

Effect of Green Hybrid Fillers Loading on Mechanical and Thermal Properties of Vinyl Ester Composites

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Abstract

The need of eco-friendly materials has been attracted due to renewability, abundance availability, low cost, and so on. Therefore, the search for bio fillers for the production of bio-based composite materials is gaining more and more attention in both academic and industry circles because it promotes sustainability. The present study represents the utilization of biomass solid waste in the hybrid form of tamarind seed and date seed powder into polymer reinforced composite which has been explored for the first time by a compression molding technique. These fillers are bio-waste that can be obtained at a minimal cost from renewable sources. An attempt has been made to use these hybrid fillers to reinforce with the matrix ranging from 0 to 50 wt.%, and their physical, mechanical, and thermal properties were investigated. In general, the inclusion of hybrid fillers increases mechanical properties, although the addition of hybrid fillers had only a minor impact on thermal properties. When compared to the pure vinyl ester resin, the hybrid fillers reinforced composites revealed a significant improvement in tensile, flexural, impact, and hardness properties, with improvements of 1.51 times, 1.44 times, 1.87 times, and 1.46 times respectively, at 10 wt.% filler loading. Filler matrix interaction of fractured mechanical testing samples was analyzed by scanning electron microscope. Based on the findings, hybrid filler reinforced composites may be suitable for applications where cost is a consideration and where minor compromises in thermal qualities are acceptable.

Introduction

Researchers all across the world are attempting to achieve an ambitious objective is to the production of high-performance engineered materials using renewable resources. Due to environmental restrictions as well as new recycling laws for composite materials, manufacturers have been forced into developing innovative new materials derived from renewable resources ¹. Because of their abundant availability and low cost of production, agricultural bio-waste fillers serve a critical and significant role in reducing environmental restraints while also serving as an outstanding possible replacement for synthetic fibre polymer goods ². There are more than 50 countries around the world, including India, Bangladesh, Sri Lanka, Thailand, and Indonesia, as well as the Gulf countries, tamarind (*Tamarindusindica* L.) seeds and date seeds (*Phoenix dactylifera* L.) seeds are grown. The seeds are underutilized in the majority of regions, despite the fact that there is potential to make them more helpful ³. We are investigating the possibility of using them as fillers in polymer composites as part of our ongoing attempt to increase their monetary value. Among the benefits of employing these materials are their low density, sustainability (since they are natural renewable resources), biodegradability, and lack of toxicity, making them more environmentally sustainable in terms of recycling and less hazardous to users and consumers ⁴. In the early stages of filler reinforced composites research and development, inorganic fillers predominated in the majority of the studies and developments. However, while inorganic filler composite materials such as silicon carbide, talc, and calcium carbonate are high-performance materials, they are non-biodegradable. They are derived from non-renewable resources than natural fillers. As a result, the usage of natural fillers may provide environmental benefits, in addition to cost benefits in some cases ⁵. Acosta et al. ⁶ investigated the mechanical and thermal characteristics of the Pecan Nutshell reinforced Poly(lactic acid) composites and found that in comparison to the clean resin, the biocomposites exhibited improved mechanical characteristics such as tensile and flexural modulus, as well as fracture toughness. In accordance with the results of the dynamic mechanical study, it has been established that the stiffness of the biocomposites is enhanced when Pecan Nutshell is used. Mittal et al. ⁷ investigated the Mechanical, Thermal, and Degradation characteristics of the Date Seed fillers (DSF) reinforced poly-L-lactide composites. The findings reveal that the tensile modulus of the DSF based composites was increased by more than 300 percent in the composite with 40 percent filler content as compared to the composite with neat resin. Rheological characteristics demonstrated that the polymer retained its viscosity behaviour even when added a high quantity of filler. Hybrid composites were materials that comprise two or

even more reinforcement components in a single matrix, which is referred to as a matrix composite. The reinforcement may be two separate fibres, two distinct filler particles, or fibres plus filler particles. These filler and particulate reinforcements with in polymer offer excellent mechanical qualities. Hybrid composites with bio waste and natural filler reinforcement provide two important benefits: first, bio waste may be reduced and utilised in a productive way; secondly, good mechanical qualities can be attained through the use of natural filler materials ⁸. Nagaraja et al. ⁹ studied the Physical, mechanical, moisture absorption properties of the Limoniaacidissima shell powder loaded vinyl ester composites and observed the alkaline treated fillers with 15 wt.% of filler loading produced better strength. In previous studies, researchers have used various natural fillers, i.e., from Rice Husk ¹⁰, walnut shell powders ¹¹, Thymus moroderi ¹², Walnut shell, Pinewood and Black rice husk ¹³, Peanut Shell Powder ¹⁴, Betel Nut Husk ¹⁵, Polyalthialongifolia seed ¹⁶ to enhance the mechanical and thermal properties of the polymer composites. A detailed investigation of the impacts of multiple parameters on the mechanical characteristics of hybrid filler composites clearly lacks in the literature, and the mechanical and thermal characteristics of hybrid filler (TSF & DSF) have not yet been explored. The knowledge gaps indicated above demonstrate that the mechanical properties of hybrid filler filled with vinyl ester resin, such as tensile, flexural, impact, as well, as hardness, must be evaluated based on a wide range of underlying parameters in order for their practical application to be feasible. We predict that the findings will provide valuable design inputs for developing a newer generation of hybrid fillers (tamarind seed filler (TSF) and DSF) that will be suited for industrial and vehicle applications as well as structural loading applications in civil engineering. The physical, mechanical, and thermal properties of hybrid fillers (TSF and DSF) reinforced vinyl ester hybrid composites were explored in the present study. We demonstrated the fabrication of natural fillers reinforced hybrid composites and subsequently tested various properties hardness, tensile, flexural, and impact properties of the composites. To establish the sustainability of the hybrid composites in various distinct aquatic environments, the moisture absorption characteristics of the composites were investigated as well. Vinyl ester resin was adopted as the matrix material as it is commonly utilized to build hybrid composites and provides high dispersion of reinforcement particles.

Materials And Methods

Materials

In order to conduct this experimental investigation, a total of 3 kg of date seeds and tamarind seeds were obtained from Manidharma Biotech dealers in Chennai, Tamil Nadu, India. The seeds were cleaned with distilled water to eliminate any excess fruit pulp that had become stuck to them throughout the cleaning process. Tissue paper was then used to wipe away any extra water that had collected on their surfaces. Finally, they were dried for 24 hours at 60 °C in an oven. Following milling in a ball mill, a good morphology of 30–60 µm was achieved, making the fillers ready to be employed as reinforcement. GSRR Resins And Polymers, Madurai, Tamilnadu, provided the industrial bisphenol-A-epoxy vinyl ester resin (styrene - 45 percent), which had a density of 1.145 g/cm³, viscosity of 400 cps, and specific gravity of 1.09, as well as N-dimethylaniline (C₈H₁₁N - promoter), methyl ethyl ketone peroxide (C₈H₁₈O₆ - catalyst) and cobalt 6% naphthenate (C₂₀H₃₄CoO₄ - accelerator) was employed for curing purposes in accordance with the supplier's recommended ratio. Table 1 shows the chemical composition of TSF and DSF with various fillers and fibres.

Fabrication of Composites

The compounding of hybrid fillers and vinyl ester has been accomplished in this current study using a typical compression molding approach. For specimen manufacturing, different filler loadings ranging between 5 to 50 wt.%

were adopted with mould specifications of approximately 200 mm long, 200 mm wide, and 3 mm thickness. The phases of preparation of the date seed filler are displayed in Fig. 1. Initially, mold removal wax (provided by Carbon black) was added to the inside surface of the mould as well as the covering plate to facilitate the removal of the cured composite plates once they had been cured. And then, a measured quantity of vinyl ester resin was Placed in a container, and 1.5 wt.% of the promoter (10 percent, N-dimethylaniline) was included in the beaker. The beaker was then agitated for another 2 minutes, and the mixture was degassed in a vacuum chamber to eliminate any air bubbles that had penetrated on where stirring procedure. A mixture of equal amounts (1.5 wt.%) of accelerator (3 wt.% Cobalt naphthenate) and catalyst (50 wt.%methyl ethyl ketone peroxide) were introduced one at a time and mixed for 2 minutes before being degassed in a vacuum chamber every after the introduction of accelerator and catalyst.

Table 1. Material characteristics of a Hybrid filler/vinyl ester (TSF/DSF) composite compared to various fillers and fiber-based composites.

Afterward, the produced mixture was started pouring into the mould, and the mould was covered with the help of a cover plate to complete the process. It was necessary to cure the composite specimen for 24 hours at atmospheric temperature before removing it from the mould and post-curing it for approximately 2 hours at 80 degrees Celsius in the oven. The cured TSF/DSF hybrid-VE composite plate was extracted from the chamber of the mould. The same process has been used to produce the hybrid-VE composite with various filler loadings.

Experimental Details

Mechanical Testing

A saw cutter was used to cut the fabricated composite plates to the desired shapes for different test specimens. Tensile and flexural experiments were carried out at room temperature, utilizing a universal testing machine (Tinius OlsenH50K). To check the repeatability of the results obtained, three specimens with respect to each weight percentage were tested. According to ASTM D638 (165 × 10 × 3 mm) test standard, a tensile test was carried out on specimens, using a set crosshead speed of 1 mm/min¹⁷. Flexural testing was carried out using the three-point bending technique with a potential of 50 kN and crosshead rate of 2 mm/min for all samples with the following dimensions: 127 mm in length, 12.7 mm in width, and 3 mm thick in accordance with ASTM D790-10 standard¹⁸. The impact strength was determined using the Charpy measurement technique in accordance with the ASTM D-256 (65 x 13 x 3 mm³) standards, and the results were analyzed. The hardness of the material was also assessed using a Barcol Hardness analyzer (Model: VBH2) in accordance with the ASTM 2583 standard. The hardness for each sample was found as the mean of 7 measurements. With the use of a Zeiss EVO 18 scanning electron microscope performing at 25 KV, the morphology and failure mechanism of the samples were investigated¹⁹.

Heat Deflection Temperature Tests

In order to perform the heat deflection temperature (HDT) measurement in accordance with the ASTM D648 standard (60×12×3 mm³), an HDT-TSP type analyzer (6012mm3mm) was utilized for composites containing 0–50 wt.% hybrid filler loading. In this experiment, the loading pressure and consistent temperature range were 455 kPa and 2°C/min, respectively. Once the testing bar deformed under flexural load, the HDT was recorded; this is a normal deflection under flexural load²⁰.

Water absorption behavior

Reinforcements	Manufacturing process	Tensile strength (MPa)	Flexural Strength (MPa)	Impact strength (KJ/m ²)	Hardness	References
TSF/DSF/Vinyl ester	Compression moulding	36.9	112	22.12	38.34	Present work
Nanoclay/banana/jute/polyester	Compression moulding	15 – 23.7	34 – 48.3	–	–	[22]
Date seed powder/Vinyl ester	Compression moulding	10.5 – 40	46 – 149	9.43 – 17	20.33 – 51	[18]
Boiled egg shell /Coir/Vinyl ester	Compression moulding	24	26	39.5	–	[23]
Tamarind seed powder/Vinyl ester	Compression moulding	10– 34	47 – 121	7 – 14	23 – 42	[17]
Nano Oil palm shell/(kenaf – coconut – kenaf fiber/polyester	Compression moulding	30 – 37.56	60 – 69.45	10 – 13.42	–	[24]
Alumina/Coir/Vinyl ester	Compression moulding	27	31	40.5	–	[23]
Shorearobustafiller/Polyester	Hand lay-up method	12–15	25–26	–	–	[25]
Rice hull/Polyethylene	Injection moulding	19–26	19–30	11–16	–	[26]
Polyalthialongifolia seed filler/Vinyl ester	Compression Molding	9–32	44–125	10–31	23–36	[20]
Rice husk/Boiled Egg shell/Coir/Polyester	Hand lay-up method	17 – 31.5	18 – 33	17 – 33	–	[27]
Roselle fiber/Sugar Palm Fiber/Vinyl ester	Hand lay up	15–24	58– 110.5	–	–	[28]
Date palm wood flour / glass fibre/polypropylene	Compression moulding	15–25	–	–	35–60	[29]
Sisal fiber/epoxy resin	Hand lay up	5–15	22–61	5–13	–	[30]
Sawdust/ Recycled Plastics	Hand lay up	9–13	21–35	–	–	[31]
carbon fiber/cement dust/vinyl ester	Hand lay up	10–19	28–34	–	–	[32]
wood flour/pulp fiber/Polyvinyl Chloride	Hand lay up	6–17	18–42	–	–	[33]
Sawdust Flour/Polypropylene	Hand lay up	25–30	50–54	–	–	[34]

The testing samples are cut from the composite plates that had been produced in accordance with the ASTM D570-99 standard. Rectangular samples with dimensions of 39 x 10 x 3 mm³ were used in this study. The materials were dried for 24 hours at 105 degrees Celsius in an oven. Following that, they were submerged in water that was at normal temperature. In each sample, three samples were immersed in four distinct watery environments, namely warm water, cold water, seawater, and normal water. The results were compared. Each of the specimens was immersed in water for two hours, twenty-four hours, twenty-four hours, and twenty-four hours at atmospheric temperature, respectively.

Utilizing an electronic weighing balance with a precision of up to 10^{-4} g, the weight of every specimen previously they were immersed in water was measured. Before every examination, a wiping cloth was utilized to wipe away the water droplets from the surfaces of all of the specimens once they were removed from the water ²⁰.

The absorbed water content of each of the specimens was determined using Eq. (1).

$$M(t) = 100 \frac{(W_t - W_o)}{W_o} \quad (1)$$

Where W_t indicates the weight of the sample after a specific soaking period and W_o means the weight of the specimen after being oven-dried.

Results And Discussions

Tensile properties

The tensile properties of a material are comprised of tensile strength, elongation at break, and tensile modulus. Fig. 2 depicts the effect of hybrid filler concentration on tensile strength and tensile modulus of vinyl ester composites at a different level of filler reinforcement. The tensile strength and the tensile modulus of pure resin (vinyl ester) samples were 24.5 MPa and 1.17 GPa, respectively. At low hybrid filler concentration (up to 10 wt.%), the tensile strength and tensile modulus showed an increase in trend due to the uniform dispersion of fillers in the matrix. In addition, adequate adhesion was developed between the hydrophilic natural fillers and hydrophobic vinyl ester. This leads to an increase in the strength and stiffness of the hybrid composites. The tensile strength and tensile modulus had reached the maximum when the hybrid filler concentration was 10 wt.%, and their values are 36.9 MPa and 1.56 GPa, respectively. Further addition of hybrid filler results in a reduction of both tensile strength and tensile modulus. The surface contact of fillers was started configured when the filler concentration within the composite was more than 10 wt.%, and this formation of contacts was vigorous when the hybrid filler concentration was more than 25 wt.%. The deterioration of strength and stiffness of the hybrid filler reinforced composites were more pronounced beyond the 25 wt.% of filler concentration. This was majorly due to the agglomeration of hybrid fillers, which can be easily disrupted by the applied force and leads to material failure. In addition, the crack was started at the filler/matrix interface, and this is more efficient where the fillers formed dense colonies. The SEM images confirmed the accumulation of fillers when the filler level reaches 25 wt.% (as shown in Fig. 4). Agglomeration tends to reduce the interfacial contact between matrix and fillers. This causes a lack of contribution of polymer chain when subjected to mechanical load and reduces the stiffening of material.

However, the elongation during the break of the vinyl ester composite has reached a maximum at 25 wt.% of hybrid filler concentration (as shown in Fig. 3). The reduced elongation of the hybrid composites owing to higher brittleness of the material when the hybrid filler concentration is below 25 wt.%.

Flexural properties:

The flexural strength of the material indicates its ability to withstand against applied bending load. The higher flexural strength of the material enables its application in the structural field. The experimented results of vinyl ester hybrid composites are depicted in Fig. 5. The flexural strength of hybrid composites was enhanced when the hybrid filler concentration was less than 10 wt.%. Further addition of fillers leads to a strength deterioration.

At low filler concentration, good interface bonding between the hybrid filler and the vinyl ester leads to an increase in flexural strength from 78 MPa to 112 MPa, which is 1.4 times higher than the pure vinyl ester. It was visualized that the void formation was under control when the hybrid filler concentration was lower than 10 wt.%, and this helped to obtain good load transfer capacity to the hybrid composites. In contrast, a relatively higher void formation was observed when the filler concentration raised from 10 wt.% to 50 wt.%. Apparently, higher filler reinforcement (more than 30 wt.%) has produced a significant reduction in flexural strength and flexural modulus. At higher filler concentration, inevitable factors such as agglomeration of fillers and air trapped during fabrication are more cause a large reduction in flexural properties. This is confirmed through SEM analysis of fractured surfaces (Fig. 6).

Hardness

The results obtained through the measurements of hardness are presented in Fig. 7 for the neat vinyl ester resin, and hybrid fillers reinforced vinyl ester composites. The reinforcement of hybrid fillers increased the hardness of the vinyl ester significantly. The hardness of the neat vinyl ester resin was 26.3, and it was reached the maximum of 38.3 when the hybrid filler concentration was 15 wt.%. An increase in hardness is evident as the concentration of the hybrid filler increases, especially in the low filler concentration level (20 wt.%) filled composites. This was due to the fact that the lignocellulosic natural fillers have noticeably higher hardness compared to the soft polymeric matrix. When assessing the wear qualities of such systems, the hardness of the material should be taken into account. In fact, hardness ratings are a measure of wear resistance because hard materials resist friction and wear better. In contrast, the hardness of the sample started to decrease when the filler concentration crossed more than 20 wt.%, and the reduction was noticeable beyond this level. The major reason for a reduction in hardness is an accumulation of fillers. This causes wide variation in hardness at a different locations. It can be noticed that the hardness of the samples revealed similar increase and decrease behavior compared to tensile and flexural tests.

Impact strength

The impact test was carried out until the impact samples were broken. Fig. 7 illustrates the impact strength results obtained from various filler weight percentages of TSF/DSF-VE composites. The impact strength achieved from the TSF/DSF-VE specimens increased between 10 KJ/m² to 22 KJ/m² as a result of a rise in the hybrid filler loads; from 5 to 50 wt.%. The strength increases from 11 KJ/m² to 14 KJ/m² when the filler loading varies from 0 to 5 wt.%. The impact of energy of 5 wt.% hybrid filler vinyl ester composite increases 1.18 times when compared to the resin is pure resin. This could be due to the low quantity of filler is added to the composites. The impact strength is low^{17,21}. For 10 wt.% filler content, the strength of TSF/DSF-VE composites is increased when compared to 5 wt.%. Significantly, the ultimate impact strength of PLSF-VE composites exhibited 22 KJ/m² at a higher TSF/DSF-VE weight content of 10 wt.%, due to high load transferred between filler and vinyl ester matrix. The impact strength increases 1.87 times when the resin is pure to an increase of 10 wt.% of TSF/DSF. Furthermore, when the filler content is raised from 10 to 20 weight percent, the impact strength of a TSF/DSF-VE composite materials is moderately reduced from 22 KJ/m² to 19 KJ/m², indicating a slight reduction in performance. Impact strength of PLSF-VE composites has been reduced by up to 10 KJ/m² once the filler volume fraction is raised from 20 to 50 wt. percent, as has been demonstrated previously. That might be due to an irregular dispersion of the filler between the matrix.

Heat Deflection Temperature Tests

HDT is a critical parameter for a material's ability to be able to resist extreme conditions ambient temperatures without deflection. The heat deflection temperature of the TSF/DSF-VE composites at different weight percentages are illustrated in Fig. 8; from the results of the graph, demonstrates that clear resin has an HDT value of 53°C. The result shows that in addition to the pure resin to TSF/DSF, the HDT values are improved. The value was then

increased to 68°C, which is 1.28 times more than the performance of virgin vinyl ester resins while adding filler content to 15 wt.%. These results clearly show that TSF/DSF filler has good thermal characteristics among different natural fillers. Moreover, after 15wt.% to 50wt.% filler weight the hardness value was decreased from 65⁰C to 40°C. The Heat deflection temperature of the TSF/DSF filler composite is superior to the Banana Ribbon Rope Straight Mat strengthened polyester, tamarind seed filler loaded vinyl ester and Date palm filler reinforced vinyl ester composites^{21, 18}.

Water absorption behavior

Figure 9 depicts the percentage of moisture absorption curves for hybrid filler-loaded vinyl ester composites. Each data point reflects the mean value of three specimens with varying filler loadings after soaking in normal, cold, salt hot water. The observed result of increasing the hybrid filler loading resulted in an increase in the water absorption percentage because of the hydrophilic character of the filler material, as shown in Figure 9. A similar trend was seen in tamarind seed filler/vinyl ester composite², and date seed filler/vinyl ester reinforced composites³. Because of the hydrophobic characteristic of the resin, there was 0% water absorption for the neat vinyl ester resin in the four different environments indicated above. The hot water atmosphere absorbed higher moisture than the other three conditions. The hot water enhanced the hybrid filler/vinyl ester composites diffusivity. As a result, micro-cracks formed in the filler-matrix interface area. For the above 35 wt.% of filler loading, the water absorption rises at times, most likely due to the hydrophilic nature of the bio-based fillers. However, due to the presence of big salt (particularly sodium chloride) molecules in seawater, the saltwater environment had lower moisture absorption relative to the other three environments. Because of the delayed penetration of big molecules into the composites, the moisture absorption percentage was the lowest.

Conclusion

In this research work, waste hybrid filler reinforced vinyl ester composites were fabricated and analyzed their mechanical properties. The following conclusions were drawn based on experimental outcomes.

- The mechanical property results like tensile, flexural, impact, Barcol hardness of the composites show an optimal strength at 10wt.% of filler content.
- The Barcol hardness and HDT of the composites show an optimal strength at 15 wt.% of filler content.
- The highest tensile strength of a material is 37 MPa occurs at 10 wt.% of the hybrid filler added comparatively higher than TSF/VE composites.
- The flexural strength is about 112 MPa and impact strength of 22 KJ/m² at 10wt.% of hybrid filler added.
- Similarly, 15wt.% of hybrid filler has a relatively good barcol hardness value of 29.67 and HDT value of 68.
- From the results, the hybrid filler composites are suitable to make the final products due to eco-friendly composite material for various industrial applications and domestic applications like fan blades, cover cases, panels, etc.

Declarations

Author contributions

Conceptualization, N.N.; Data curation, N.N. and V.V.; Formal analysis, S.B., S.R., PD.L., LT.J., K.S and R.A.; Investigation, N.N.; Methodology, N.N.; V.V and KB.NB.; Project administration, K.R.; Resources, K.R., KB.NB., and N.N.;

Software, K.R.; Supervision, S.B.; Validation, S.B. and K.S.; Visualization, S.B. and N.N.; Writing—original draft, N.N., V.V., KB.NB.; Data Visualization, Editing and Rewriting, N.N.

Competing interests

The authors declare no conflict of interest.

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Figures

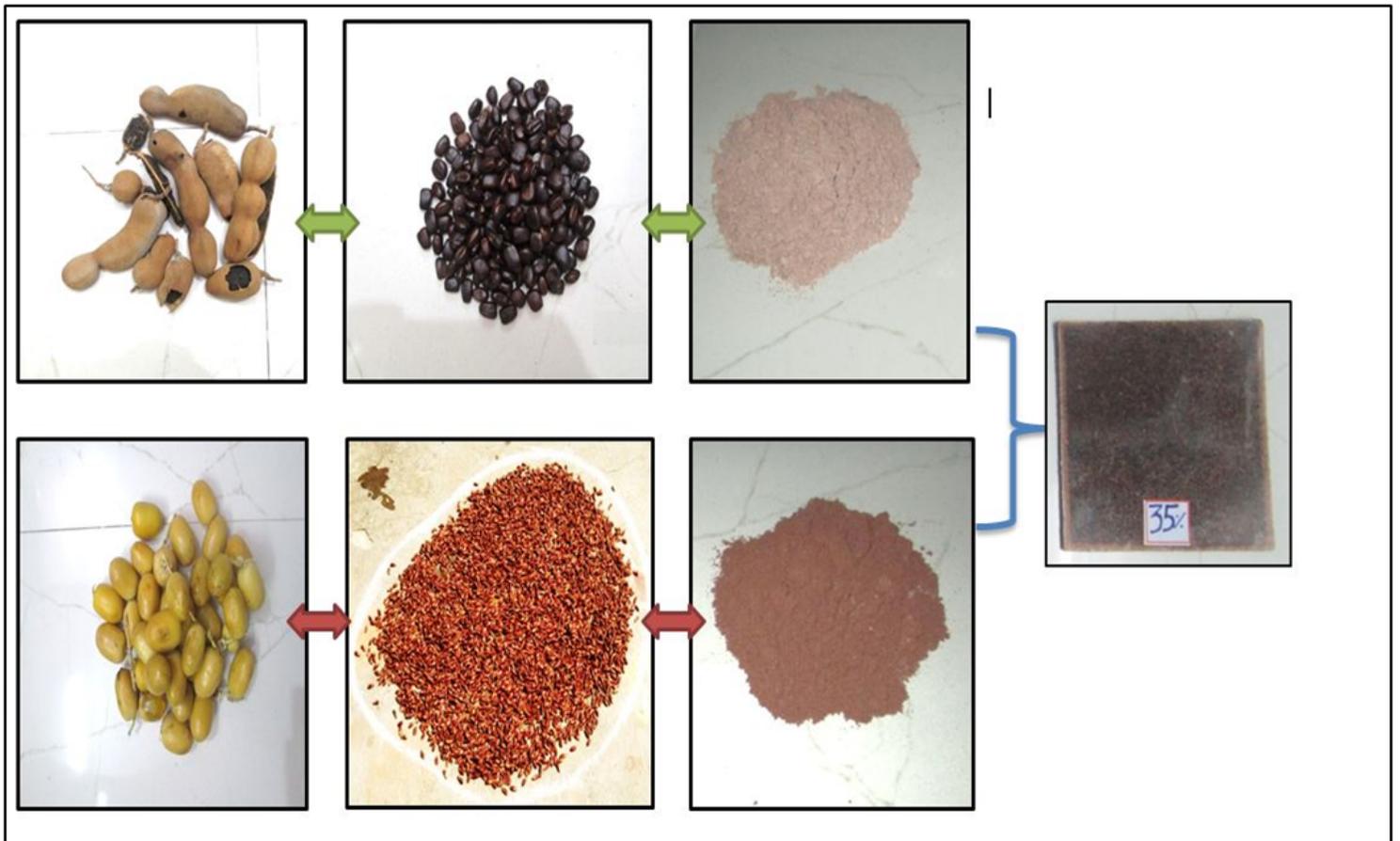


Figure 1

Stages of TSF/DSF filled vinyl ester composites.

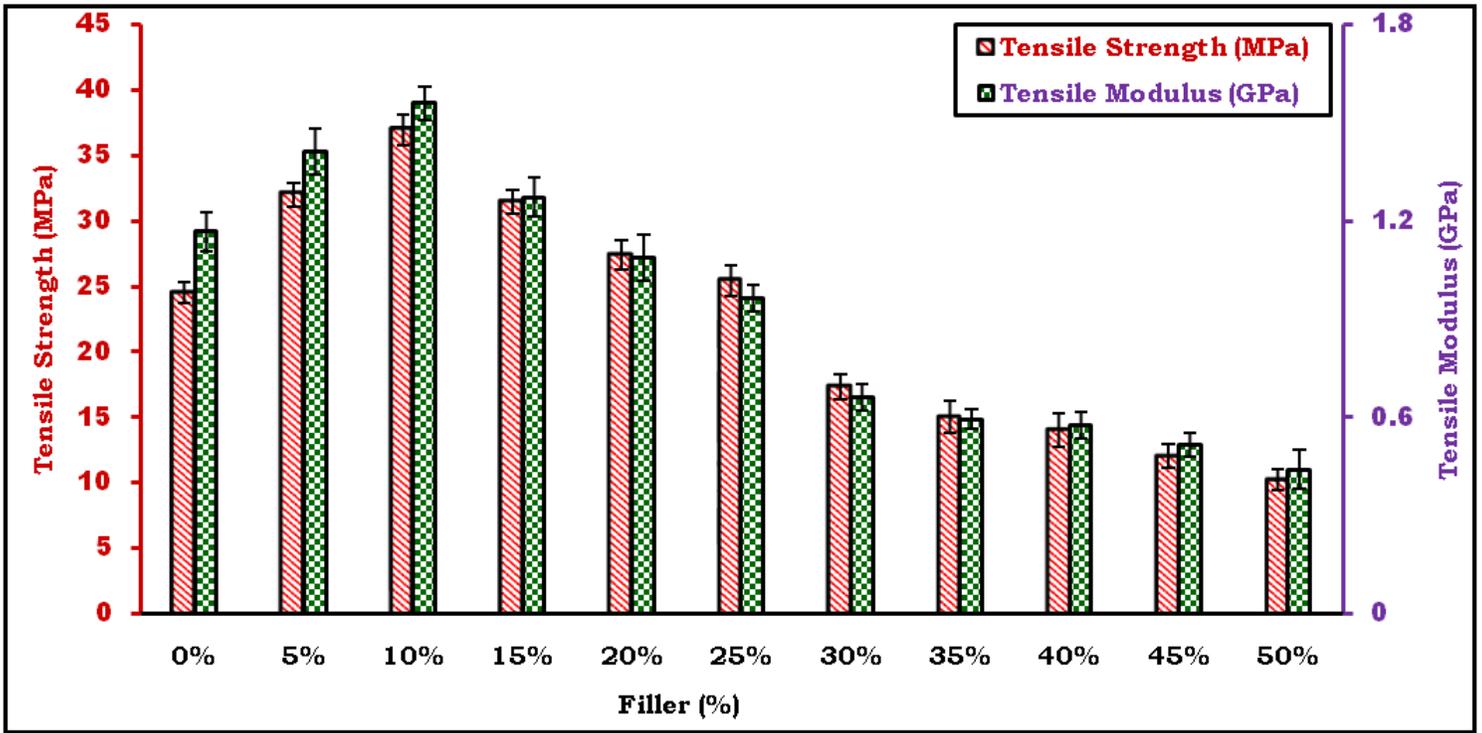


Figure 2

Variation of tensile strength and tensile modulus of hybrid composites at different levels of filler concentration.

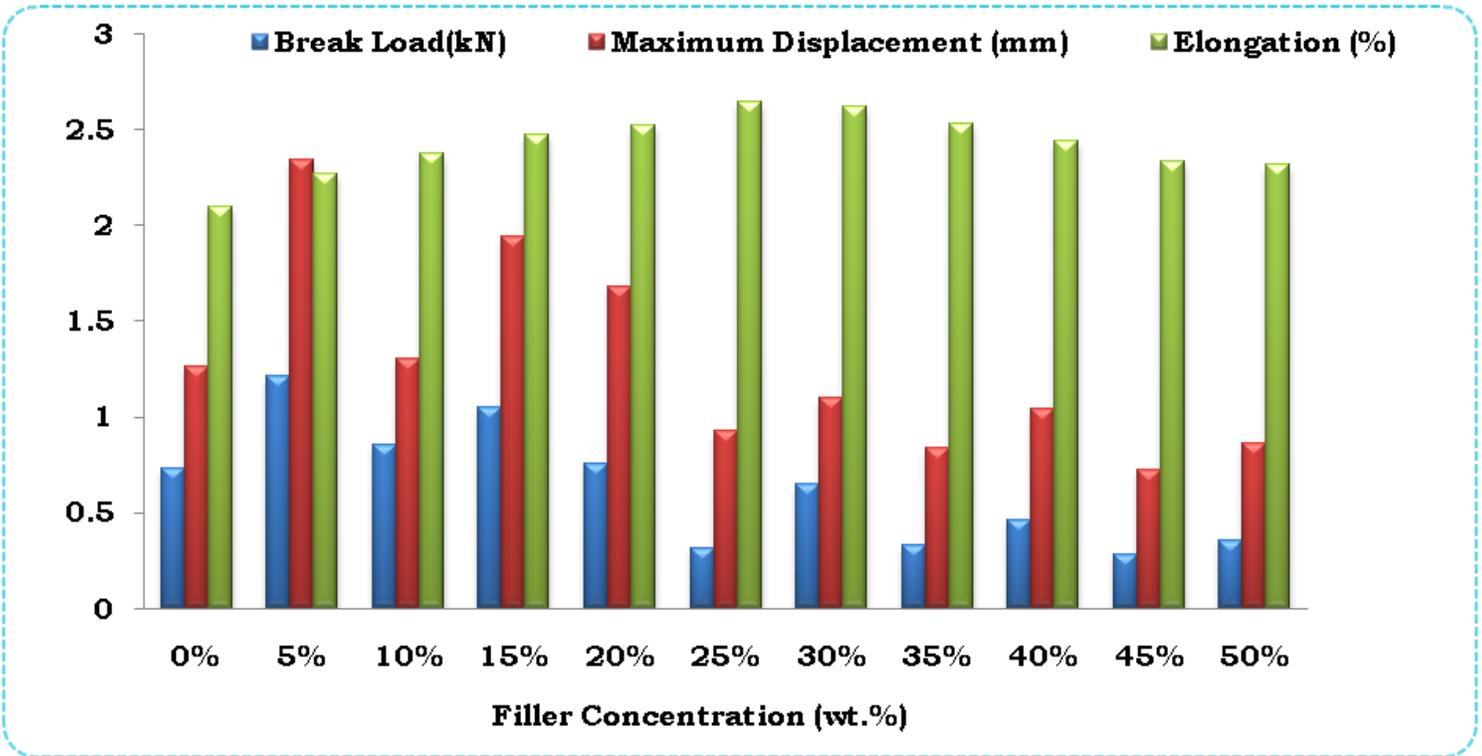


Figure 3

Variation of break load, peak displacement and deformation of hybrid composites at various filler proportions.

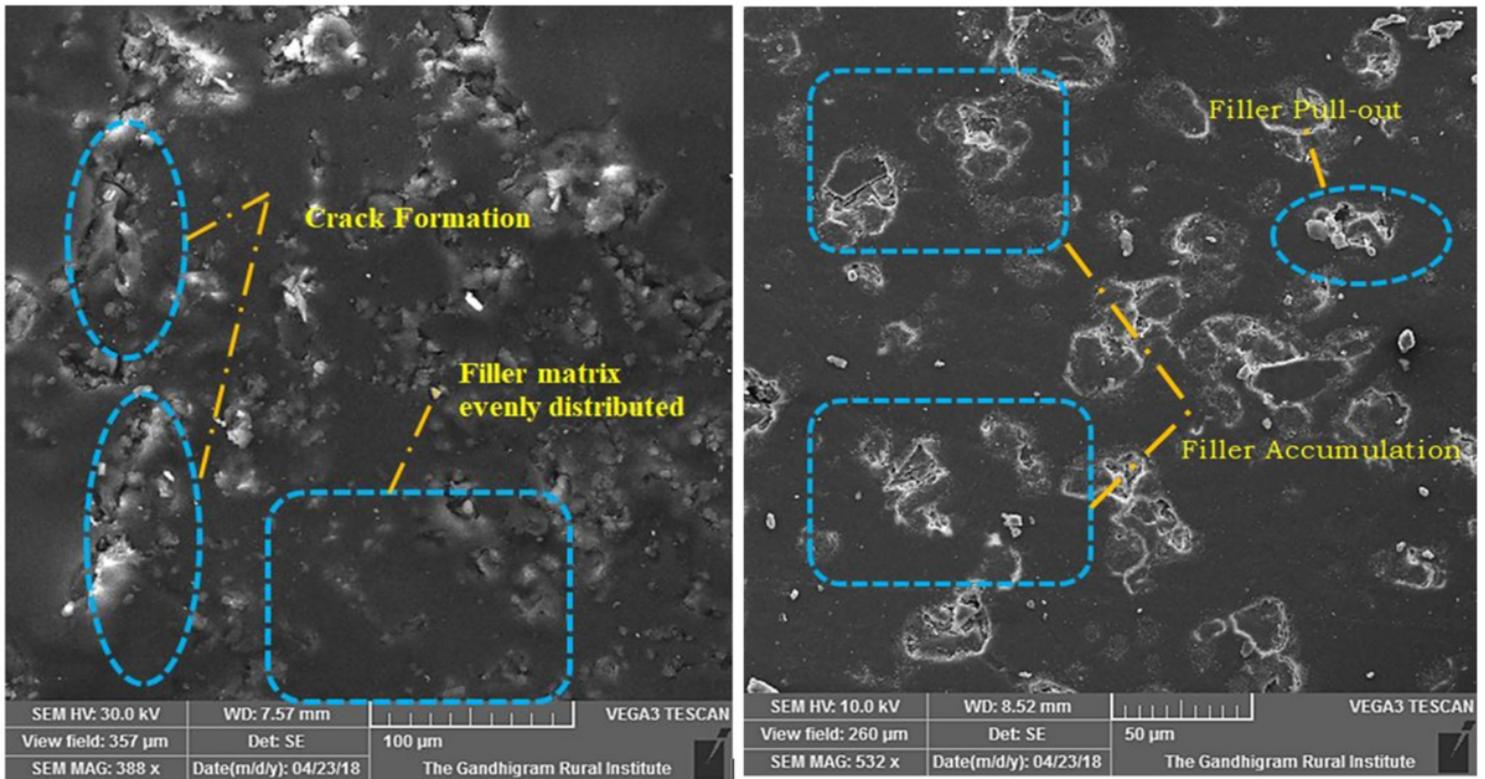


Figure 4

Fractured surface morphology of tensile tested sample contain 25 wt.% hybrid filler.

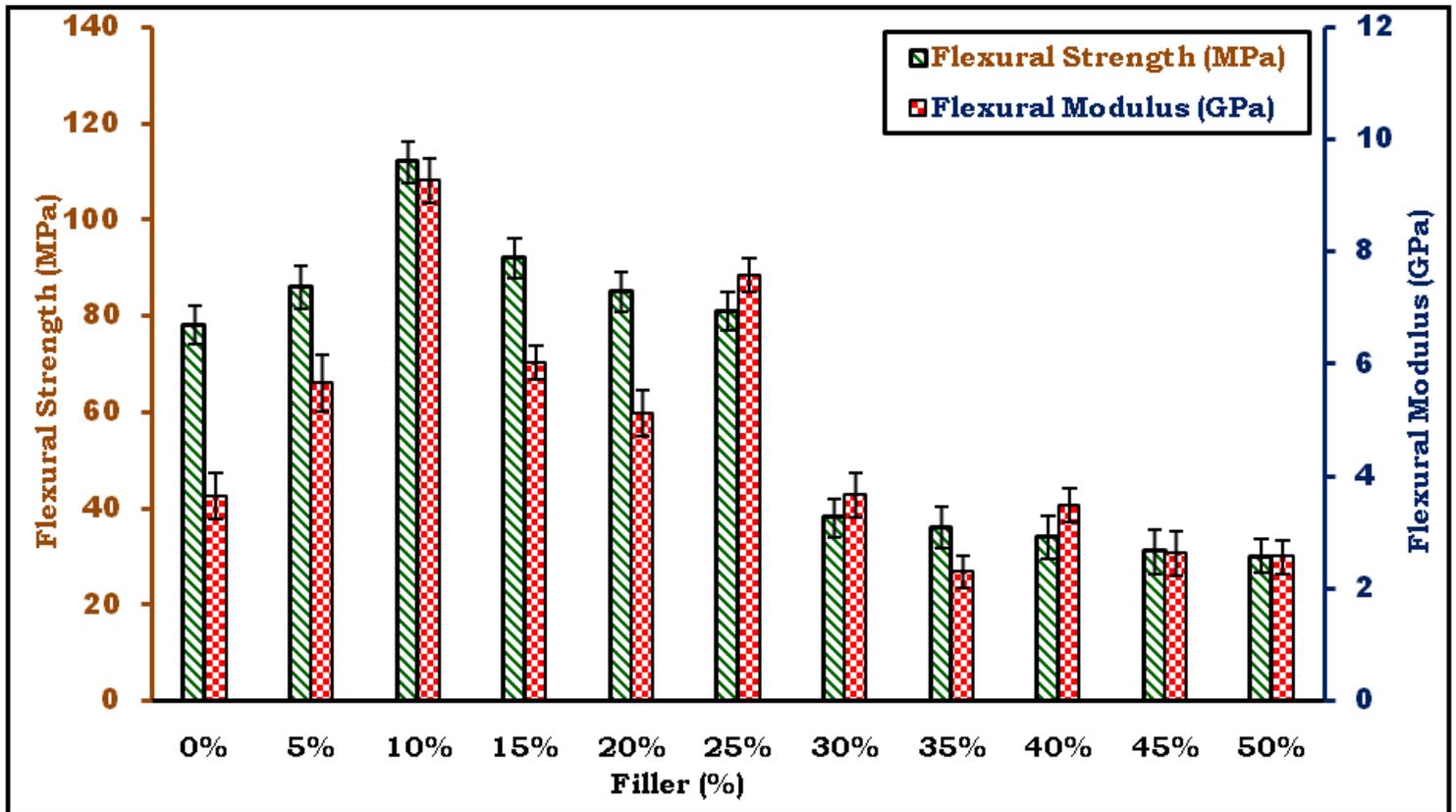


Figure 5

Variation of flexural strength and flexural modulus of hybrid composites at different levels of filler concentration.

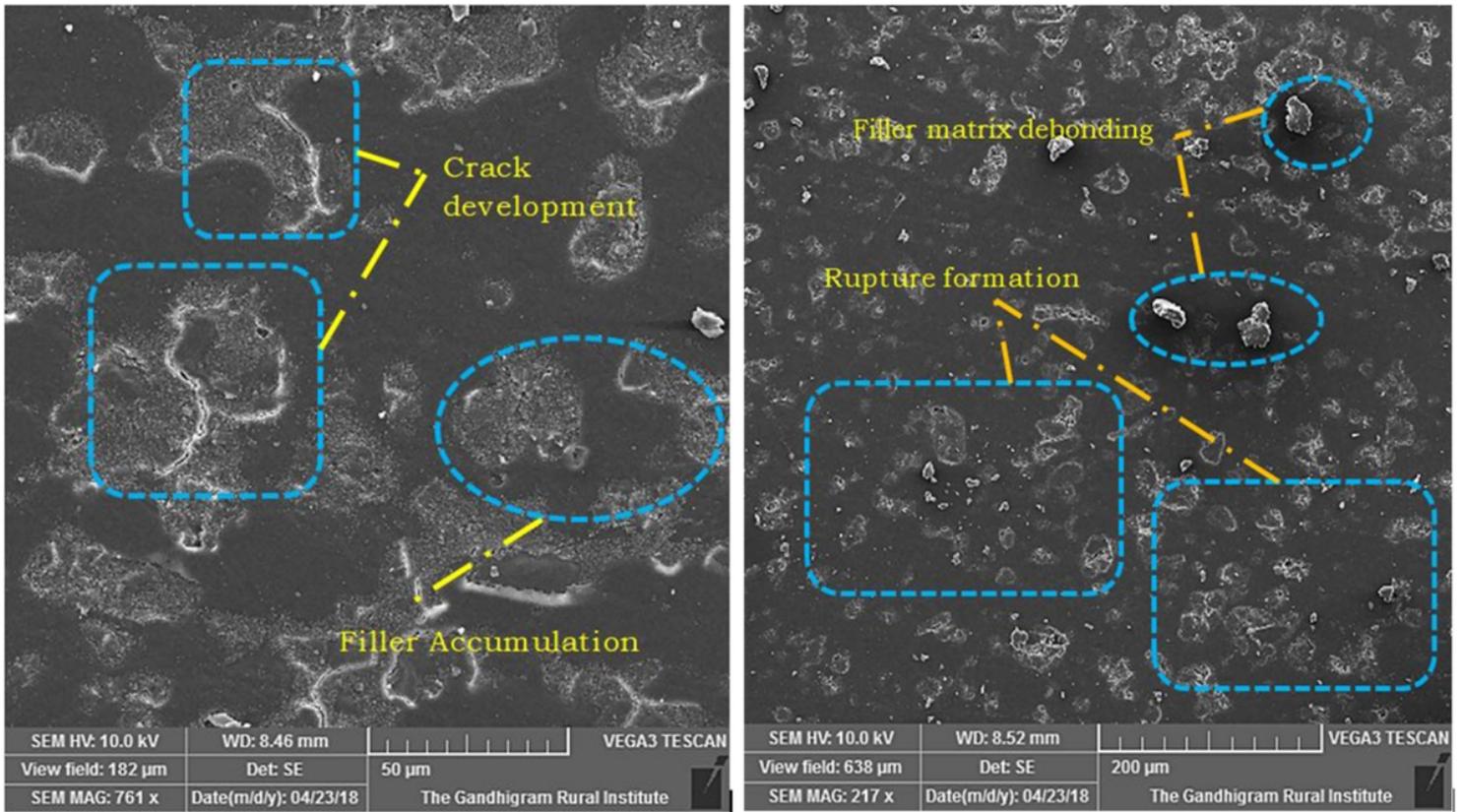


Figure 6

Fractured surface morphology of flexural tested sample contain 30 wt.% hybrid filler.

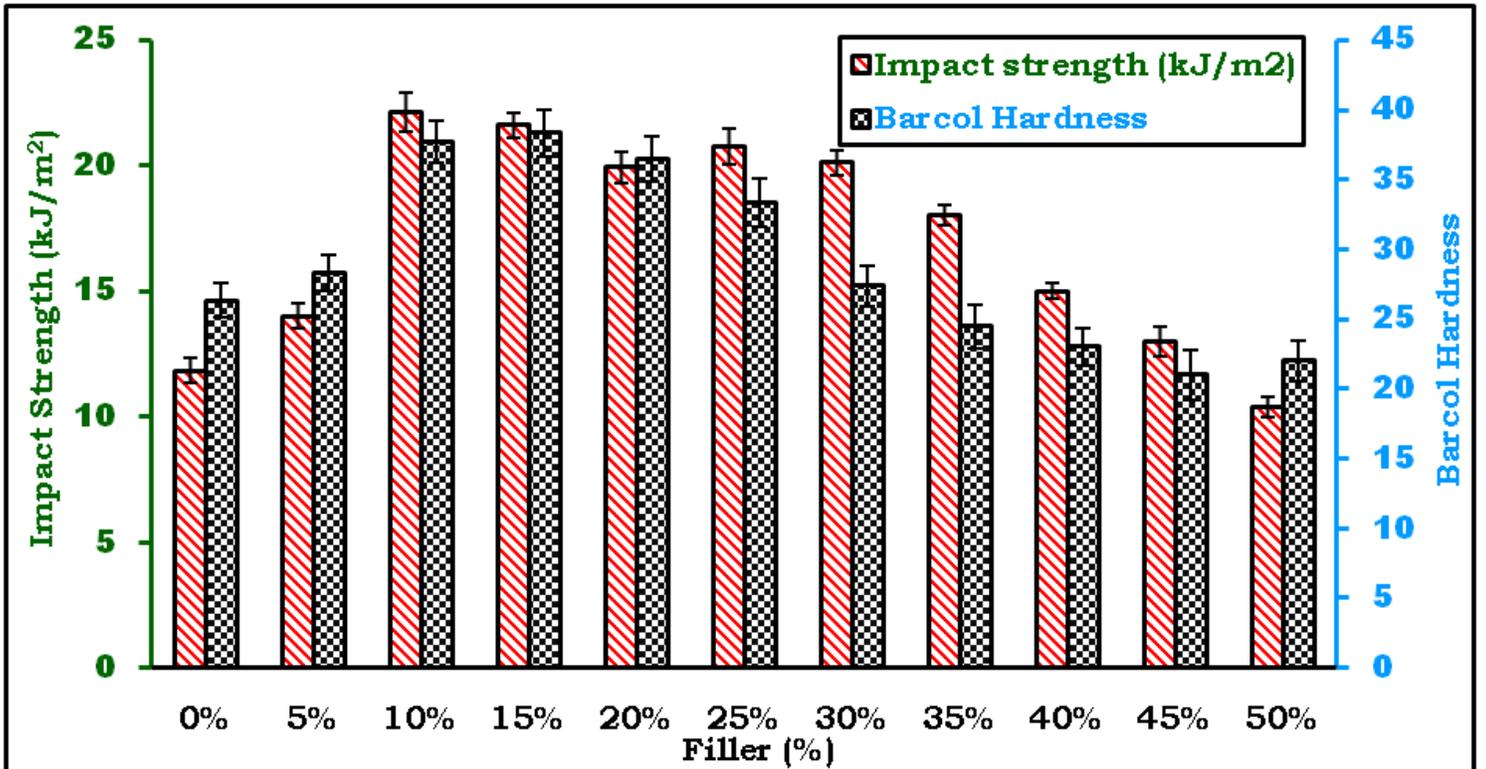


Figure 7

Impact Strength, Hardness of TSF/DSF filled VE composites as a result of varying filler loading levels.

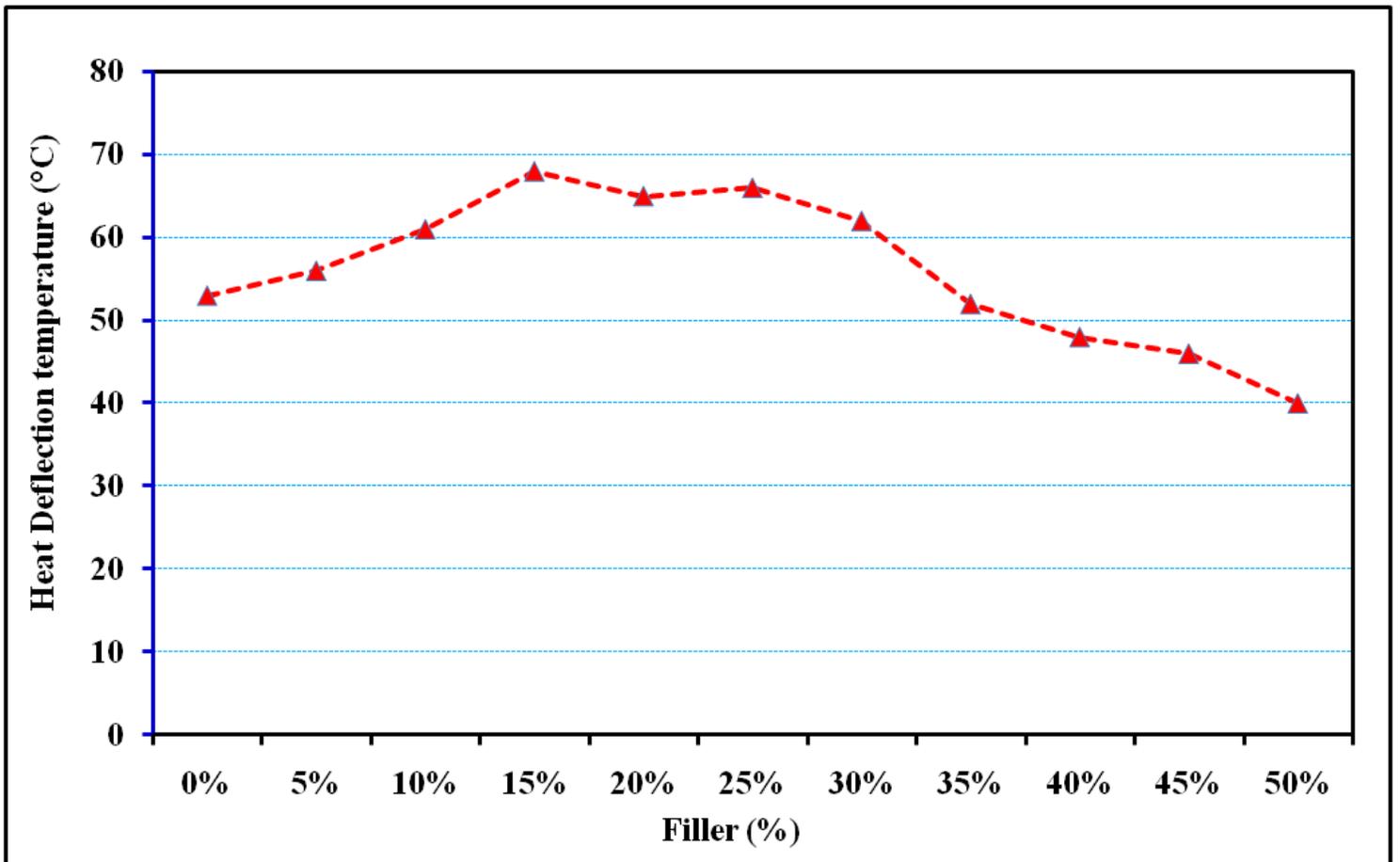


Figure 8

Heat deflection temperature against % of TSF/DSF loaded VE composite.

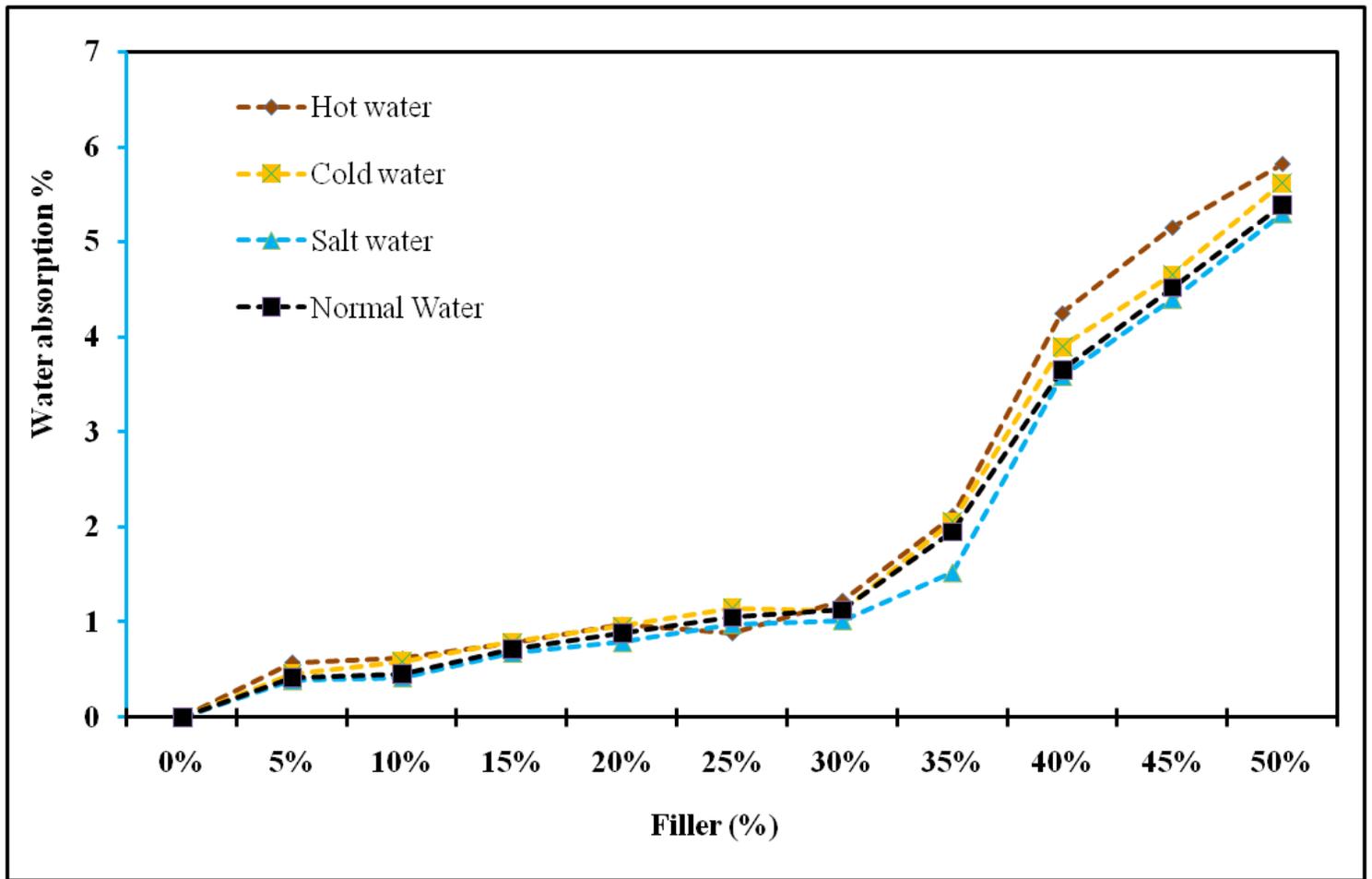


Figure 9

The effect of processing on moisture absorption vs filler quantity in TSF/DSF-filled VE composites.