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Investigations of structural, chemical and physical properties of natural lac and its reinforced composites

Sukhvir Singh[a]*, Vandana Singh[b] & Ashish Kumar Gupta[a]
[a]CSIR- National Physical Laboratory, New Delhi 110 012, India
[b]National Museum, Janpath, New Delhi 110 001, India

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Natural lac resin is secreted by the small parasitic insect Kerria Lacca on various host trees in India. It has been conventionally used as filling, protective, adhesive, binder and insulating material. Cultivated by tribal people for various applications, the earliest popularly known reference to its use is found in the Mahabharata epic. Because of the imminent danger of environmental degradation, mankind is now veering towards a refreshing global awareness of the need to use, natural products because of their organic, non-toxic and biodegradable nature. This way, the present study is focused to understand the physical, structural and chemical properties of these natural lac and its applied form chapadi (a mixture of lac and sand), which has been used, for more than 500 years, as an adhesive and filling material by traditional Swordsmiths in Rajasthan (India). In addition, new lac-based composites reinforced with carbon nanotubes and carbon fibres have been synthesised and studied for their structural and physical properties. Surface morphology and elemental composition of as synthesized samples have been carried out by scanning electron microscope (SEM) and energy dispersive spectrometer (EDS). FTIR spectra have been recorded in order to identify the organic functional group. Samples of CNTs and carbon fibre reinforced with pure lac have been found to be better adhesives. The study aims to understand the nature of these reinforced composites as a new material that can be used for various applications in future.

Keywords: Natural lac, Chapadi, Multiwall carbon nanotubes, Carbon-fibre-reinforced composites, Strength

1 Introduction

Lac is a natural resin product with interesting properties and an exceptional versatility. It is the only known commercial resin of animal origin. The material forms a dense secretion on the branches of host plants infested by the insects (Fig. 1(a)) and, when harvested in this form, it is referred to as stick lac[1]. After cleaning, the semi-refined material is known as seedlac and, with subsequent refining processes, it becomes a purified commercial resin, known as shellac. The most common and most widely occurring species of lac insect in India, Thailand and other parts of Southeast Asia is Laccifer lacca (Kerr). These produce the bulk of commercial lac and are found on various host trees[2].

The Vedas provide a great deal of information on the traditional aspects of this natural product which has been used for centuries for a variety of purposes, such as coating (wood finish), skin cosmetic, decorative inlay material and dyes. It has also been used as adhesives in bonding mica splitting to form mica board and in abrasives. It is characterized by high adhesive strength, and high plasticity. Products created from lac can meet the crucial requirements of environmental protection, because shellac presents unique characteristics, as non-toxicity, physiologically harmless and listed as GRAS (Generally Recognized as Safe) by the FDA (Food and Drug Administration). One such lac-based adhesive, locally known as chapadi, has been used by traditional swordsmiths of Rajasthan (India) for fixing sword blades for centuries (Fig. 1(b,c)). According to smiths, chapadi is a mixture of lac and sand river and its adhesive properties makes it very useful for bonding metals.

Lac is a natural material with a complex mixture of esters and polyesters of polyhydroxy acids. The molecular structure of the ingredients was analysed and revised several times until the structure of the main components, aleuritic acid and shellolic acid, was clarified[3]. In later studies, butolic acid and other sesquiterpenic acids, related to shellolic acid, were identified as further components of the lac resin[4-8]. Besides the individual acids, also several esters have been identified[9]. These findings have been confirmed and further specified by modern analytical methods, such as liquid and gas chromatography or combined

*Corresponding author (E-mail: sukhvirster@gmail.com)

pyrolysis and mass spectrometry[10-14]. However, in spite of all this attention, the composition of lac is still not completely understood because of the highly variable composition depending on its origin and the type of refining.

In the present work, pure lac and chapadi were characterized by FTIR and HPLC analysis, in order to identify the organic nature of the material. Efforts have also been devoted to synthesizing reinforced lac with modern materials, such as carbon fibres and carbon nanotubes. They were also characterized to observe their properties, including density, hardness, stress-strain behaviour and microstructural characteristics. The overall aim of this study was to develop new composite materials that can perform better as adhesives and replace the existing synthetic resins.

2 Specimen Preparations

2.1 Preparation of lac sample

The raw lac obtained from the tree were grounded into powder form and poured into a clean die with the internal dimensions 48 mm × 15 mm × 2.5 mm and a die of dimension 13 mm × 13 mm × 3 mm . Then, at 90 °C, the die was closed and a load of 4 kg was applied. After 15 h, the die was cooled to room temperature and the samples were collected in the shape of solid bars. The images of the lac in all the cited process can be seen in Fig. 2(a-d).

2.2 Preparation of Chapadi sample

Chapadi block, as received from traditional swordsmiths, is shown in Fig. 3(a). The block was further reduced into small pieces (Fig. 3(a)) which were then cut, grounded and polished to the size of 48 × 15 × 2.5 mm and 8 × 4 × 3 mm using cutting, grinding and polishing machines. A small piece taken from the chapadi sample was used to investigate surface morphology and the elemental compositional analysis.

2.3 Preparation of carbon nanotubes-reinforced lac (CNT-RL) composite sample

A carbon nanotube (CNT) is a tube-shaped material, made of carbon with a diameter that measures on the nanometre scale. CNTs are

Fig. 1 — (a) Twigs fully encrusted with lac, (b) chapadi and (c) attaching a sword blade to the hilt with softened chapadi.

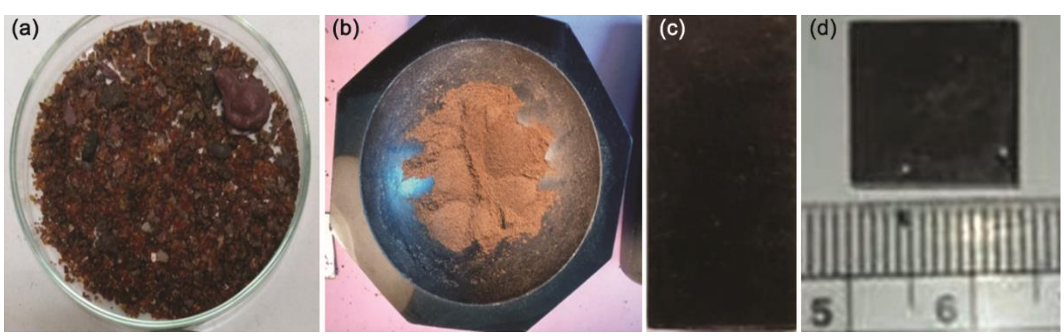

Fig. 2 — Steps of the sample preparation (a) raw lac encrustations, (b) powder of lac encrustation and (c, d) solid bar of samples of lac obtained from die.

essentially formed from graphite sheet. The name is derived from their long and hollow structure with walls formed by one atom thick sheets of carbon, called graphene. CNT are the strongest, most flexible and stiffest materials discovered in terms of tensile and elastic modulus. The hardness (152b Gpa) and bulk modulus (462-546 Gpa) of CNT are greater than diamond, which is considered the hardest material.

A few grams of pure lac were ground in the mortar and pestle with 2% of CNTs procured from M/s Alfa Aiser. After proper mixing of the seed lac and CNTs, the same procedure was followed to prepare the sample of pure lac. The final shape and size of the sample after reinforcement with CNTs is shown in Fig. 4(b). The dimensions of the CNT- reinforced lac sample are 48 mm × 15 mm × 2.5 mm and 8 mm × 4 mm × 3 mm. Figure 4(a) depicts a SEM image of CNTs used for the reinforcement of the lac.

2.4 Preparation of carbon fibre-reinforced lac (CF-RL) composite sample

Carbon fibres (CF) or graphite fibres are about 5–10 micrometres in diameter and composed mostly of carbon atoms. The properties of CFs, such as high stiffness, high tensile strength, low weight, high chemical resistance, high temperature tolerance and low thermal expansion, make them very popular in aerospace, civil engineering, military, etc. However, they are relatively expensive when compared with similar fibres, such as glass or plastic fibres.

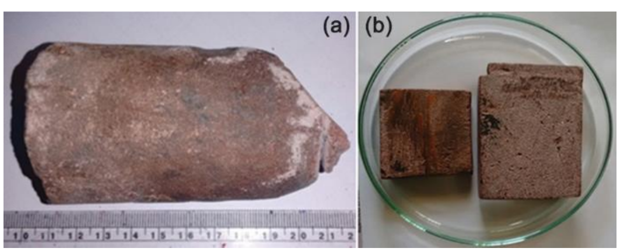

Fig. 3 — (a) Sample of chapadi as collected from smiths and (b) pieces cut out from the chapadi sample for the analysis.

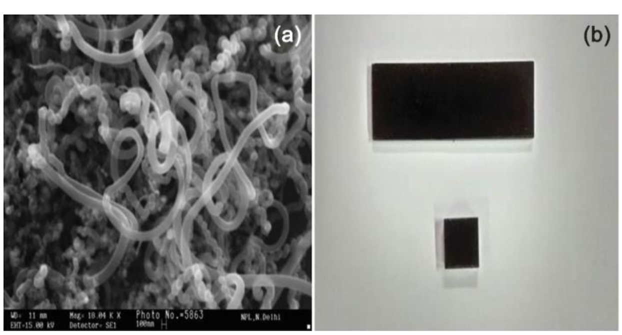

Fig. 4 — (a) SEM image of carbon nanotubes and (b) multiwall carbon nanotubes (MWCNT-RL) reinforced with lac sample.

CFs is usually combined with other materials to form composites. When combined with a plastic resin and wound or moulded, carbon-fibre-reinforced polymer is formed. It has a very high strength-to-weight ratio and is extremely rigid although somewhat brittle. Carbon fibres also form composites with other materials, such as graphite, to form carbon-carbon composites, which have very high heat tolerance[15]. About 90% of CFs produced are made from polyacrylonitrile (PAN) and the remaining 10% are made from rayon or petroleum pitch. These materials are organic polymers, characterized by long strings of molecules bound together by carbon atoms[16]. The dimensions of carbon fibre-reinforced lac for the bigger sample were 48 mm × 15 mm × 2.5 mm and for the smaller sample were 13 mm × 13 mm × 3 mm (Fig. 5).

3 Experimental

Surface morphology of pure lac and chapadi was carried out by SEM, using a Ziess EVOMA10 at 20 kV. The elemental composition of the samples was analysed by energy dispersive spectrometer (EDS) attached to the SEM. FTIR spectra were recorded in attenuated total reflectance (ATR) mode in the 400 – 4000 cm^{-1} wave range, using an Agilent FTIR spectrometer to identify the organic functional group present in the material. High performance liquid chromatography (HPLC) analysis was done on the pure lac sample using a HPLC-UV detector (220 nm). In HPLC analysis, acetonitrile/water was used as the mobile phase, whereas a C-18 reversed-phase (RP) column was used as the stationary phase. An aliquot of the pure lac samples was dissolved in methanol (30 mg/10 mL), and further diluted as per the requirement of the analysis. The hardness of the pure lac sample was measured using the Vickers Hardness method and the density of the sample was determined by the Archimedes principle.

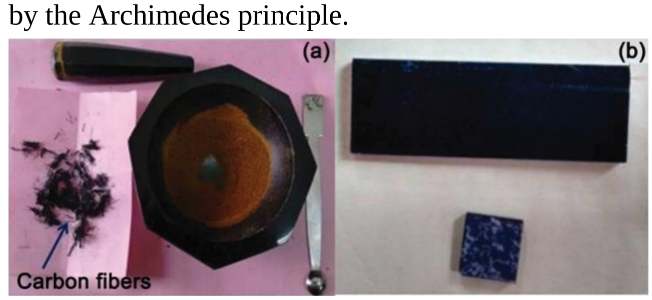

Fig. 5 — (a) Grinding process of pure lac with carbon fibres and (b) carbon fibre-reinforced lac composite sample.

The compressive strength of all four samples with the dimensions of 13 × 13 ×3 mm was measured using a universal 4411 INSTRON testing machine. For bending/flexural strength measurement, a new lac sample was prepared by filling a clean die with the internal dimensions 48 cm × 15 mm × 2.5 mm with lac powder. The die was then closed and a load of 4 kg was applied at 90 °C. After 15 h, the die was cooled to room temperature and the samples were collected in the shape of a solid bar. The same procedure was followed to make the composites reinforced with carbon fibre and carbon nanotube. However, the chapadi sample was made by cutting, grinding and polishing to achieve the size of 48 cm × 15 mm × 2.5 mm.

4 Results and Discussion

4.1 SEM/EDS analysis

The surface morphology of the pure lac sample, observed by SEM, revealed a smooth surface without any pores or micro-cracks (Fig. 6(a)). The elemental composition of the corresponding sample area analysed with EDS showed the presence of only carbon and oxygen, as can be seen in Fig. 6(b).

The surface of the chapadi sample when scanned with SEM revealed a large number of nano and micro sized pores on the surface (Fig. 7). These pores may have been introduced during the process of mixing sand river and small pieces of crushed glass in the pure lac sample, as noted by local smiths. It is expected that swordsmiths may have reinforced the matrix of the pure lac sample with river sand and glass intentionally in order to achieve a high strength and light weight material. The presence of a large number of pores in the lac matrix resulted in brittleness of the chapadi sample. EDS analysis (Fig. 7) depicts the presence of Mg, Al, Si, Ca and Fe apart from the C and O, which is due to the presence of river sand and small pieces of crushed glass.

A SEM image of the pure lac reinforced with 2% MWCNTs' composite sample is shown in Fig. 8. The SEM image revealed the reinforcement of MWCNTs in the pure lac as depicted in the high magnification images of the sample. Apart from the existence of MWCNTs on the sample surface, some crater like pits were also found. The surface morphology of the pure lac sample reinforced with 2% carbon fibre clearly revealed reinforcement of carbon fibres in the pure lac (Fig. 8). The top surface of the sample does not reveal any pores and pits on the surface. However the carbon fibres are found to be well aligned in a zig-zag manner which makes the surface appear very compact.

4.2 FTIR analysis of raw lac

IR spectroscopy can be used to enhance the understanding of degradation processes, causes and rates of change. This knowledge can, in turn, aids in the development of conservation strategies to extend the lifetime of an object. FTIR spectra of the pure lac

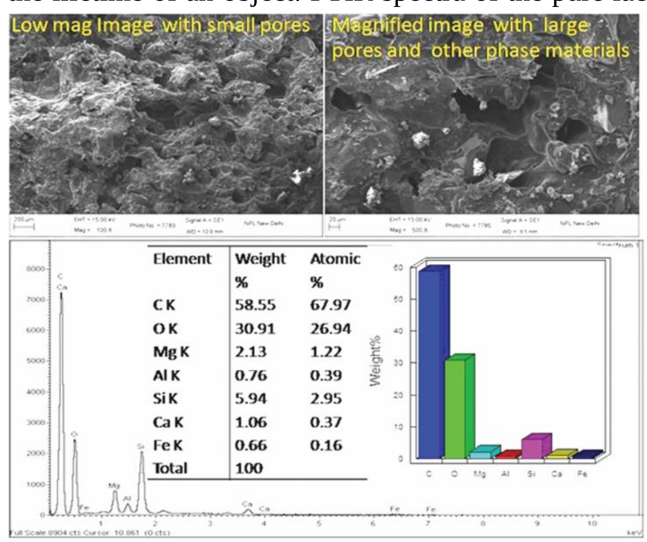

Fig. 7 — Low and high magnification SEM images of chapadi sample showing pores of varied sizes on the surface of the sample and EDS spectra of the corresponding area.

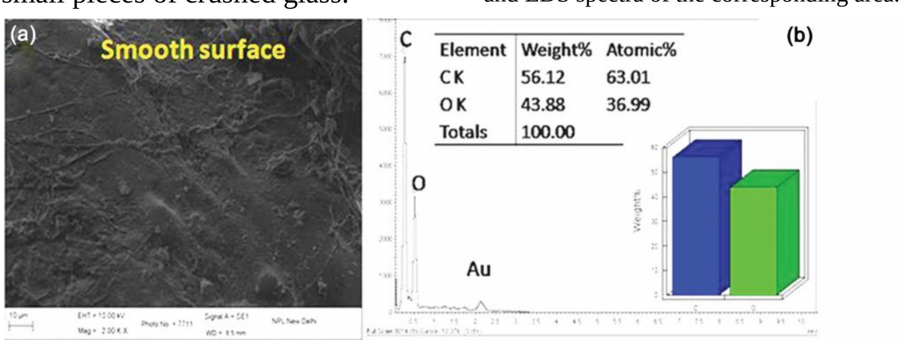

Fig. 6 – (a) SEM image and (b) EDS spectra of corresponding area pure lac sample.

sample (Fig. 9(a)) showed the dominant characteristic signatures of O-H, C-H stretch (2915 cm^{-1} may be alkane), C=O stretch (1709 cm^{-1} may be carbonyl) and C-O stretch (1033 cm^{-1} may be ester) for which transmittance is low (or absorbance is high). The pure lac sample may comprise these functional groups.

4.3 HPLC analysis of raw lac

The HPLC of the pure lac showed retention time (RT) against intensity data (Fig. 9(b)). Two major peaks were identified in the UV chromatogram, which appeared around 1 and 2.30 minutes' RT. By looking at literature data and analysis, these peaks are indicative of mono-ene alkylphenols which are largely identified in red lacquer sap[17].

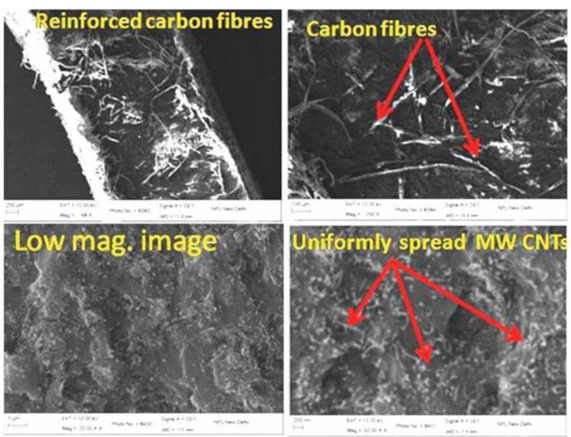

Fig. 8 — Low and high magnification SEM images of pure lac reinforced with the carbon fibres and carbon nano tubes.

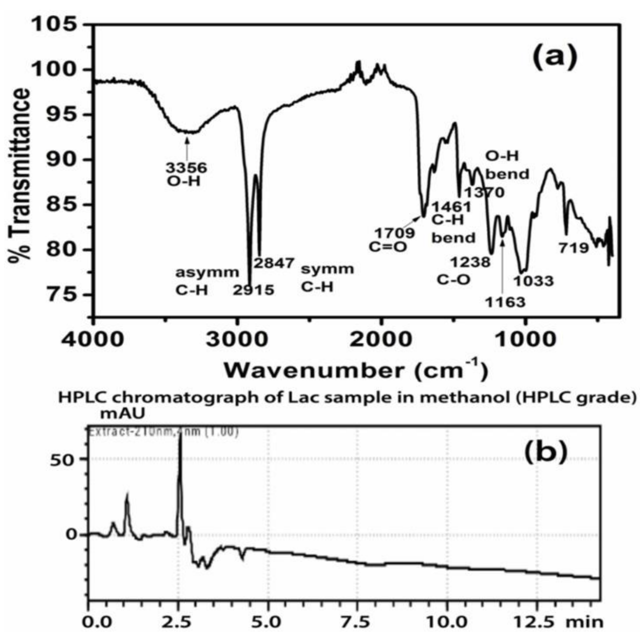

Fig. 9 — (a) FTIR spectra and (b) HPLC chromatogram of pure lac sample.

4.4 Density and hardness measurements

Density represents the degree of compactness of a material measured in mass per unit of volume. Hardness and density of pure lac, chapadi, CNT-RL and CF-RL composite samples were measured and are listed in Table 1. It is evident that CF-RL composite has the highest hardness value (19.5 Hv) and lowest density (1.191 g/cc) as compared to the pure lac, chapadi and MWCNT-RL. It is clear that pure lac reinforced with carbon fibres (2% wt) is found to be the best amongst all four materials as it provides a light weight and high strength adhesive material. It's important to mention here that chapadi, which is still being used as an adhesive by swordsmiths to fix sword blades, is heavy in weight and brittle in nature. It breaks easily when the sword is struck with shield, as evident from surface morphology of the chapadi sample shown in Fig. 7.

4.5 Compressive and flexural strengths

Compressive strength is one of the essential requirements of composite materials, because compressive forces are often encountered during self-life of any application. Therefore, compressive/ flexural strength of composite materials should be sufficient enough to avoid any form of structural damage. The compressive/flexural strength of composite materials depends mainly on two factors: (i) microstructure and (ii) density.

Figure 10(a-d) shows graphs for the compressive load and displacement/extension of pure lac, chapadi, carbon fibre reinforced pure lac and MWCNTs reinforced pure lac composite samples. In the graph for the chapadi sample, it can be observed that the maximum extension is about 0.12 mm only at maximum compressive load of about 250 N. It is also noticed that the chapadi sample breaks suddenly after 0.12 mm of extension, which indicates the brittle nature of the chapadi sample. This is also confirmed from the SEM images (Fig. 7), revealing the presence of nano and micro pores responsible for making the

Table 1 — Details of hardness and the density of the samples.

S. No.	Sample details	Hardness	Density
1	Pure lac	19.1 Hv	1.610 g/cc
2	River sand + Pure lac	***	1.824 g/cc
3	2 % MWCNTs reinforced with pure lac	18.5 Hv	1.329 g/cc
4	2 % Carbon fiber reinforced with pure lac	19.5 Hv	1.191 g/cc

*** Vickers hardness of this sample could not be determined as the surface of the sample was not smooth.

materials porous in nature. There is no deformation area in the graph (Fig. 10 (a)). However, sufficient deformation areas exist in other samples of pure lac, CFs reinforced pure lac and MWCNTs reinforced pure lac composites. This also indicates that the chapadi sample presents brittle nature. Reinforcing MWCNTs and CFs shows increase in compressive strength may be due to energy absorbed in fibre pull out during the measurement of flexural and compressive strength.

On the other hand, pure lac reinforced with CFs and pure lac reinforced with MWCNTs can bear a compressive load of 450 N and 600 N and an extension of 0.55 mm and 0.70 mm, respectively, and does not show any sudden breakage as depicted in Fig. 10(c-d). From the study, it is observed that pure lac reinforced with CF and MWCNTs are found to be better material to bear greater loads with higher extension.

The bending properties also known as flexural strength of all the four samples was also tested by a three-point flexural test (Fig. 11). As can be seen from the graph in Fig. 11(a), the maximum load supported by the rectangular chapadi sample in the 3 point flexural test was 55 N, with the extension of 0.18 mm only. The sample shows a very high level of brittleness as there is a sudden decrease in load after breakage. The area under the curve of load versus extension is much lower than for pure lac and lac reinforced with carbon fibres and MWCNTs. The flexural strength of the chapadi sample is very low, because it stored very little energy.

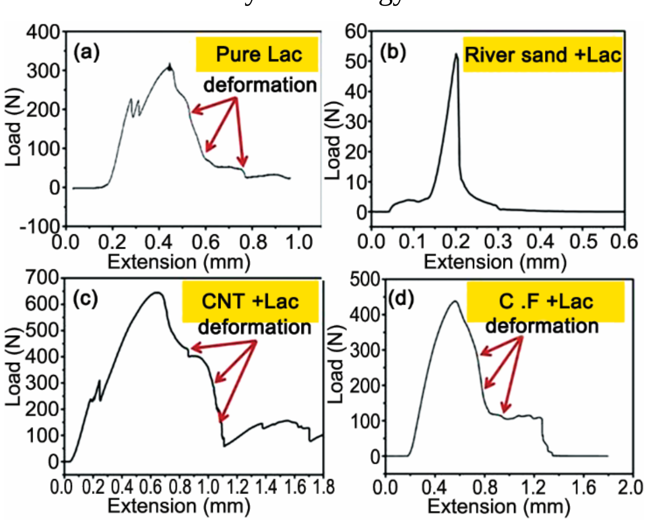

Fig. 10 — Compressive load (*N*) versus displacement/extension (mm) curve for (a) pure lac, (b) chapadi, (c) CFs reinforced with lac and (d) CNTs reinforced with lac.

4.6 Advantages of lac-based resins over epoxy resin

Natural resin from lac has an advantage over synthetic resin, because it is non-toxic and biodegradable. Figure 12(a) represents commercially available epoxy resins used for gluing stacks (pieces) of substrate material for cross-sectional specimen preparation for transmission electron microscopy (TEM) to study microstructural details at the interface of films and substrate. For example, epofix resin is developed especially for mounting of irregularly-shaped specimens, where low shrinkage and good mechanical properties in the cured state are required. This study plays a key role in deciding these materials for suitable electronic devices and various sensors. After curing, epofix can be cut, ground, polished and grilled to prepare electron transparent cross-TEM specimen. It's important to mention here that epofix resin is not safe from a health point of view, because it contains Bisphenol-A-Diglycidylether, which is (i) irritating to eyes and skin and (ii) may cause sensitization by skin contact. Furthermore, epofix hardener contains tri-ethylenetetramine which causes burns and may cause sensitization by skin contact. Details of toxic components presented in the epofix are shown in Fig. 12(a). Suitable medical precautions should be taken when such synthetic resins are used for TEM specimen preparation.

Based on investigation carried out during this study, lac is suggested as an alternative suitable adhesive that can be a good replacement to the commercially available synthetic resin. FTIR and HPLC studies of pure lac did not reveal the presence

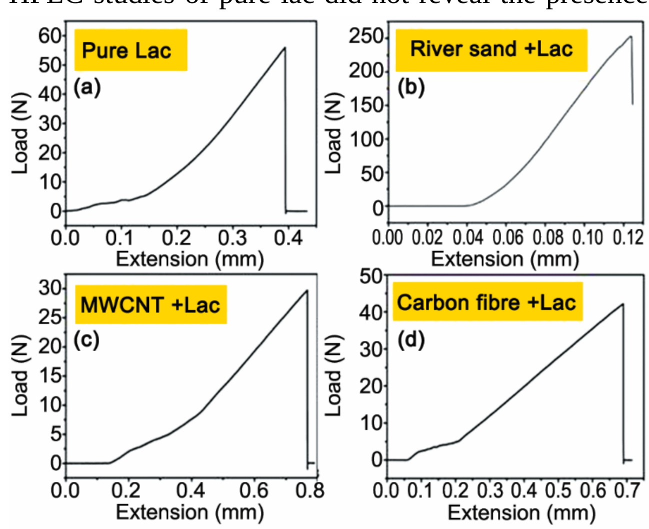

Fig. 11 — Flexural load versus displacement/extension curve for (a) pure lac sample, (b) chapadi sample (river sand mixed with pure lac), (c) carbon fibre reinforced with lac and (d) CNTs reinforced with lac.

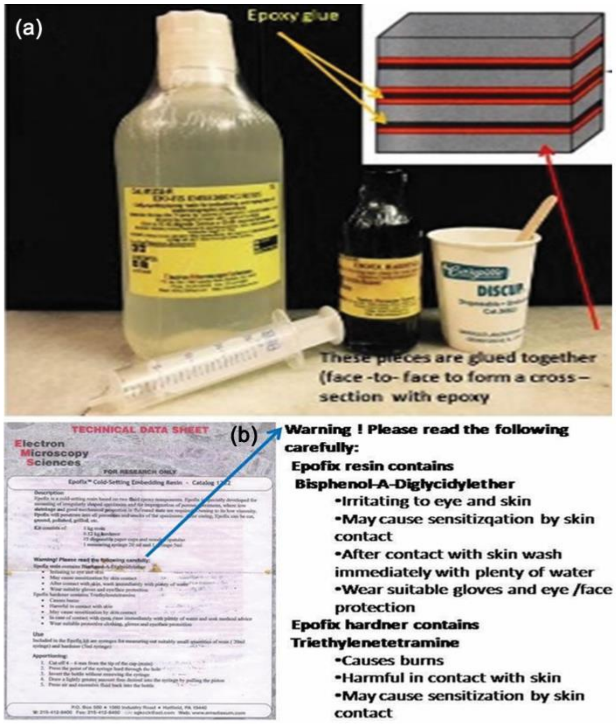

Fig. 12 — (a) Photograph of the commercially available epoxy cold-setting resin based on two fluid epoxy components and /’(b) technical data sheet showing toxic components of epofix.

of any health hazardous components of organic compounds. Lac is naturally abundant and is a very safe natural product, eco-friendly and economical to be used in place of commercially available adhesives.

5 Conclusions

Samples of CNTs and carbon fibre reinforced with pure lac were found to be better adhesives. This is due to these two can bear higher compressive loads as compared to pure lac and chapadi samples. Data obtained from analysis of lac sample used in the present study was also compared with epoxy resin. Although the compressive strength of lac is lower than that of synthetic resin, lac can replace the epoxy resin if reinforced with carbon fibre, carbon nanotubes or fibre glass. Since commercially available epoxy resins are costly and toxic in nature and there is now a renewed global consciousness towards the use of safer natural products. Hence lac synthesized in pure form is suitable alternative to the commercially available epoxy resins. Therefore, natural resin obtained from lac can replace the epoxy if synthesized in highly pure form.

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