



Utilization of waste leather for the fabrication of composites and to study its mechanical and thermal properties

Ravindra D. Kale¹ · Nilesh C. Jadhav¹

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Abstract

In this present work the preparation and characterization of waste leather-reinforced epoxy resin composites were assessed. Composite sheets of various leather loadings were prepared with thicknesses ranging from 2.5 mm to 5 mm to 7.5 mm and studied using response surface methodology by employing a central composite design. The final optimized sample of composites was tested for tensile, flexural, impact and chemical resistance, and their assessment was carried out. Composites exhibited excellent mechanical properties as the loading percentage of leather was increased. Bonding between the matrix and leather was analysed using SEM looking at the fractured surfaces, which showed that at the highest leather loading the composite demonstrated close packing and adhesion. TGA and DTA analysis proved excellent thermal stability with an increase in leather loading. The DMA analysis of composites indicated an increase in storage modulus and loss modulus and decrease in $\tan \delta$ peak with an increase in leather loading. Composites showed no deterioration, thereby having excellent chemical resistance.

Keywords Design expert · SEM · TGA · DMA

1 Introduction

Leather enterprises are amongst the most polluting industries in India. More than 20–30% of leather is disposed of during the preparation of footwear and leather products. The final products of the leather industry result in significant solid waste, so the leather industries are continuously observed owing to their danger to the environment [1]. Some statistics obtained from the United Nations Industrial Development Organization demonstrate that leather products are utilized by more than one fourth of the entire world population. Leather industries contribute substantially to the financial improvement of the nation. However, there is continuous pressure from the experts in the pollution control division. Ecological awareness requires industries to use various new sustainable strategies and clean methods by using environmentally friendly enzymes,

waste minimization techniques and so on. Therefore, it is critical to appropriately dispose of or utilize the leather waste from the finished and used products, which otherwise might become a serious environmental problem. Since waste and discarded leather materials contribute the overall maximum percentage of solid waste, fundamental research has been carried out on the utilization of used leather products and converting them into useful value-added products, which will provide an economically beneficial way to ameliorate environmental pollution issues. Composites are made up of two components and consist of a matrix and reinforcement [2]. The composite has properties that outperform the features of the individual constituents. Composites of various types surround us in everyday life, both natural and human-made. Some examples of natural composites are human bones and wood [3]. Humans have utilized composite materials throughout the ages in

✉ Ravindra D. Kale, rd.kale@ictmumbai.edu.in; Nilesh C. Jadhav, nilesh.jadhav890@gmail.com | ¹Department of Fibers and Textile Processing Technology, Institute of Chemical Technology, Mumbai 400019, India.



various applications such as natural fibres and mud to build houses using bamboo sticks and clay to make roof-tops, bricks reinforced with natural fibres, etc. Steel as a composite material used for reinforcement in cement concrete is already being implemented [4, 5]. Currently, fibre-reinforced polymeric materials are utilized for many structural applications in various aspects because of their excellent mechanical strength compared with metal. Since the 1950s advanced composites have mostly found applications in the industrial and automotive sectors, e.g., in building materials such as high-performance sporting goods, electrical circuit boards, yachts and so on. Generally, commercially available composites are manufactured using non-biodegradable resins such as epoxy resins, phenolic and unsaturated polyester resins in combination, which possess high-tensile-strength fibres such as glass, graphite and aramids. These composites are intended for applications where strength, stiffness and long-term durability are required [5]. The only hindrance is that most of the composites are derived from petroleum sources since composites are produced using two different components that are bonded together and have a specific shape, so they cannot be recycled or reused; currently > 90% of composites are disposed of in landfills. Degradation in landfills can take several decades or even centuries, which makes that land unusable and infertile for any other purpose. The ever-growing amounts of plastic and composite waste have increased environmental pollution, which has raised the consciousness of manufacturers, consumers and government officials. Currently, we are utilizing petroleum resources at an unsustainable level of 100,000 times the rate at which it has been created in nature [6]. To eradicate these pollution problems, governments worldwide have established and implemented specific laws encouraging us to use recycled bio-based green products [7]. Due to the environmental awareness and diminishing rate of natural petroleum resources, the concept of sustainability and some new environmental regulations have triggered the search for new products and processes that are environmentally friendly. Most global manufacturers are marching towards green or recyclable products. To the best of our knowledge, the utilization of leather waste as a reinforcement material in composites has never been investigated. In this work, we endeavoured to develop leather waste-reinforced composites, viz., chrome shavings or buffing dusts with epoxy resin. Composite sheets of 2.5 mm, 5 mm and 7.5 mm thickness and leather loadings of 10%, 20% and 30% were employed. The work was carried out using Design-Expert software 7.0 with a central composite design and 13 runs of experiments. Prepared composites were tested

for their mechanical performance, thermal stability and sensitivity to various chemicals.

2 Materials

Waste scrap leather was purchased from Dharavi leather market, Mumbai, India; epoxy resin B47 and hardener AH 416 were supplied by Atul Vapi India Ltd. Mould size of 18 × 18 cm was used on a 300T compression moulding machine (Santosh Engineering Ltd., Vapi, India) for composite fabrication.

3 Methods

3.1 Preparation of composites

Waste scrap leather was chopped into small pieces using scissors and ground in a mixer. Epoxy resin and the hardener were used in 100:60 w/w proportions according to the manufacturer's recommendations. This resin and hardener were thoroughly mixed with the assistance of an overhead stirrer, poured on the randomly powdered scrap leather present in the mould and then evenly spread by using a hand roller; excess resin was squeezed out. The composite was laid in between two greased PET sheets, compressed between two steel plates and cured at 120 °C for 1 h in the 300T compression moulding machine. The vertical cutting machine was employed to cut the sample for tensile, flexural and impact testing according to the standard ASTM techniques. Five samples were made for each test, and the average value was reported. The leather volume fraction (VF) was in the range of 10%, 20% and 30% when changing the thickness to 2.5 mm, 5 mm and 7.5 mm, respectively.

4 Mechanical characterization of composites

4.1 Tensile strength

Tensile properties of the leather-reinforced epoxy resin composites were examined on an H50KT Tinius Olsen Universal Testing Machine as per the ASTM D 638 standard technique. The testing was performed at a crosshead speed of 5 mm/min.

4.2 Flexural strength

The flexural tests were conducted as per ASTM D 790 on an H50KT Tinius Olsen tensile testing machine. A sample

size of 120 × 13 × 3 mm was used. The test specimen was placed on two supports having an 80-mm span length between them. A load range of 500 N with a 10 mm/min extension range at the crosshead speed of 2 mm/min was set for this test.

4.3 Impact strength

Izod impact tests were conducted on an Izod impact tester to obtain the fracture of specimens. The dimensions of the samples used were 65 × 13 × 3 mm according to the ASTM D 256 standard.

4.4 Scanning electron microscopy (SEM)

The surface morphology of fractured composite samples was observed using a Philips XL-30 SEM (The Netherlands). The samples were coated with gold by the sputtering method before recording the micrographs.

4.5 Thermogravimetric analysis (TGA)

Thermal stability of the neat and leather-reinforced epoxy resin composites was determined by thermogravimetric analysis (TGA) (DTG-60 H, Shimadzu Co., Japan). TGA analysis was carried out under inert atmosphere. The heating rate was kept at 10°C/min, and the samples were heated from 30 to 500°C.

4.6 Dynamic mechanical characterization

The three-point bending mode was used for the dynamic mechanical analysis using the METRAVIB RSO Vibco Analyzer VA 4000 (Germany). The testing was performed in

the range of 30–180°C temperature at a 3°C/min rate of heating. The frequency was fixed at 1 Hz, the preload was about 0.1 N, and the amplitude was 20 μm with 125% force track. Samples having 12 mm width, 2.5 mm thickness and 50 mm span length were used for DMA. Maximum two-sample testing was carried out, and the average values were reported.

4.7 Chemical resistance test

The chemical resistance was carried out as per ASTM D 543-87. In each case, five pre-weighed samples of the same size were taken and immersed in the respective chemical reagents for 24 h at room temperature. These samples were removed after 24 h, washed with distilled water and dried by sandwiching them between filter paper to remove the excess water sticking on the surface of the composites at room temperature. The increase in percentage weight gain of the samples was calculated and the increase in original weight was determined. Experiments were performed as per the central composite design matrix to optimize the amount of leather and thickness of the composite sample.

5 Results and discussion

The experimental design matrix is given in Table 1. The responses studied were tensile strength, Young's modulus, flexural strength, flexural modulus and Izod impact. As observed in Table 2, the model result was significant ($P < 0.05$) for all the responses. The lack of fit was not significant ($P > 0.05$) for all the responses, which proved this model was valid for this work. The independent variable

Table 1 Design matrix for waste leather-reinforced epoxy composites

Run	Leather loading (%)	Thickness (mm)	Tensile strength (MPa)	Youngs modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Izod impact (kJ)
1	20	5	12.5	1037.93	32.6	1514	0.108
2	20	5	13.16	1011.25	31.68	1552	0.107
3	30	7.5	20.58	981.49	45.27	3711	0.208
4	20	5	14.1	1065.21	33.57	1533	0.106
5	20	5	14.58	1029.33	32.59	1565	0.108
6	30	5	17.81	1313.89	40.48	2688	0.207
7	10	5	10.2	786.93	12.11	808	0.096
8	10	2.5	10.68	891.35	12.92	920	0.098
9	20	7.5	14.07	914.73	35.22	2994	0.106
10	20	5	15.1	1051.81	32.52	1788	0.108
11	10	7.5	10.58	849.67	12.33	1216	0.097
12	30	2.5	20.43	1575.69	44.14	2218	0.205
13	20	2.5	14.17	1207.65	35.52	1640	0.108

Table 2 ANOVA for the response surface quadratic model

	Tensile strength (MPa)	Young's modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Izod impact (kJ)
Model (<i>P</i> value)	0.0003	< 0.0001	< 0.0001	< 0.0001	< 0.0001
Lack of fit (<i>P</i> value)	0.5228	0.1139	0.12540	0.0628	0.2511
<i>A</i> (<i>P</i> value)	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.0001
<i>B</i> (<i>P</i> value)	0.9847	< 0.0001	0.9225	0.0003	1.0000
<i>AB</i> (<i>P</i> value)	0.9066	< 0.0001	0.4053	0.0180	0.1052
<i>A</i> ² (<i>P</i> value)	0.2589	0.5282	< 0.0001	0.6039	< 0.0001
<i>B</i> ² (<i>P</i> value)	0.2001	0.2531	0.0031	0.0035	0.9590
<i>R</i> ²	0.946533	0.987482	0.995741	0.968348	0.999669
Adj <i>R</i> ²	0.908342	0.978541	0.992699	0.945575	0.999433

fibre fraction was significant for all the responses while the composite thickness was significant only for the Young's modulus and flexural modulus. Similarly, the interaction of independent variables was only significant for the Young's and flexural modulus. The quadratic term for the fibre fraction was significant for flexural strength and Izod impact and thickness for the flexural strength and flexural modulus. The fitness of the model was further confirmed by a satisfactory value of the determination coefficient *R*², which was > 90% for all responses.

5.1 Final equation in terms of coded factors

$$\text{Tensile strength} = 13.70448 + 4.56A - 0.00833B + 0.625AB + 0.7591A^2 + 0.87431B^2 \tag{1}$$

$$\text{Young's modulus} = 1045.009 + 223.8533A - 154.8B - 138.13AB + 8.584828A^2 + 19.36483B^2 \tag{2}$$

$$\text{Flexural strength} = 32.64828 + 15.42167A + 0.04B + 0.43AB - 6.49397A^2 + 2.581034B^2 \tag{3}$$

$$\text{Flexural modulus} = 1653.621 + 945.5A + 523.8333B + 299.25AB - 63.6724A^2 + 505.3276B^2 \tag{4}$$

$$\text{Izod impact} = 0.107276 + 0.054833A + 0B + 0.001AB + 0.044534A^2 + 3.45E - 05B^2 \tag{5}$$

To gain a better understanding of the results, the 3D response surface plots for different responses used in the study are presented in Figs. 1a–c and 2a, b, respectively. The results show that all the input process parameters had a significant effect on the responses. The mechanical properties showed tremendous improvement in the thickness and amount of leather present in the composites. This may be because as the leather loading increased, there was remarkable improvement of the strength and rigidity

of the matrix due to the larger contact area between the leather and matrix. According to the RSM, the results anticipated by the model demonstrated that the maximum values of the tensile strength, Young's modulus, flexural strength, flexural modulus and Izod impact could be accomplished with 30% leather loading at 2.5 mm thickness (Table 3). The predicted values for all the responses matched the experimental values closely.

5.2 SEM analysis

The SEM images were taken for an optimized sample predicted by the software. Figure 3 shows 2.5 mm thickness

with 10%, 20% and 30% loaded leather-reinforced epoxy composites to investigate the reasons for an increase in mechanical strength. The uniform distribution of the leather is visible in the images, as seen in Fig. 3. At 10% leather loading (Fig. 3a), air gaps and voids are visible because of the poor adhesion of the resin to the leather. With an increase in leather percentage, i.e., 20% and 30%, as observed in Fig. 3b, c, the air gaps and voids almost disappeared because of the close packing of the leather

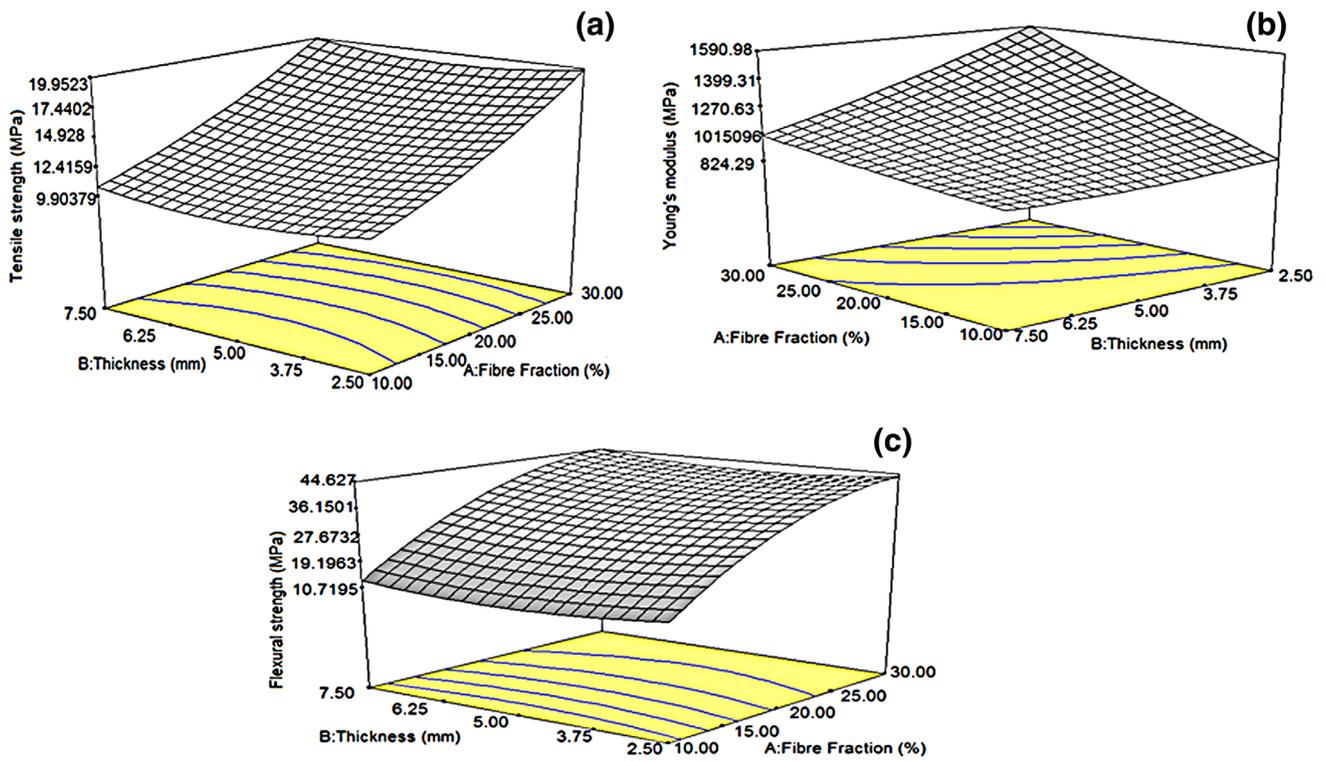


Fig. 1 Three-dimensional response plot for the **a** tensile strength, **b** Young's modulus and **c** flexural strength of leather-reinforced composites

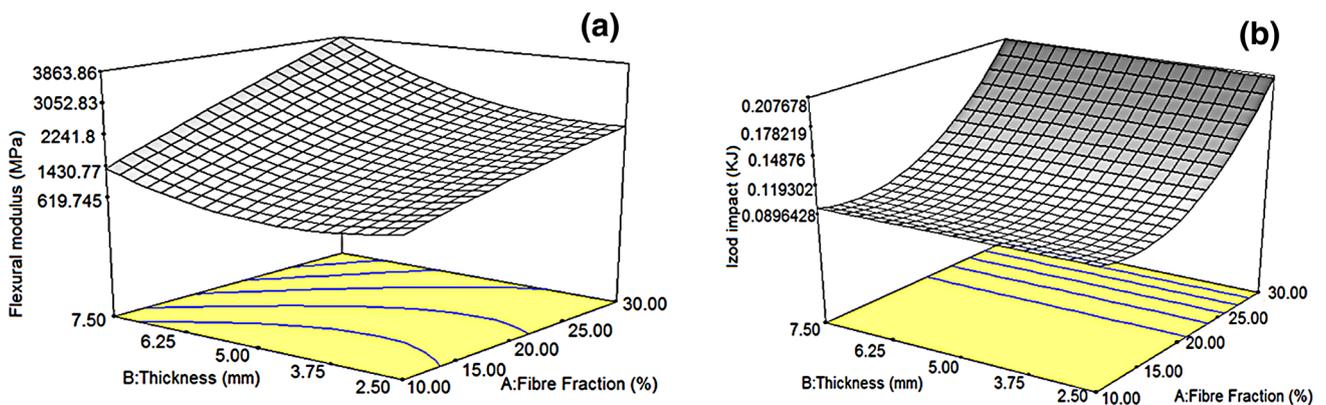


Fig. 2 Three-dimensional response plot for the **a** flexural modulus and **b** Izod impact of leather-reinforced composites

Table 3 Optimization

Sample	Fibre fraction (%)	Thickness (mm)	Tensile strength (MPa)	Young's modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Izod impact (kJ)
Predicted value	30	2.5	20.43	1575.69	44.14	2218	0.205
Experimental value	30	2.5	19.90	1571.93	42.14	2210	0.209

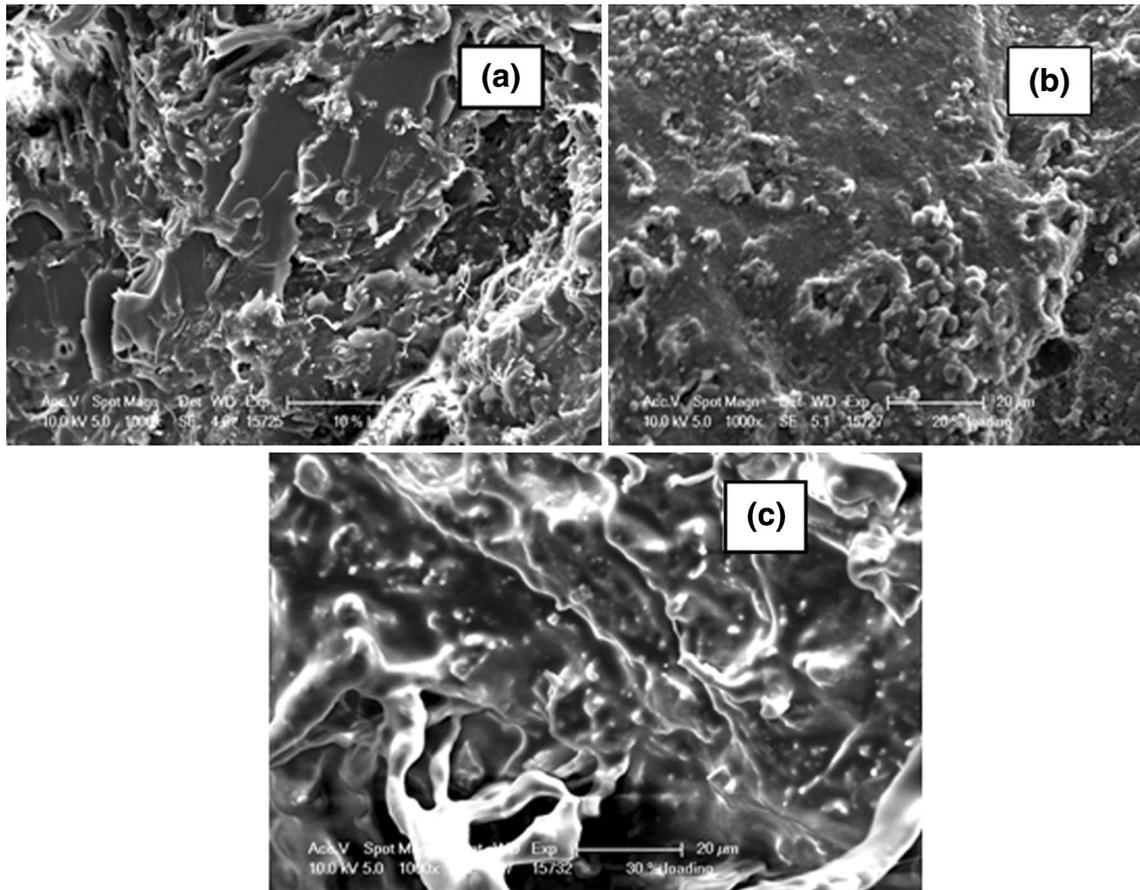


Fig. 3 SEM analysis for a 10%, b 20% and c 30% leather-reinforced composites

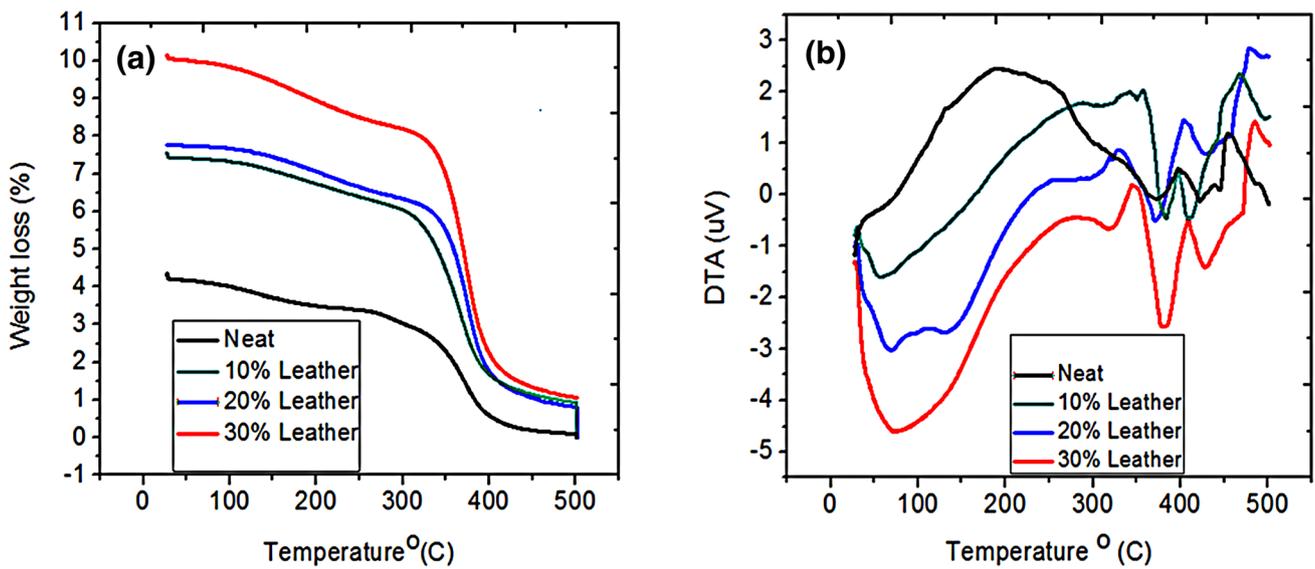


Fig. 4 a TGA and b DTA analysis for neat epoxy and leather-reinforced composites

with the resin, indicating enhanced interfacial adhesion of the leather and epoxy resin. This resulted in excellent mechanical properties of the composites.

5.3 TGA analysis

Thermogram and DTA curves of the neat epoxy and leather-loaded epoxy composites are shown in Fig. 4a, b. This demonstrates that the neat epoxy exhibited lower thermal stability than the leather-loaded composites, which is reflected in the curve shift towards higher temperatures due to increments in the leather percentage of 10%, 20% and 30%. The presence of higher leather loading increased the interfacial adhesion, which improved the compatibility between the leather and epoxy matrix. This enlarged the area of contact between the leather and matrix, which bound the material more tightly, restricting the molecular mobility on exposure to elevated temperature. The neat epoxy decomposed in the range of 330.49–360.60°C. However, after incorporation of leather, the thermal stability improved with enhancement of the decomposition temperature to the 354.34–390.83°C range for 30% leather loading. The neat epoxy showed a 7.9% final residue, which was the lowest as no char was

Table 4 Thermogravimetric analysis obtained for the leather-reinforced epoxy composite

Composites	Degradation temperature (°C)		Char residue
	T_{IDT}	$T_{FDT} (d_{max})$	
Neat epoxy	330.49	360.60	7.9
10% Leather	332.42	364.24	8.54
20% Leather	336.95	368.35	13.71
30% Leather	354.34	390.83	15.77

present. The leather-reinforced epoxy composites with 10% loading, 20% loading and 30% loading had final residue percentages of 8.54%, 13.71% and 15.77%, respectively, (Table 4). The above results show that the last residue percentage increased as the loading per cent of the leather increased.

5.4 Dynamic mechanical analysis (DMA)

The DMA results are generally expressed in terms of the storage modulus E' , loss modulus E'' and $\tan \delta$, which are dependent on certain factors such as temperature, time and frequency, respectively. Figure 5a shows the effect of temperature on the E' of the neat epoxy and leather-reinforced composites [8]. There was a gradual decrease in E' with the increase in temperature because of the transition from a glassy to rubbery state. Compared with the leather-loaded composites, the neat epoxy showed the lowest E' over all the specified temperature ranges. The stiffening effect obtained because of the interaction between the leather and matrix increased the E' of the composites. Also, its value increased with the loading [9, 10]. This could be because the enhanced interfacial adhesion between the matrix and reinforcement, which enlarged the area of contact between the two components, restricted the molecular mobility on exposure to elevated temperature [11]. Figure 5b presents the loss modulus (E'') versus temperature of different leather-reinforced composites. E'' is the contribution of the viscous components present in the material and is indicative of the energy dissipated as heat from the system during a deformation cycle due to viscous motions inside the material [12]. This is shown in Fig. 5b. The value of E'' increased and then gradually decreased with the increase in temperature for all the samples. The

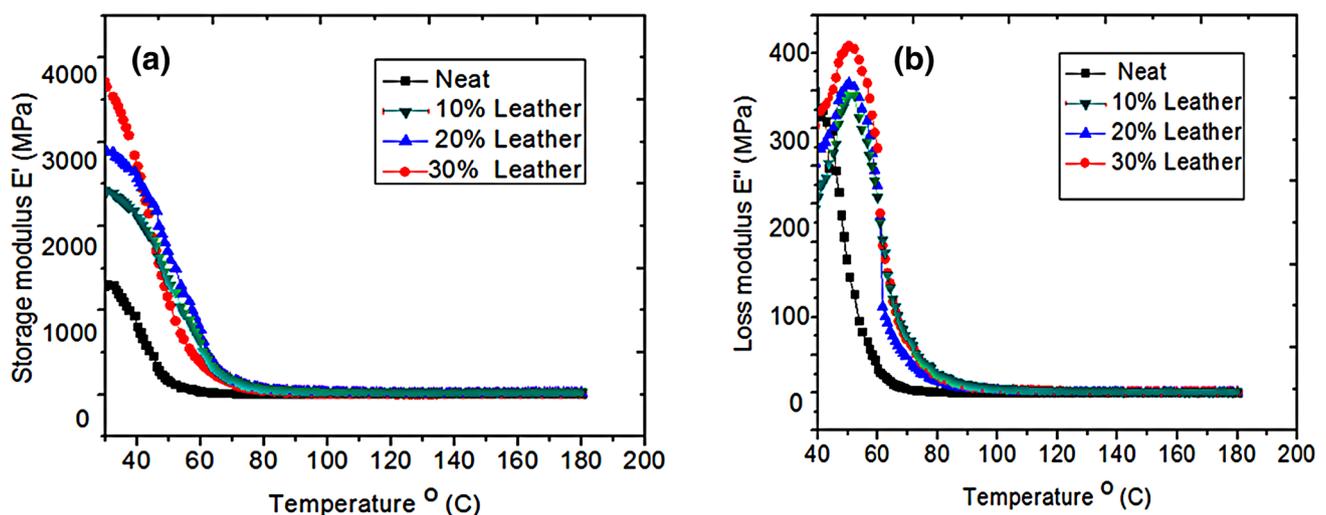


Fig. 5 Dynamic mechanical analysis for **a** the storage modulus and **b** loss modulus for neat epoxy and leather-reinforced composites

maximum heat dissipation was found at the temperature at which the value of E'' was maximized, representing the glass transition temperature (T_g) of the system [13]. The rapid rise in E'' in an order shows an increase in the polymer chains' free movements at higher temperatures due to a relaxation process that allows considerable amounts of motion along the chains, which is not possible below the T_g . It is also noted that the value of E'' increased proportionately with the amount of leather [14].

The dissipated energy of a material under a cyclic load is called damping. The potential of a material to dissipate or absorb energy is measured with the damping factor or tangent of the phase angle, $\text{Tan } \delta$. The change in the $\text{Tan } \delta$ values, measured over a range of temperatures, for the composites and neat epoxy is shown in Fig. 6a. In general, the $\text{Tan } \delta$ for any composite material may depend upon several factors, such as the matrix cracking leather-matrix interfaces, frictional resistance and interphase zones. The neat epoxy had the highest $\text{Tan } \delta$ value of the glass transition region. However, there was a decrease in the height of the $\text{Tan } \delta$ curve because of the increased leather component. The $\text{Tan } \delta$ was decreased because of the reduced energy-loss rate. Another reason could be the lesser degree of molecular displacement found during heating. The increased stiffness of the composite specimen would limit the degree of freedom in the polymer chain at an atomic level [15]. Because of the restricted molecular mobility, the increased stiffness of the reinforced composite would lower the $\text{Tan } \delta$ value of the material. Among the various leather loadings in the present work, the 30% leather-reinforced composites showed the lowest $\text{Tan } \delta$ values. This proves the effectiveness of the adhesion with the leather-matrix interface. The width of the $\text{Tan } \delta$ peak became broader for leather-reinforced epoxy composites.

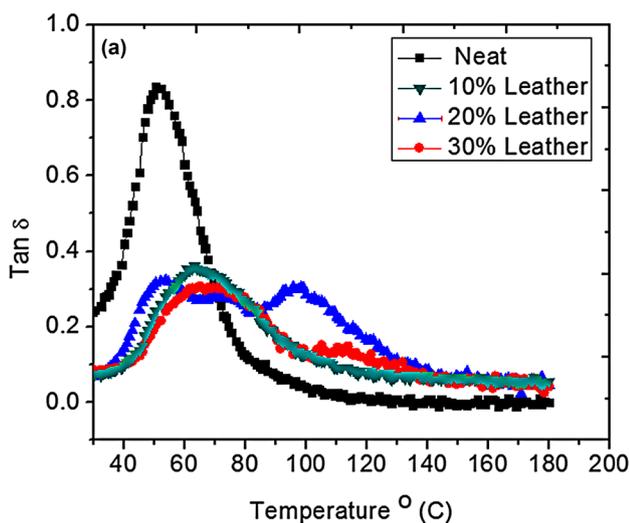


Fig. 6 a $\text{Tan } \delta$ for neat epoxy and leather-reinforced composites

This increase in the width of the $\text{Tan } \delta$ peak suggests the increased volume of the interface and an increase in the inhibition of relaxation processes in composites [16]. In polymer composites, the T_g value is determined with the peak of either the E'' or $\text{Tan } \delta$. It is seen that the T_g values of the E'' are more accurate than the $\text{Tan } \delta$. The highest value for the $\text{Tan } \delta$ peak, which was (0.83), was observed for neat epoxy, giving rise to more energy dissipation. On the other hand, a reduction in the $\text{Tan } \delta$ peak height was seen for all the composites. The peak height gradually reduced to 0.30 for the 30% loaded composite, representing a drastic 36.11% decrease (Table 5), thus indicating that both strong intermolecular and physical interactions are found, which contribute to more significant molecular restrictions at the interface and less energy dissipation.

5.5 Chemical resistance

Table 6 shows an increase in the weight gain of the composite samples for all the chemicals and solvents used in the study. This indicates that no disintegration of composites has occurred. Due to the hydrophilic properties of the leather, swelling of the composite samples occurred in water or nonaqueous solutions, which resulted in weight gain of the samples. The collagen groups present in leather, which are hydrophilic, were responsible for the increased hydrophilicity of the system [16].

Table 5 Peak height of $\text{Tan } \delta$ and T_g of E''

T_g values obtained from E'' curves and $\text{Tan } \delta$ peak height of composites		
Composites	T_g from E'' max curve (°C)	$\text{Tan } \delta$ peak height
Neat epoxy	42	0.83
10% Leather	55	0.37
20% Leather	56	0.32
30% Leather	58	0.30

Table 6 Chemical resistance of the leather-reinforced epoxy composite to chemical reagents of the optimized sample

Chemicals	Weight gain (%)
Toluene	4.7
Benzene	6.3
Carbon tetrachloride	3.3
8% Acetic acid	3.7
10% Hydrochloric acid	1.2
10% Sodium hydroxide	2.9
20% Sodium carbonate	0.6
Distilled water	1.8

6 Conclusion

This study showed that scrap leather can be used to fabricate composites based on epoxy. The mechanical strength of the composites increased with leather loading. SEM images showed excellent adhesion of the leather to the matrix. Thermal stability of the composites was found to be unique with a higher percentage of loading. DMA investigation demonstrated that the storage and loss modulus increased with an increase in leather per cent loading and a decrease in the $\tan \delta$ peak was seen. Composites exhibited excellent resistance towards acids, bases and solvents. We anticipated that these results would contribute to and help in utilizing leather-reinforced epoxy composites in the development of unique and cost-effective advanced composites possessing desirable stiffness, thermal stability and chemical resistance. These composites can be considered for applications in various fields such as automotive, tabletops, building, storage tanks, construction industries and aerospace.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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