Original Article

Evaluation of dynamic properties of nano oil palm empty fruit bunch filler/epoxy composites

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1. Introduction

Since 1947 epoxy shows the wide industrial applications from coatings, to adhesive and marine to aerospace fields where toughness and resistance to high temperatures are required [1–4]. However, the cured epoxy resins pretense a constraint on many engineering applications due to their intrinsically fragile and brittle nature and most important inferior thermal management, low thermal conductivity and large thermal expansion that limits its end use application scope [5–8]. Natural fibers such as oil palm empty fruit bunch (OPEFB), jute,
Table 1 – Recent reported literature on the dynamic mechanical analysis of epoxy nanocomposites.

<table>
<thead>
<tr>
<th>Polymer matrix</th>
<th>Nano filler reinforcement</th>
<th>References</th>
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<tbody>
<tr>
<td>Epoxy</td>
<td>Graphene nanoplatelets (GNP)</td>
<td>[12]</td>
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<tr>
<td></td>
<td>Functionalized kaolinite (KGS)</td>
<td>[13]</td>
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<tr>
<td></td>
<td>Copper phenylphosphinate (CuPP) nanofibers</td>
<td>[14]</td>
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<td></td>
<td>Jack pine and spruce softwood cellulose nanofibers</td>
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<td></td>
<td>Bare or starch-modified ZnO particles</td>
<td>[16]</td>
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<td></td>
<td>Ramie fibers cellulose nanocrystals</td>
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<tr>
<td></td>
<td>Amine-modified graphene oxide</td>
<td>[18]</td>
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<td></td>
<td>Multi-walled carbon nanotubes</td>
<td>[19]</td>
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<td></td>
<td>Boehmite, γ-alumina and α-alumina nanoparticles</td>
<td>[20]</td>
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<td>Modified clay (cloisite 20A)</td>
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<td></td>
<td>Modified clay</td>
<td>[22]</td>
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<tr>
<td></td>
<td>Polyhedral oligomeric silsesquioxane (POSS)</td>
<td>[23]</td>
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<td>Polypropylene-graphene oxide</td>
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<td>Reduced graphene oxide</td>
<td>[25]</td>
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<td></td>
<td>Sodium montmorillonite (pristine clay)</td>
<td>[26]</td>
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<td></td>
<td>Nano silica</td>
<td>[27]</td>
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<td>Nano cellulose from cellulose acetate (ECA)</td>
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<td>Silanized fullerenes (C60)</td>
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<td>Cloisite 30B</td>
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<td>Silane-functionalized montmorillonite</td>
<td>[31]</td>
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<td></td>
<td>Vertically aligned carbon nanotubes</td>
<td>[32]</td>
</tr>
<tr>
<td></td>
<td>Silica nanoparticles</td>
<td>[33]</td>
</tr>
</tbody>
</table>

Fig. 1 – $E'$ of nano OPEFB/epoxy nanocomposites.

2. Materials and methods

2.1. Materials

Same materials including ground OPEFB fibers, epoxy resin (D.E.R. 331), hardener Jointmine 905-35, stainless steel mold and teflon sheets are used directly without any further purification like in our previous published study [36].

2.2. Composites fabrication and DMA characterization

Similar fabrication technique for epoxy composites and nano OPEFB/epoxy composites were applied, samples were prepared [36] and their dynamic properties ($E'$, $E''$, tanδ and Cole–Cole plot) [37] were characterized as per ASTM D4065-01.

3. Results and discussion

3.1. Storage modulus ($E'$)

Fig. 1 shows the $E'$ versus temperature of 0%, 1%, 3%, 5% nano/OPEFB filler loading to the epoxy composites. From the graph it is seen that epoxy with 0% filler showed the minimum $E'$ values. In other studies it was reviewed that epoxy offers low degree of stiffness and consequently have lower $E'$ [38,39]. But considerable enhancement in $E'$ for all nano OPEFB/epoxy composites were noticed during examination, merely due to toughness and rigid behavior of incorporated nano OPEFB, which improved the stiffness and virtuous resistance toward heat of all epoxy nanocomposites.

Result clearly revealed that nano OPEFB filler has a considerable effect on the viscoelastic properties of the epoxy as it efficiently inhibits the epoxy polymeric chains segmental motion ensued by the better dispersion. Remarkably, 3% loading confers highest $E'$ value when compared to 5% and 1% nano OPEFB filler loading (Fig. 1) due to better nanoparticle dispersion, effective reinforcing effect and physical filler–epoxy matrix interaction. However an increase in nano OPEFB filler loading beyond 3% increases the density resulting in the accumulation of nanoparticles within the polymeric matrix due to...
to strong particle–particle interaction [39]. All this creates vacant spaces and voids within the polymer that enhance the rotational movement or segmental motion [40], ultimately lowering the $E'$ and $T_g$ values. Comparable trend in $E'$ value and justifications are noticed with incorporation of nano-Al$_2$O$_3$ particles to the epoxy [41].

Fig. 1 also shows that below $T_g$ the $E'$ values of all epoxy nanocomposites shows decreasing trend with increase in temperature. Interestingly, near $T_g$, a sharp decrease in $E'$ value was noticed revealing transition from glassy to rubbery stage of composite constituents. But above $T_g$ the $E'$ values of all composites shows no remarkable change in the rubbery region revealing reduction of the moduli above 80 °C to almost zero (0), as the nano particles are practically not in contact with epoxy due to high amplitude of polymer segmental motion. Hence composite components lost its ability as hard and stiffer material and became more moveable. Similar trends and agreement were noticed for silicon carbide/carbon fibers/epoxy composites having no remarkable change in $E'$ in the rubbery region [42]. Satisfactory increase in $E'$ for 3% nano OPEFB/epoxy justifies the perfect dispersion, distribution and better physical interaction on account of its higher surface area. Comparable statements were also reported in literature [43,44]. Apparent result also governed the enhanced thermal degradation temperature and stability of 3% nano OPEFB/epoxy composites [45].

3.2. Loss modulus ($E'$)

$E'$ is also referred as dynamic modulus to define viscous response and “internal friction” of the materials [46–48]. Fig. 2 illustrates the compiled curves of $E'$ versus temperature of epoxy composites and nanocomposites at a frequency of 1 Hz. Fig. 2 revealed that $E'$ possess similar trend with the $E'$ at different nano OPEFB loading in epoxy composites system.

Addition of nano filler enhance the $E'$ peak height of the epoxy composites, but more remarkable for 3% filler loading compared to 1% and 5%, emphasizing the case of better dispersion, distribution with no void and aggregated filler within the epoxy matrix comparative of 5% loading. Researchers also reviewed that aggregated structure within polymer matrix conferred the non-homogenous distribution and dispersion resulting in lowering of $E'$ [49].

![Fig. 2 – $E'$ of nano OPEFB/epoxy composites.](image)

3.3. Damping factor (tan δ)

Tan δ define the damping factor [50,51] and relate the internal energy dissipation of the matrix/filler interphase of composites system [52], presented in Fig. 3.

It is clear from the tan δ graph that epoxy possess highest value (0.75) revealing higher degree of molecular rotation/mobility. However, filled composites display moderately lower tan δ peak height as the added nano OPEFB lowered the damping of the epoxy matrix. Thus $E'$ was found highly influenced by the addition of nano filler compared to $E'$ in the composites [49].

Lowered tan δ value for 1% loading with relative to epoxy composites indicates perfect filler dispersion and certain constraint in polymer movement, however lowering in tan δ are apparent for 3% while its value get increased instead of further reductions when loading goes beyond 3%. Remarkably 3% nano OPEFB filler loading displays the lowest damping factor followed by 5%, as the agglomeration increases at higher loading generating more void for the polymer chain to rotate or move which ultimately improves the viscoelastic damping behavior. Analogous and comparable results were reviewed where epoxies are modified with MWCNT, nano Al$_2$O$_3$ particles, activated carbon black from biomass (bamboo stem, OPEFB fiber and coconut shells), amino-functionalized and carboxyl-functionalized [7,39,53,54]. Moreover, from tan δ plot it is also evident that damping increases to its maximum in the transition region at higher temperature followed by considerable reduction in the rubbery region.

3.4. Glass transition temperatures ($T_g$)

$T_g$ can be obtained either from the peak position of tan δ or $E'$ however $T_g$ values from the $E'$ are more lowered but realistic and substantial as compared to $T_g$ value from tan δ curves [47,51]. Table 2 tabulated the $T_g$ values obtained from $E'$, tan δ and the peak height of tan δ curve.

Table 2 illustrates that the epoxy has comparatively lower $T_g$ (60.11 °C) obtained from both $E'$ and tan δ peak compared to all nanocomposites due to the existence of certain movable and flexible epoxy polymer chain within the epoxy matrix [49,55,56]. Additionally, all the epoxy nanocomposites offered higher $T_g$ with respect to epoxy composites, as the
incorporated nano OPEFB acts as hindrance and decreases the empty/free spaces consequently altering the polymer segmental motion/rotation within the epoxy systems. All this results in a prominent restraint in the polymer chain mobility which eventually increase the \( T_g \) of all nanocomposites system. Relatively closer declaration also has been made in the literature report [57,58].

### 3.4.1. Cole–Cole plot

Cole–Cole plot or wicket plot is regarded as the highly valuable and ideal tool to analyze the relationship between \( E' \) with \( E'' \) [59]. Cole–Cole plot having smooth, semicircular arc suggest homogenous polymeric system having better compatibility between the reinforcement and polymer matrix [60], while imperfect or irregular shape having deviation from semicircular arc are defined phase heterogeneity, nonhomogeneous dispersion, phase segregation and micro sized nano materials aggregation due to immiscibility [47]. Fig. 4 displays the comparative Cole–Cole plot for epoxy nanocomposites.

Fig. 4 illustrates that epoxy composites and 1% nano OPEFB/epoxy composites conferred alike smooth and semicircular arc revealing homogenous and perfect dispersion of filler within matrix. However, in the case of 3% loading the graph shows slight deviation from semicircular, but still delivers a very smooth semi arc plot. Moreover no upward inflection was observed directing highly dispersed and miscible single polymeric phase.

But at 5% loading a strong deviance from semicircular shape display irregular arc revealing immiscibility of filler within matrix. Clumping of filler leads to irregular and heterogeneous distribution with relatively weak interfacial adhesion among nano filler-matrix. Analogous reports were also reviewed [61,62]. Interestingly, upward inflection was also noticed in 5% loading revealing high ordered two phase system structures. Overall 3% nano OPEFB filler found optimal to enhanced both \( E' \) and \( E'' \) and \( T_g \).

### 4. Prospective applications of nano OPEFB/epoxy composites

Developed nanocomposites offers considerable dynamic properties and would act as promising substitute materials to the customary and expensive structural materials such as steel, cement, aggregates, aluminum rods, ceramic bricks and wood for several advance applications. Manufactured filled epoxy nanocomposites can also extend epoxy industrial applications such as batteries, supercapacitors, electrical/electronic, automotive/aerospace thermally stable components, adhesives, coatings, exterior components in constrictional partitioning materials and in high performance industrial applications.

### 5. Conclusions

In this study nano OPEFB were successfully incorporated in epoxy and their dynamic properties were evaluated. DMA result revealed that \( E' \), \( E'' \) and \( T_g \) in the glassy and rubbery regions of epoxy composites get enhanced after the addition of nano OPEFB filler, however it is more pronounced for 3% loading. Moreover, it is also observed that the peak height of \( \tan \delta \) get reduced indicating good interfacial interaction between the matrix and the added nano filler. We concluded that 3% filler loading is the effective, ideal and minimal as it displays considerably improved dynamic mechanical properties with relative to 1% and 5% loading for various structural applications.

### Conflicts of interest

The authors declare no conflicts of interest.

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