Compression and fracture behavior of leather particulate reinforced polymer composites

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Abstract
Strategies are suggested for the waste utilization of industrial leather by preparing composites with epoxy and high-density polyethylene (HDPE). The addition of leather improves the average specific compression toughness of epoxy by 29%. The fracture surface analysis suggests the incorporation of leather microparticles leads to a transition of failure mode of epoxy from brittle to ductile. In addition, the dynamic strength of the leather/epoxy composite is found to be 69% higher than that of neat epoxy. However, no significant changes are observed when HDPE is infiltrated with leather. Apart from dispersing the leather particles directly in polymer, a novel strategy is presented here in which leather/HDPE microfibers are prepared and then used to reinforce the epoxy matrix. The specific compression modulus of this composite blend is 8% and 65% higher than epoxy and HDPE, respectively. Fractography is further carried out on the failed specimens to understand the failure mechanism in each composite. A change in the failure mode is observed when epoxy is reinforced either with leather particles or the microfiber. While the failure strength of the microfiber is found to be higher than epoxy, the strength of microfiber/epoxy interface is lower than that of epoxy.

1. Introduction

Processing of leather generates large quantities of solid waste, amounting up to 600 000 tons worldwide [1]. Inappropriate disposal of leather waste may lead to leaching of trivalent chromium present in leather into the Earth. Under suitable conditions, trivalent chromium oxidizes to form hexavalent chromium, which is carcinogenic and can have devastating effects if it comes in contact with humans [2]. One possible solution to this problem can be recycling through reuse and recovery of leather constituents or by burying and incineration. However, where restoration of constituents is a costly affair, burying degrades soil health, and incineration causes air pollution. Therefore, a simple and cost-effective way is to reuse the waste leather directly in some form, for example, to make useful products such as footwear, insulation material, board, etc by infiltrating polymers [3–6]. In this manner, we can take advantage of low density, recyclability, and renewability of leather particles, similar to the use of other bio-fillers like leather, rice husk, and pistachio shell [7, 8].

Now the question arises, which type of polymer is to be considered to reinforce with leather. Incorporation of leather particles in rubber polymers has been reported to improve its mechanical properties [3]. However, since, we are tackling vast amounts of waste, which is generated consistently every year, we need a polymer that is widely used and applicable in wide range of application areas. To this end, we have shortlisted two different types of polymers: thermoset epoxy and thermoplastic high-density polyethylene (HDPE). Owning to their low weight and tailorable mechanical, thermal, and electrical properties, reinforced epoxy composites are used in broader range of engineering applications [9]. Epoxy is the most popular thermoset polymer used in structural applications such as aircraft wings, helicopter rotors, and wind turbine blades [10]. Thermoplastic HDPE is
another such polymer due to its recyclability, moldability, low cost, low density, and low friction properties [11–13]. To name few, HDPE is used in boats, ballistic plates, and piping for fluid transfer [14].

Henceforth, in present work we report the procedure to prepare leather infiltrated composites with epoxy and HDPE matrix. Leather microparticles at 15 wt% are incorporated in the matrix, and the mechanical properties of the resulting composite under compressive loading are evaluated. Apart from dispersing the leather particles directly in polymer, a novel strategy is presented to prepare leather/HDPE microfibers. These microfibers are then used to reinforce the epoxy matrix to get a blended composite having the characteristics of both the thermoset epoxy and thermoplastic HDPE. Later on, fractographic analysis is performed on the broken test specimens to understand the failure mechanism of all five types of composite samples.

2. Materials and methods

2.1. Preparing the composites

Leather particles are first sieved in a mechanical sieve shaker (sieve size 20 μm to 1700 μm) to get fine leather microparticles. Leather particles of size less than 800 μm are then segregated and heated in an oven at 125 °C for 30 min to remove moisture. This is followed by the preparation of composite samples with epoxy (Trans Oceanic Chemical Pvt. Ltd India) by whisking 15 wt% of leather particles in bisphenol-A epoxy resin ER-099 SPL for 10 min. Epoxy polyamine hardener EH-100 is then added to this mixture at a ratio of 1:2 for hardener to resin and mixed thoroughly. The composite mixture is then filled in a rectangular mould and allowed to cure for 24 h at room temperature. After solidification, the composite brick is post-cured at 100 °C for 4 h. The leather/HDPE composite is prepared by mixing 15 wt% leather particles and HDPE pellets (UC Enterprises, India) in a three-zone (130 °C, 140 °C and 150 °C) twin-screw extruder to prepare a homogeneous mixture. The melting screw speed is set at 50 rpm. The obtained mixture is then supplied to an injection moulding machine at 6.37 bar and 230 °C to get rectangular samples. In order to process the blended composite, first the leather/HDPE microfiber is prepared by carefully extruding the 15 wt% leather/HDPE mixture from the circular opening of injection moulding die without filling any cavity. The microfiber is then affixed from edge to edge within a rectangular cavity with the help of an adhesive (see figure 1), and the cavity is then filled with epoxy matrix. The processed leather/HDPE-epoxy blended composite is then subjected to curing and post-curing procedures, as already discussed above. From the processed samples, square-prism test specimens with size 12.7 × 12.7 × 25.4 mm³ are cut for compression test as per ASTM D695-15 [15]. The blended composites are cut in such a way that the micro-fiber lies parallel to the longitudinal direction of the specimen (see figure 1) with each specimen having ~95 wt% of epoxy. In a similar manner, the neat epoxy and HDPE composites are processed, without infiltrating leather particles, and subjected to curing and post-curing reactions.

2.2. Characterization

The average density is calculated on MS105, Mettler Toledo, USA from at least 15 readings for each test specimen as per ASTM D792-07. The hardness of each sample is measured on a Vickers’s hardness tester (402MVD, Wilson Instruments) under a load of 200 grams applied for 10 s as per ASTM E384. Thirty-four readings are taken for each sample, and the average value with the standard deviation is evaluated. Compression tests are performed at crosshead...
speeds of 1 mm min$^{-1}$ and 50 mm min$^{-1}$ on a universal testing machine (UTM, Shimadzu Corp., Japan) as per ASTM D695-15. The contact faces of all the test specimens are lubricated with petroleum jelly to reduce friction and to avoid cracking of resin near the loaded ends. At least five specimens are tested at each test speed. High strain rate testing is conducted on an in-house built split Hopkinson pressure bar (SHPB) system. For this purpose, the dimensions of the sample are slightly different from those used at low-speed testing on UTM. The test specimens for dynamic testing on SHPB are in the form of cubes of side 12.7 mm as per ASTM D695-15. The cross-section of all the neat, as well as leather reinforced composites, are analysed using a scanning electron microscope (SEM, JEOL, JSM-6610LV, Japan) without the application of any conducting coating on samples. The failed test specimens are also viewed inside the SEM to get an idea about their failure mechanisms.

3. Results and discussion

3.1. Surface morphology, density, and hardness

Figure 2(a) shows the scanning electron micrographs of leather particles and the composites processed thereof. The variation in the particle size as a result of using particles less than 800 μm is clearly visible in figure 2(a). Figures 2(b)–(e) shows the cross-section of neat and leather modified composites. The cross-section of neat epoxy (figure 2(b)) appears rough while the cut section of HDPE is smooth and flat (figure 2(d)). The images of the cross-sections of leather particulate composites with epoxy (figure 2(c)) and HDPE (figure 2(e)) show the uniform dispersion of particles in the matrix. Figure 2(f) represents the SEM of the blended composite in which one can see, on careful observation, the presence of leather/HDPE microfiber completely surrounded by epoxy matrix.

Next, the physical and material properties of each composite in terms of density and hardness are evaluated, and the results are presented in figure 3. The density of epoxy decreases after the addition of leather particles (figure 3(a)), possibly because of an increase in the porosity level in leather/epoxy composite owing to large size particulates. However, the density of HDPE remains almost unaltered with the incorporation of leather particles. Due to the presence of epoxy in large quantity compared to HDPE, the density of blended composite is higher than that of HDPE (figure 3(a)) but below that of neat epoxy. The density measurements are followed by hardness testing (figure 3(b)) on each composite, except for the blend because of its inhomogeneous nature. The hardness of neat epoxy and its composite is higher than that of HDPE and leather/HDPE composite. This is because of the hard and brittle nature of epoxy than HDPE [16]. Since the indenter makes an indent on the surface of the sample, and we do not see much variation in the mean value of hardness of neat epoxy and HDPE after the incorporation of leather particles in them (figure 3(b)), it can be said that the leather particles are entirely wetted by both epoxy and HDPE. However, this is accompanied by large error bars, which is attributed to the considerable variation in the size of leather particles (<800 μm) used to prepare the composites.

3.2. Compression response

Figure 4 presents the average stress ($\sigma$) versus strain ($\varepsilon$) response of epoxy and leather/epoxy composite (figure 4(a)) and that of HDPE and leather/HDPE composite (figure 4(b)) under compressive loading at crosshead speeds of 1 and 50 mm min$^{-1}$. One can clearly distinguish between the $\sigma$–$\varepsilon$ curves for epoxy and
HDPE, there is clear indication of yielding in case of epoxy and its leather composite (figure 4(a)). However, such a phenomenon is missing in HDPE and leather/HDPE composite (figure 4(b)). As a result, the specific failure strength and failure strain for HDPE and leather/HDPE composite are not reported in figure 5 as the kink or load drop is not visible in their stress-strain plots. From the recorded data, various mechanical properties are calculated such as specific toughness (figure 5(a)), modulus of resilience (figure 5(b)), specific strength (figure 5(c)), failure strain (figure 5(d)), and specific modulus (figure 5(e)). For ease of comparison, the results for all mechanical properties are summarized in table 1.

It is observed that the average specific toughness (W/ρ) increases after the incorporation of leather micro-particles in epoxy (figure 5(a)). We see a 29% increase in the average specific toughness of epoxy from 21 kN-m/kg to 27 kN-m/kg on adding leather in epoxy. A similar trend has been observed when rubber microparticles were incorporated in epoxy, showing improved toughness [16–19]. However, as expected, an increase in toughness of epoxy leads to a decline in specific modulus (figure 5(e)) and specific failure strength (figure 5(c)). Neat epoxy shows
weak resistance to crack initiation and crack propagation compared to when it is reinforced with micro-fillers. Debonding of leather and yielding of the epoxy matrix is the possible toughening mechanism [20].

Compared to hard and brittle epoxy, HDPE is soft and ductile (see figure 3(b)), that is why the specific toughness of HDPE and its composite is relatively higher than neat epoxy and leather/epoxy composite (figure 5(a)). Where the

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Figure 5. Compression properties extracted from the stress-strain curves: (a) specific toughness, (b) modulus of resilience, (c) specific failure strength, (d) failure strain, and (e) specific modulus.
results for specific toughness of epoxy, HDPE, and their composites indicate the efficacy of dispersing leather micro-particles in polymer, the least toughness of blended composites (figure 5(a)) implies that leather particles are not efficient in energy dissipation when present in concentrated form as a leather/HDPE micro-fiber. Figures 5(c), (e) shows the effect of the inclusion of leather micro-particles on the specific failure strength and compression modulus. A decrease in both these properties is observed with the addition of leather particles. A similar trend has been reported by other researchers [21, 22] and is attributed to the softness of leather particles. It is noteworthy that the difference in the standard deviation of the failure strength of epoxy and its composite has reduced (figure 5(c)) [23]. The decrease in the compression modulus of epoxy (figure 5(e)) on adding leather is attributed to the lower modulus of leather particles, which leads to a decline in the compression modulus of the overall composite. Whereas, no significant decrease is observed in the case of HDPE and leather/HDPE as HDPE is already softer compared to epoxy (figure 3(b)) [24]. The decrease in failure strength (figure 5(c)), in case of epoxy and its micro-composite, could be because of the irregularity in the shape of leather micro-particles when compared with fibers such as carbon, glass, etc that have a uniform cross-section area and high aspect ratio. Thus, the capability of such fillers to support the stress that is transmitted through the matrix decreases radically. Due to reduced stress transfer in particulate filled composites at filler/polymer interface, a discontinuity is created, which generates a weaker structure as discontinuities lead to stress concentration. Micro-voids between fillers and matrix are caused due to weak interfacial bonding, which hinders stress propagation [15]. The presence of leather micro-particles leads to the formation of defects, i.e., micro-cracks, which spread when acted upon by external loading. This might lead to a decrease in modulus and failure strength of the composite [25]. Moreover, the failure strain decreases with the addition of leather particles, and a further decrease is seen in the case of the blend (figure 5(d)).

However, the presence of leather micro-particles in concentrated form, rather than dispersed form, shows a different trend. The specific modulus of blended composite is 8% and 65% higher than that of neat epoxy and HDPE, respectively (see figure 5(e)). Therefore, we can say that the toughness of a polymer can be increased by reinforcing it with dispersed particles, while the modulus or stiffness can be improved when the same reinforcing filler is present in the concentrated form [26].

The increase in the specific compression modulus of epoxy (figure 5(e)) with an increase in the loading speed is attributed to the viscoelastic behavior of epoxy. Another reason could be because of the reduction in molecular mobility of polymer chains, which results in higher stiffness [27]. However, such a phenomenon is missing in HDPE and hence no change in modulus with changing crosshead speeds. The failure strain decreases for all the samples with increasing strain rate (figure 5(d)) because there is not enough time for polymer chains in epoxy matrix to follow instant changes in strain, which results in a decrease in mobility of the polymer chains. A decline is observed in the specific failure strength with an increase in strain rate (figure 5(c)), while no significant change is observed in specific toughness (figure 5(a)).

Next, the dynamic compression response (figure 6) of composites is evaluated on an in-house built SHPB setup. The signals received from strain gauges mounted on incident and transmission bar are processed to plot the final true stress-true strain plot. The peak strength of the leather/epoxy composite is 69% higher in comparison to epoxy, but only marginal improvement is observed for HDPE and HDPE/leather (figure 6). Accordingly, the failure strain of epoxy and leather/epoxy composite decreases drastically compared to their values at low-speed testing (see figure 5(d)).
3.3. Fractography

The compression response of all the five types of samples viz neat epoxy, leather/epoxy, HDPE, leather/HDPE, and blended composite are presented in figure 7 at different points of time during the compression testing. To get a
realistic experience of the compression behavior of various samples, images are taken at different time intervals during the testing, as shown in figure 7(a). These images are then related to their respective locations on the stress-strain plot given in figures 7(b), (c). Where stage-I correspond to the original configuration of the test specimen, stage-V shows the image of the failed specimen. In-between these two stages are stage-II and III pertaining to yielding, and stage-IV representing plastic deformation. Bulging of all the samples occur with applied load from stage I to stage III.

The failed test specimens are further examined under optical and scanning electron microscopes (figures 8, 9) for a better understanding of the mechanisms behind the failure of each type of composite. Brittle fracture of neat epoxy analogous to sharp knife cuts can be seen clearly in figure 8(a) (arrows marked). The cracks are visible on all the surfaces, as well as the edges of neat epoxy samples (figure 8(a)). In contrast, the surface of the epoxy modified with leather micro-particles appears rough with blunt cracks, as marked by arrows in figure 8(b). Where epoxy depicts weak resistance to crack initiation and propagation and fails catastrophically [20], the presence of leather micro-particles leads to debonding and shear yielding [19] at the interface of inclusion and matrix. In leather/epoxy composite, the failure is not catastrophic but progresses slowly. Crack initiation and crack propagation occur only on the surface of the leather/epoxy composite (see figure 6(a), leather/epoxy). No visible cracks are
noticed along the edges of the sample (figure 8(b)). Also, the crack in leather/epoxy composite is roughly aligned at an angle of 45° from the axis of loading (see figure 8(b)). Such a failure is the characteristic of ductile materials, which under the action of an applied normal load, fail in shearing. Moreover, the leather particles are found to instil a bridging kind of behavior in epoxy (encircled in figure 8(b)). Hence, there is a drastic change in the mode of failure from brittle to ductile when it is reinforced with leather micro-particles.

Where the mode of failure of neat epoxy changes from brittle to ductile failure on the addition of leather particles in epoxy (figure 8), no such change can be seen in the case of HDPE and leather/HDPE composite (figure 9). Both these materials undergo a change in shape, and no visible cracks have been identified. In other words, there is only shape change occurring in these materials with an expansion in volume of the samples.

The failure behavior of the blended composite of leather/HDPE-epoxy is discussed next and is demonstrated in figure 10. Visible inspection of the blended composite indicates a drastic change in the failure mode of neat epoxy. On comparing figure 10 with figure 8, one can easily distinguish that the catastrophically brittle failure of neat epoxy is suppressed when epoxy is reinforced with leather/HDPE micro-fiber. Failure takes place on the surface of the blended composite (figure 10) and not along edges or on corners (stress concentration sites), which was the case with neat epoxy samples (figure 8(a)). Two observations can be made on investigating the failure images of the blended composite. One is that the micro-fiber remains intact (figure 10(c)), with no visible crack in fiber (figure 10(d)). This implies that the strength of the microfiber is higher than the failure strength of neat epoxy. The second observation is that crack initiation in blended composite possibly starts at the interface of micro-fiber and the surrounding epoxy (figure 10(c)). Then the crack propagates outward into the epoxy matrix leading to failure of the composite. This is confirmed from the fact that after the completion of the compression test, epoxy recovers to some extent, but the fiber reinforcement does not (figure 10(b)). Hence, we can state that the interfacial strength of the leather/HDPE micro-fiber with the surrounding epoxy is lower than the failure strength of epoxy itself.

4. Conclusion

Epoxy matrix is versatile when it comes to mechanical, chemical, and physical properties. It has been used extensively in the industry as coatings, adhesives, laminates, etc. However, when it comes to structural application, epoxy is either brittle or notch sensitive or both. Hence focus needs to be shifted towards improving the toughness of epoxy so that it can be used for more comprehensive structural applications. In this study, an effort is made to improve the specific toughness of epoxy while maintaining other properties by combining it with waste leather micro-particles. The SEM analysis and visual analysis show that leather microparticles are effectively embedded and uniformly distributed in the epoxy matrix. The fracture surface analysis suggests the incorporation of leather microparticles leads to the transition from brittle to a ductile mode of failure of epoxy. Although, no significant changes were observed when it comes to HDPE and leather/HDPE composite. The
decline in specific compressive modulus after the inclusion of leather particles in polymer is countered by a novel strategy in which leather/HDPE micro-fibers are prepared and used to reinforced epoxy to get a blended composite. Further, the failure strength of the leather/epoxy composite is higher than that of neat epoxy by as much as 69%. The insights of this study will help the design engineers to consider leather particles in structural composites and will surely help in tackling the huge problem of leather waste.

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References

[1] Garcia N G et al 2013 Natural rubber/leather waste composite foam: a new eco-friendly material and recycling approach J. Appl. Polym. Sci. 132 41636
[2] El-Sabbagh Salwa H and Mohamed Ola A 2011 Recycling of chrome-tanned leather waste in acrylonitrile butadiene rubber J. Appl. Polym. Sci. 121 979–88
[3] Rajaram J, Rajnikanth B and Gnanamani A 2009 Preparation, characterization and application of leather particulate-polymer composites (LPPCs) J. Polym. Environ. 17 181–6
[4] Senthil R, Hemalatha T, Kumar B S, Uma T S, Das B N and Sastry T P 2015 Recycling of finished leather wastes: a novel approach Clean Technol. Environ. Policy 17 187–97
[5] Sundar V, J Raghavaran J, Muralidharan C and Mandal A B 2011 Recovery and utilization of chromium-tanned proteinous wastes of leather making: a review Crit. Rev. Environ. Sci. Technol. 41 2048–75
[6] Senthil R, Hemalatha T, Manikandan R, Das B N and Sastry T P 2015 Leather boards from buffing dust: a novel perspective Clean Technol. Environ. Policy 17 571–6
[7] Karaqağ, Başçalı 2014 Use of ground pistachio shell as alternative filler in natural rubber/styrene–butadiene rubber-based rubber compounds Polym. Compos. 35 245–52
[8] Sae-Oui P, Rakdee C and Thanmathorn P 2002 Use of rice husk ash as filler in natural rubber vulcanizates: in comparison with other commercial fillers J. Appl. Polym. Sci. 83 2485–93
[9] Gabr M H, Elrahman A M, Okubo K and Fujii T 2010 A study on mechanical properties of bacterial cellulose/epoxy reinforced by plain woven carbon fiber modified with liquid rubber Compos. Part A Appl. Sci. Manuf. 41 1263–71
[10] Mishnaevsky L, Branner K, Petersen H N, Beauson J, McGugan M and Sørensen B F 2017 Materials for wind turbine blades: an overview Materials (Basel) 10 1–24
[11] Khalaf M N 2015 Mechanical properties of filled high density polyethylene J. Saudi Chem. Soc. 19 88–91
[12] Herrera-Franco P, Valadez-Gonzalez A and Cervantes-Uc M 1997 Development and characterization of a HDPE-sand-natural fiber composite Compos. Part B Eng. 28 331–43
[13] Fu Q and Wang G 1992 Polyethylene toughened by rigid inorganic particles Polym. Eng. Sci. 32 94–7
[14] Patrick I 2002 Use of composite pipe materials in the transportation of natural gas INEL Field Work Proposal 02-00992 Idaho National Engineering and Environmental Laboratory Idaho Falls, Idaho 4340–70 64 (https://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.163.1183&rep=rep1&type=pdf)
[15] Shadlou S, Ahmadi-Moghdam B and Tabarir F 2014 The effect of strain-rate on the tensile and compressive behavior of graphene reinforced epoxy/nanocomposites Mater. Des. 59 439–77
[16] Unnikrishnan K P and Thachil E T 2006 Toughening of epoxy resins Des. Monomers Polym. 9 129–52
[17] Jayan J S, Saritha A and Joseph K 2018 Innovative materials of this era for toughening the epoxy matrix: a review Polym. Compos. 39 E1959–86
[18] Giannakopoulos G, Massania K and Taylor A C 2011 Toughening of epoxy using core–shell particles J. Mater. Sci. 46 327–38
[19] Tang L C, Wang X, Wan Y J, Bin Wu L, Jiang J X and Lai G Q 2013 Mechanical properties and fracture behaviors of epoxy composites with multi-scale rubber particles Mater. Chem. Phys. 141 333–42
[20] Kimloch A J, Shaw S I and Huston D L 1983 Deformation and fracture behaviour of a rubber-toughened epoxy. II. Failure criteria Polymer (Guildf). 24 1355–63
[21] Tang L C et al 2013 Fracture toughness and electrical conductivity of epoxy composites filled with carbon nanotubes and spherical particles Compos. Part A Appl. Sci. Manuf. 45 95–101
[22] Sobyh M S and Tammam M T 2010 The influence of fiber length and concentration on the physical properties of wheat husk fibers rubber composites Int. J. Polym. Sci. 2010 1–8
[23] Zhang G, Rasheva Z, Karger-Kocsis J and Burkhardt T 2011 Synergetic role of nanoparticles and micro-scale short carbon fibers on the mechanical properties of epoxy resin Express Polym. Lett. 5 859–72
[24] Kokta B V, Raj R G and Daneault C 1989 Use of wood flax as filler in polypropylene: studies on mechanical properties Polym. Plast. Technol. Eng. 28 247–59
[25] Valaśek P 2015 Polymeric microparticles composites with waste EPDM rubber powder Agron. Res. 13 723–31 (https://pdfs.semanticscholar.org/8ff0/041eb5b771812947d37f688d4813b06.pdf)
[26] Fourquet-Bandeira C, Montoro S R and Brooks T 2016 Thermoset-Thermoplastic Nanostructured Blends In Design and Applications of Nanostructured Polymer Blends and Nanocomposite Systems (Norwich, New York: Elsevier Inc)
[27] Okóli O I 2001 The effects of strain rate and failure modes on the failure energy of fibre reinforced composites Compos. Struct. 54 299–303