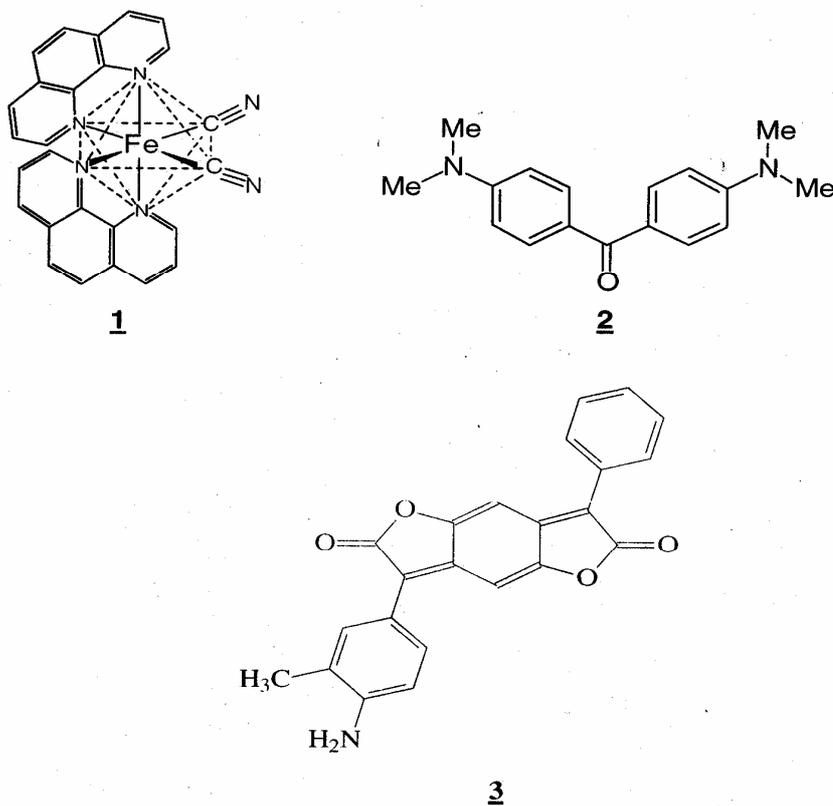


Fig. 2.2 Formulae of the probe dyes used 1. Iron dye 2. Michler's ketone, 3. Furan dye

$$\alpha = -7.9 = 0.453 \nu_{\max}(\mathbf{1}) \cdot 10^{-3} [\text{cm}^{-1}] + 0.021 \nu_{\max}(\mathbf{2}) \cdot 10^{-3} [\text{cm}^{-1}] \quad (2.1)$$

$$\pi^* = 13.889 - 0.251 \nu_{\max}(\mathbf{1}) \cdot 10^{-3} [\text{cm}^{-1}] - 0.32 \nu_{\max}(\mathbf{2}) \cdot 10^{-3} [\text{cm}^{-1}] \quad (2.2)$$

$$\beta = \frac{18.6 + 0.97\alpha - v_{\max} (\underline{3}) \cdot 10^{-3} - 0.91\pi^*}{2.93} \quad (2.3)$$

$$AN = 0.013732 v_{\max} (\underline{1}) \cdot 10^{-3} [\text{cm}^{-1}] - 207.8 \quad (2.4)$$

$$E_T (30) = 31.2 + 15.2 \alpha + 11.5\pi^* \quad (2.5)$$

2.4 Fourier transform infrared analysis (FTIR)

The modified fibre surfaces were characterised by IR spectroscopy. KBr disk method was followed. The instrument used was Shimadzu infra red spectrophotometer IR. 470.

2.5 Optical microscopy studies

The optical photographs of the untreated and silane treated fibres were taken using Leica DMRX Microscope provided with a digital camera DC 300 F. The dimensions of PALFs were also determined using this optical microscope.

2.6 Composite processing

2.6.1 PALF/PER and GF/PER composites

The PALFs were chopped to desired length, washed with water and dried at 60-70°C for 2 hours. Hand lay-up method followed by compression moulding was used for composite preparation. Composite sheets of size 150 mm × 150 mm × 3 mm were prepared. The polyester resin was mixed with 1 vol % cobalt naphthenate (catalyst) and 1 vol % MEKP. The resin mixture was poured onto the fibre mat of uniform thickness prepared of definite weight which is placed in the mould. The air bubbles were removed carefully with a roller. The closed mould was cured at room

temperature for 24 hours under constant pressure (1MPa) and post cured at 50°C for a further period of 24 hours.

Pineapple leaf/polyester (PALF/PER) composite sheets were prepared by varying the fibre length, keeping fibre loading constant at 0.3 V_f (fibre 0.3 and matrix 0.7) and varying fibre loading keeping the fibre length constant at 30 mm. Glass fibre reinforced polyester (GF/PER) composites were prepared by varying fibre loading using glass fibre mat. Unfilled polyester resin samples were also prepared by curing the resin with MEKP and cobalt naphthenate. PALF/PER composites of different fibre loading 15, 30, 40 and 50 wt% (volume fractions 0.12, 0.25, 0.33, 0.41) and GF/PER composites of fibre loading 16, 24, 35, 40 and 50 wt% (volume fractions 0.08, 0.12, 0.20, 0.23, 0.33) were prepared.

2.6.2 Chemically modified PALF/PER composites

Using chemically modified PALF, composite sheets were prepared keeping the fibre loading constant at 40 wt% (0.3 V_f).

2.6.3 PALF/GF hybrid polyester composites

Randomly oriented intimately mixed (IM) hybrid composites were prepared by uniformly mixing the two fibres PALF and GF of required weights corresponding to different volume fractions of each fibre. Glass fibres of length 50 mm and PALF of 30 mm were used for the preparation of IM composites.

Hybrid composites of different layering patterns such as trilayer GPG (GF/PALF/GF), and PGP (PALF/GF/PALF) were also prepared by hand lay-up technique mentioned above. Glass fibre mats were sized. Both PALF and glass fibre mats of required weights were used in the

preparation of the layered composites. Trilayer PALF/GF hybrid fibre polyester composites (GPG) were prepared by placing glass fibre mats on both sides and PALF in between and PGP by placing PALF mats on both sides of the GF mat. Bilayer GP (Glass/PALF) hybrid composites were prepared using mats of chopped PALF and GF, one placed above the other. The mats were arranged in such a manner so as to get the two types of fibres uniformly intermingled.

The total fibre loading is kept constant at $0.3 V_f$ and the GF content of the hybrid composite was first varied from 0 to $1 V_f$, i.e., the volume ratio of PALF/GF was varied from 100:0, 90:10, 80:20, 70:30, 50:50, 30:70, 10:90 and 0:100. A schematic representation of different hybrid configuration used in the study is given in Fig. 2.4. IM and GPG hybrid composites of different loading were also prepared keeping PALF/GF ratio constant at 90/10. The relative volume fraction of the two fibres was varied in all these patterns keeping the total fibre volume fraction constant at $0.3 V_f$.

2.7 Scanning electron microscopy analysis

The morphological characterisation of PALF and the fracture morphology of the composites were observed using scanning electron microscope JEOL –JSM-840 A and JEOL –JSM 6390. The tensile and impact fractographs of the composites were taken to study the fracture mechanism and interface adhesion of the composites.

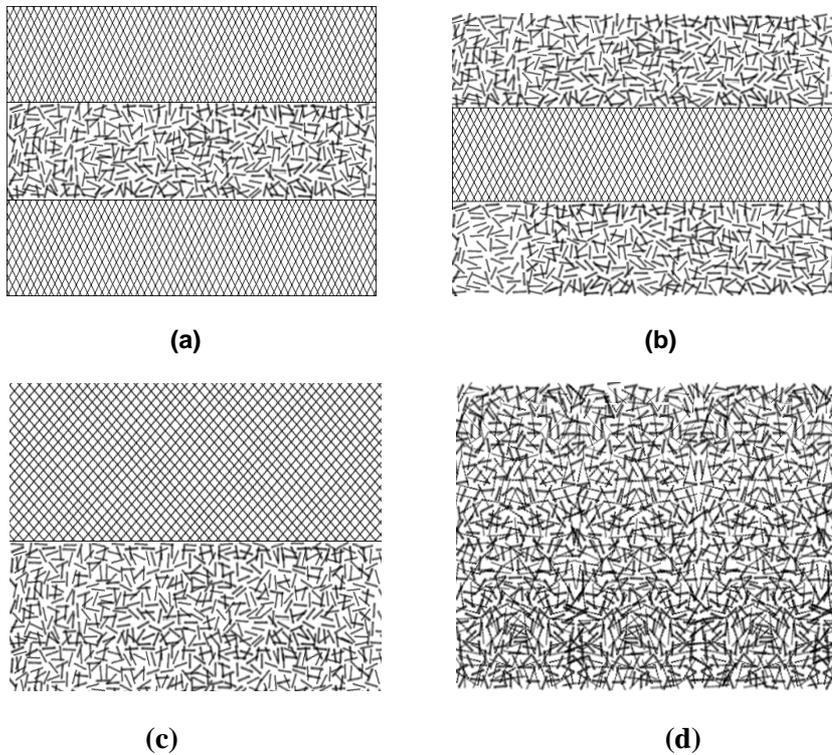


Fig. 2.3 Schematic representation showing different hybrid configurations
(a), (b) Fibre skin and fibre core arrangement (c) Bilayer
(d) Intimately mixed

2.8 Mechanical property measurements

Test specimens were cut from the composite sheets of dimensions $120 \times 15 \times 3 \text{ mm}^3$. Tensile tests were carried out using a FIE universal testing machine as per ASTM-D 638 at a crosshead speed (CHS) of 50 mm/min and a gauge length of 100 mm. Flexural tests were conducted on the same machine using a three point bending system according to ASTM D 790. Izod impact tests on notched specimens were performed using a

pendulum impact testing machine (International Equipments, Mumbai, India) as per ASTM D 256. Rectangular specimens of size 75 mm×15 mm×3 mm were used for testing. Five samples have been taken for each test to obtain average value.

2.9 Hardness measurement

Hardness of the composites was measured using shore D durometer according to ASTM D 2240. The size of the samples used was 100 mm × 10 mm × 3 mm³.

2.10 Dynamic mechanical analysis (DMA)

The dynamic mechanical analysis (DMA) was carried out using TA Instruments, Thermal Analyser in dual cantilever mode. The dynamic mechanical properties of the composites were evaluated at three frequencies 0.1, 1 and 10 Hz and temperatures ranging from 30 to 200°C. Rectangular specimens of size 35 mm × 10 mm × 3 mm were used for the measurement.

2.11 Thermogravimetric analysis (TGA)

Thermogravimetry (TG) was employed to analyse the thermal stability of fibres and composites. Simultaneous DTA-TG measurements were carried out using a thermogravimetric analyser (DTG 60) on approximately 10 mg samples, over a temperature range 30 to 500°C.

2.12 Thermophysical measurements

A periodical method developed by Boudenne et al. [3,4]. was used to estimate simultaneously thermal conductivity, diffusivity and specific heat of polymer composite materials at room temperature This method is

based on the use of a small temperature modulation in a parallelepiped-shape sample (44 mm of side and 4 mm of thickness) that allows obtaining all of these thermophysical parameters in only one measurement with their corresponding statistical confidence bounds. The composite sample is fixed between two metallic plates. The usage of conductive grease ensures a good thermal exchange between the different plates and the sample. The front side of the first metallic plate is heated periodically using a sum of five sinusoidal signals and the temperature is measured with thermocouples placed inside both front and rear metallic plates [4]. The thermophysical parameters of the samples are identified by comparison of the experimental and theoretical heat transfer functions [4]. The system under study is modelled with one-dimensional quadrupoles theory. The experimental heat transfer function H is calculated at each excitation frequency as the ratio between the Fourier-transform temperatures of the front and rear plates. A parameter estimation technique is then applied to estimate simultaneously both thermal conductivity (k) and diffusivity (a). The identification of the set of thermophysical parameters is a non-linear optimisation problem that is solved iteratively: by starting with sufficiently accurate initial guesses for the unknown parameters. By using the Levenberg–Marquardt method, the estimates can be successively refined.

The specific heat capacity (C_p) values of the composite samples were determined using the density (ρ) and thermal conductivity (k) and diffusivity (a) values:

$$Cp = \frac{k}{\rho a} \quad (2.6)$$

The density (ρ) measurements were achieved using the square plates samples used for thermal measurements. A Mettler- Toledo TM AT61 delta range balance was used to measure sample weight. The size of the samples was measured using a caliper square. Fig. 2.5 shows the schematic representation of the thermophysical measurements set up.

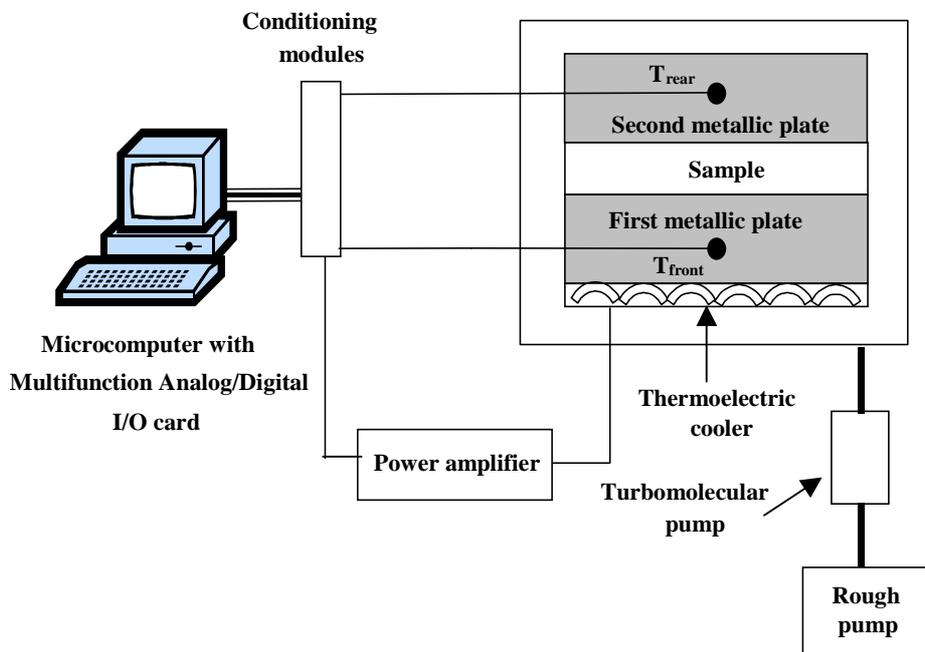


Fig. 2.5 Schematic representation of the thermophysical measurements set up

2.13 Water absorption studies

Water absorption is evaluated in terms of weight increase for composite specimen immersed in distilled water at temperatures 28, 60 and 90°C.

Samples of approximate dimensions 10 mm × 10 mm × 3 mm were used for the measurements.

The corners of the samples were curved to avoid non-uniform water diffusion. The thickness and weight of the samples were measured. The weighed samples were then immersed in distilled water at different temperatures. The samples were periodically taken out of water, surface dried with adsorbent paper and reweighed. The weight gain of the samples was measured as a function of time until equilibrium or the saturated state of water uptake has been reached. At each temperature, three specimens of the same material were tested. The molar percentage uptake Q_t of water by 100 grams of the polymer was calculated using the equation

$$Q_t = \frac{M_{(w)}/M_{r(w)}}{M_{i(s)}} \times 100 \quad (2.7)$$

where, $M_{(w)}$ is the mass of water at time t , $M_{r(w)}$ is the relative molecular mass of water i.e, 18 and $M_{i(s)}$ is the initial mass of the sample. When equilibrium was reached, Q_t becomes equal to the mole percent uptake at infinite time, Q_∞ .

2.14 Ageing studies

Composite samples were cut to specified dimensions according to ASTM D 638-76 and ASTM D 256 and used for the following experiments. Tensile and impact tests were done after the ageing experiments.

2.14.1 Cold water immersion

Pre weighed composite samples were immersed in distilled water at 28°C for 2 hours. The samples were taken out, surface water was wiped off, reweighed in an electronic balance and used for tensile and impact tests.

2.14.2 Dimensional stability tests

The dimensions of the samples were remeasured after cold water immersion; the moisture absorption and swelling in thickness of the composites were calculated as per the following equations from the mass of the samples before and after immersion.

$$\text{Moisture absorption (\%)} = \frac{(M_2 - M_1) \times 100}{M_1} \quad (2.8)$$

M_1 is the mass of the sample before immersion.

M_2 is the mass after immersion

$$\text{Thickness swelling (\%)} = \frac{(t_w - t_0) \times 100}{t_0} \quad (2.9)$$

t_w is the thickness of the sample after immersion and t_0 is the thickness before immersion.

2.14.3 Boiling water immersion

Samples of required size were kept in boiling water for 2 hours. After wiping of the water adhering to the surface of the samples, they were weighed in an electronic balance and used for tensile and impact tests.

2.14.4 Thermal ageing

In thermal ageing, the samples cut into specified dimensions and placed in an air oven at a temperature of 100°C for about 3 days. The samples were then allowed to cool to room temperature and tests of these aged samples were performed.

2.14.5 Soil burial test

Samples were completely buried in natural soil and allowed to be in constant contact with soil. They were taken out after 6 months, removed the soil using a brush, dried in an air oven at 50°C for 5 hours and used for tensile and impact testings.

2.14.6 Outdoor weathering studies

Weathering evaluation of the composites was carried out for a period of six months by natural weathering. For this, the samples were exposed to outdoor to get rainfall, solar radiation and all conditions of local climate. The samples were collected after six months of exposure, dried in an air oven at 50°C for 5 hours and subjected to tensile and impact tests.

References

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