

Effect of plasticizer, molecular weight, and cross-linking agent on glass transition temperature of polymer composites

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13.1 Introduction

Nowadays, polymer-based composites are playing an important role in day-to-day life, having applications in various fields. There is not even a single area where polymer composites cannot be applicable (Verma, Baurai, et al., 2020; Verma, Budiya, et al., 2019; Verma, Kumar, et al., 2019; Verma, Negi, et al., 2019; Verma et al., Parashar, et al., 2018a, 2018b; Verma & Singh, 2019). If we take the basic definition of a composite, it is defined as a combination of two or more materials designed for a specific task as per the requirement. Most composite materials are divided into two constituents: (1) reinforcement material, which provides strength to the material, and (2) matrix material, which binds the reinforcement material to develop composite material. If the matrix material is polymer, then the composite is known as a polymer-based composite. With further increase in demand for superior materials, researchers used other constituents such as plasticizers, cross-linking agents, coupling agents, stabilizers, and so forth to enhance the thermomechanical characteristics of polymer composites. Furthermore, polymer composites are being divided into two categories based on the type of polymer, that is, thermoplastic polymer composites and thermosetting polymer composites. Thermoplastic composites can be molded into any shape by softening them at elevated temperatures and subsequently cooling them, which results in a one- or two-dimensional polymer structure. In the case of thermosetting polymer composites due to their highly cross-linked structure, they are rigid and cannot be softened under high-temperature environments (Faruk et al., 2012; Ticoalu et al., 2010). In this chapter, our major focus is on plasticizers and cross-linking agents used in developing polymer-based composites and their effect on the glass transition temperature of polymer composites.

13.2 Plasticizers and their classification

In today's scenario, many researchers are using plasticizers as an additive to alter the degree of plasticity/flexibility of the polymer composites (Sejidov et al., 2005). Plasticizers, as per the International Union of Pure and Applied Chemistry, are "a substance incorporated in material (mainly plastic or elastomer) to increase its flexibility, workability, and distensibility." Plasticizers are linear or cyclic carbon chains having low molecular weight polymer chains ranging from 300 to 600 (Greener Donhowe & Fennema, 1993; Wilson, 1995). Some other features of plasticizers are their nonvolatile nature, high boiling point, and low molecular weight, resulting in a wide range of applications such as consumer goods, constructions, packaging, automobile, and so forth (Yesid, 2014). Due to their low molecular weight, it is easily facilitated in between the molecular chain of the polymer and results in reduction of secondary forces between the molecular chains and restructuring of the molecular chain in three-dimension space such that amount of energy required for the mobility of the molecular chain is minimum (Wypych, 2017). Due to restructuring, a large amount of free space is present and hence ductility/flexibility of the polymer composites increases, as shown in Fig. 13.1. The degree of plasticity depends upon the molecular structure, function group attached, molecular weight, and chemical composition of the plasticizer (Moreno, 1992).

Based on the processing technique, plasticizers are classified as (1) internal plasticizers: these plasticizers chemically modify the polymer structure by forming

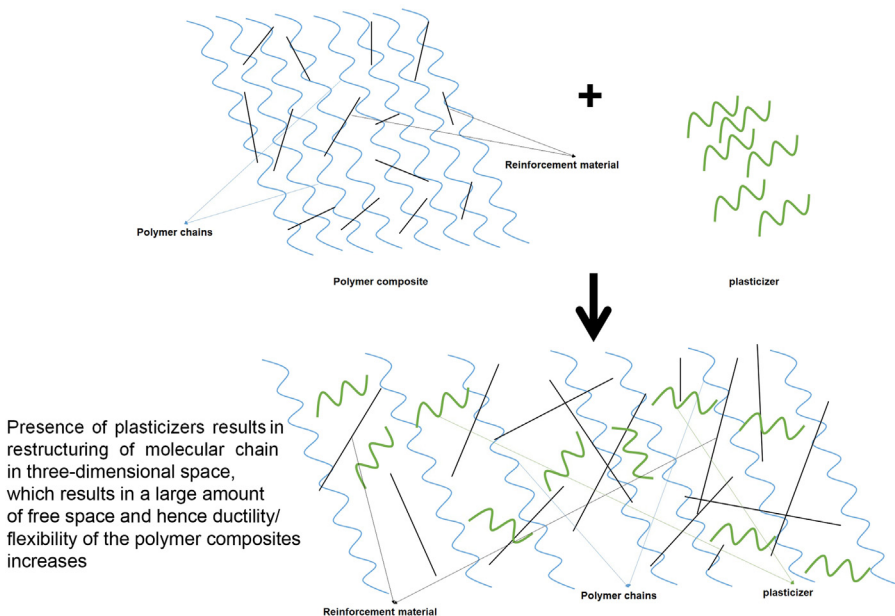


Figure 13.1 Effect of plasticizers on the structure of polymer composites.

certain bonds by chemically attaching to the polymer chains to increase the ductility/flexibility of polymer composites. During the process, low glass transition temperature (T_g) plasticizers either copolymerize or react with a high T_g polymer such that they become the integrated part of the main chain (Frados, 1976), for example, vinyl acetate and vinylidene chloride. They lower the glass transition temperature of overall polymer composites, resulting in a softened effect; (2) external plasticizers: they are low volatile materials that interact with polymer chains without forming any primary bonds with the main structure. The commonly use an external plasticizer, polyvinyl chloride in most cases, which acts as a solvent at a higher temperature. External plasticizers are further divided into two groups based on solvation capacity (Godwin & Krauskopf, 2008): (1) primary plasticizers: when the solubility of the polymer in the plasticizer is high, it is termed the primary plasticizer. It acts as the sole plasticizer forming a gel-type substance with the polymer at normal processing environmental conditions and does not exude from the plasticized material, for example, citrates, adipates, and so forth; (2) secondary plasticizers: they have limited solubility/gelation capacity (due to a less polar or nonfunctional group) with the main polymer chain and therefore blend with the primary plasticizer (Chanda & Roy, 2006; Krauskopf & Godwin, 2005; Vieira et al., 2011) to alter the properties of the parent material, for example, chlorinated paraffin and epoxidized esters. Extenders are a special category of secondary plasticizers; they are also incompatible with the parent polymer, extend the material, or fill out its bulk at a low cost without causing a significant loss of flexibility, as would occur if a solid filler is used as an extender. Examples are naphthenic hydrocarbons, aliphatic hydrocarbons, and chlorinated paraffin (Altenhofen Da Silva et al., 2011; Bortel, 2008). According to chemical compositing, plasticizers are classified as adipate (such as DEHA and DIDA), benzoate (such as benzoate esters), energetic (such as BTTN, DNT, and BDNPA), biobased (vegetable oils), phthalate ester (such as DEHP, DINP, and DIDP), citrates (TOC, ATOC, and ATBC), and trimellitate ester (TINTM, TIDTM, and TEHTM) (Langer et al., 2020). In this chapter, our major focus is to study the effect of plasticizers on the viscoelastic properties such as glass transition temperature, Young's modulus (storage and loss modulus), percent of elongation, and thermal stability of the polymer composite material in detail.

13.3 Cross-linking agents

To improve the properties of polymer composites such as solubility, strength, thermal stability, rigidity, and so forth, many cross-linking agents were used in past few decades. A study of cross-linking was first done in 1839 by Goodyear (Datta, 2002), which investigated the cross-linked rubber structure. It was found that sulfur cross-linked rubber had superior properties than without cross-linked rubber. In most cases, a chemical reaction will occur between the agents and the main polymer chain, which compacts the structure. It results in alteration of properties such

as decrease in flexibility as the free space between the main polymer chains reduces, which imparts brittleness and lower viscosity; insolubility of the polymer composite in solvents (may absorb) due to a strongly tied structure by covalent bonds; increased glass transition temperature (Miyazaki et al., 2010), strength, and toughness; the thermoplastic nature may change to thermosetting; and depending upon the crystallinity of the final structure, thermal stability may increase or decrease. The cross-linking structure may be regular, highly irregular, tightly cross-linked, loosely cross-linked, or highly imperfect with intramolecular loops and many free ends, and molecules may get trapped in the network but become unattached to it (Nielsen, 1969). Many of the properties depend upon the final network of the cross-linked polymer composite; therefore, the study of their structure is an important aspect for researchers nowadays.

Depending upon the polymer's nature (i.e., nature may change depending on the thermoplastic, elastomer, and thermosetting), many cross-linking techniques have been employed by different researchers, either by polymerization of the polymer having one or more functional groups (there may be self-cross-linking without any use of additive or required additives) or by forming covalent bonds between the parent polymer and cross-linking agent, as shown in Fig. 13.2, through different techniques such as UV radiation, chemical reaction, and sulfur vulcanization (Maitra & Shukla, 2014). There may be pre or postcross-linking, that is, they may be partially cross-linked or can undergo time-dependent cross-linking. Therefore, concentration, environmental conditions, and cross-linked networks play an important role, which helps in the characterization of polymer composites. In this chapter, our major focus will be on the study of the effect of cross-linking agents and molecular weight on glass transition temperature and dynamic mechanical analysis properties of polymer composites.

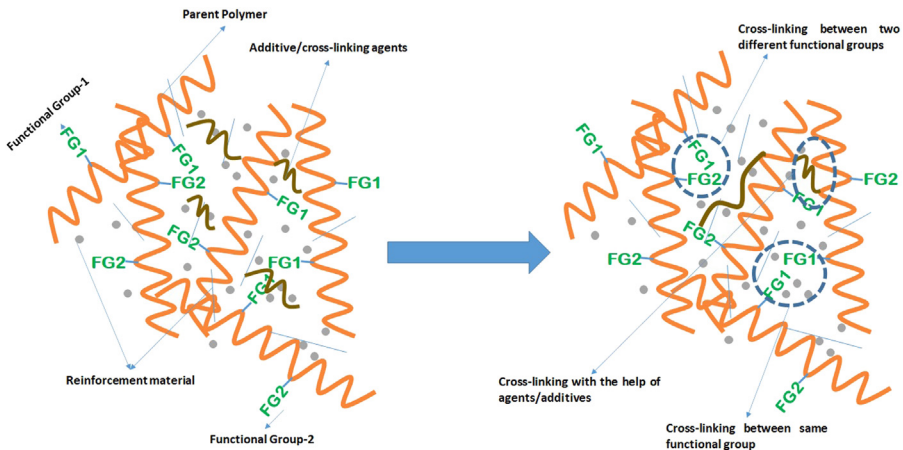


Figure 13.2 Cross-linking of polymer composites.

13.4 Glass transition temperature

The dimensional stability of a material as a function of temperature and time is best measured through a property known as glass transition temperature (T_g). T_g is the temperature at which the state of amorphous material changes from a glassy to a rubbery state (Bandeira et al., 2015; Menard & Menard, 2020). At this temperature, mobility of the polymer chains increases at a significant level, resulting in a change in the thermal stability of the material. The most commonly employed techniques for determining the glass transition temperature are dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). In DMA, oscillating force generates sinusoidal stress that has been applied to the composite material and sinusoidal strain response has been recorded. Values such as amplitude at peak and phase lag between two sinusoidal waves are being recorded to determine the properties such as different modulus (storage and loss) and glass transition temperature of the material. The behavior of the material under the sinusoidal force is of two types, that is, Hookean or elastic behavior and Newtonian or viscous behavior. Storage modulus, also known as elastic modulus, is defined as the amount of energy stored in a material under the application of stress, which states the elastic nature of the material. For elastic materials, their response is in the same phase as applied oscillation stress, as shown in Fig. 13.3. Loss modulus is the amount of energy that disappears under the application of stress in the form of heat. The viscous material response of the material is out of phase. In general, the composite material shows the viscoelastic response to the material, which resulted in phase lag between applied stress and strain output; this phase lag represents the viscous nature of the material.

Mathematically

$$\text{Applied oscillating stress } \sigma(t) = \sigma_0 \sin \omega t$$

where σ_0 is maximum amplitude of stress, t is the time period, and ω is oscillating frequency.

Response of elastic material $\sigma = E\varepsilon$

$$\varepsilon(t) = \frac{\sigma}{E} = \frac{(\sigma_0 \sin \omega t)}{E} = \varepsilon_0 \sin \omega t$$

where $\varepsilon_0 = \frac{\sigma_0}{E}$ is the maximum strain produced in the material.

Response of viscous material $\sigma = \eta \dot{\varepsilon} = \eta \left(\frac{-d\varepsilon}{dt} \right)$

$$\varepsilon(t) = - \int \frac{\sigma_0 \sin \omega t dt}{\eta}$$

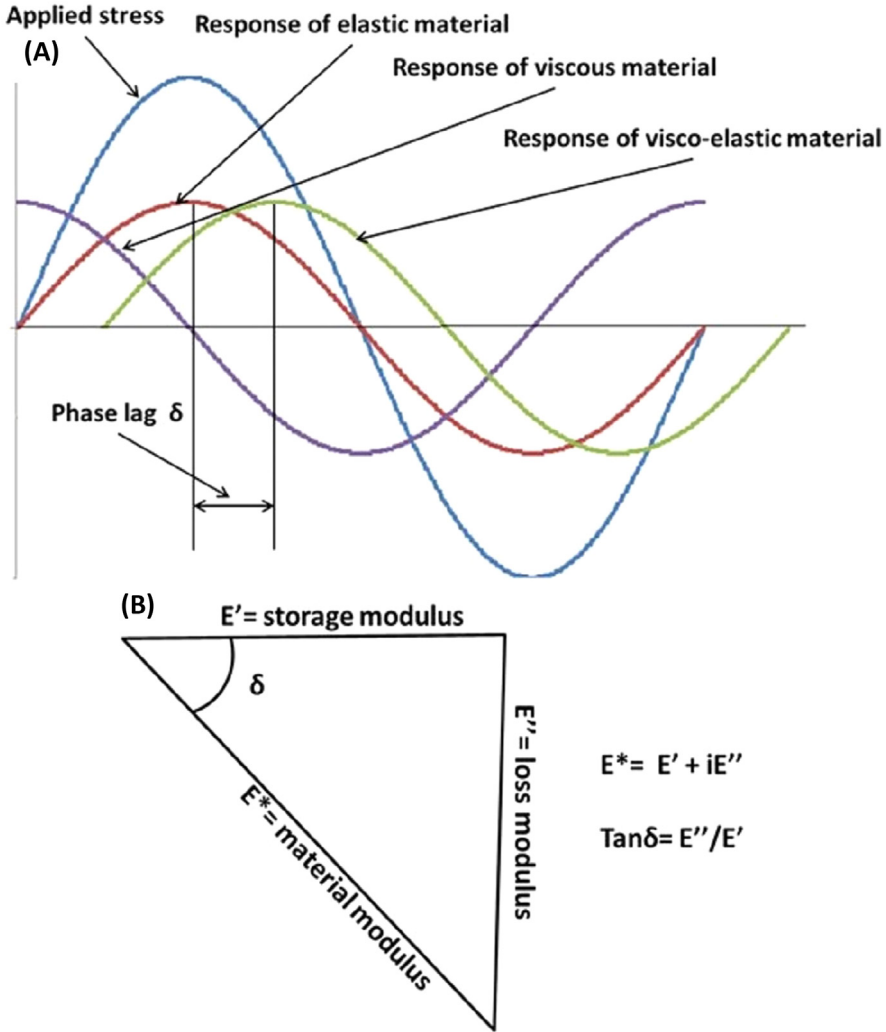


Figure 13.3 (A) Response of materials under the application of oscillating stress and (B) relationship between storage and loss modulus.

$$\epsilon(t) = \frac{\sigma_0 \cos \omega t}{\eta} = \epsilon_0 \sin(\omega t + \pi/2)$$

where σ , E , ϵ , γ , and η are stress, Young’s modulus, strain, strain rate, and viscosity, respectively.

Another important application of DMA is that it measures the effect of temperature on stiffness of materials, which governs its working range in real file conditions, that is, at higher temperatures, stiffness of composites decreases, leading to

serious problems. For composite materials, variation of storage modulus concerning temperature is presented in Fig. 13.4. In composites when the temperature is low, polymer molecular chains are closely packed and are in a solid (glassy) state. Under the application of load, with increase in temperature, free volume is increased, which facilitates stretching, bending, and rotation of the molecular chain and is represented as gamma transition (T_γ), as shown in Fig. 13.5. Further, with an increase in the temperature, free volume of the material gets increased, resulting in movement of the side chain known as beta transition (T_β); this may also be associated with movement of cross-linked/additive branch chains, as shown in Fig. 13.5. At elevated temperatures, the composite behaves like fluid, that is, there is sliding/

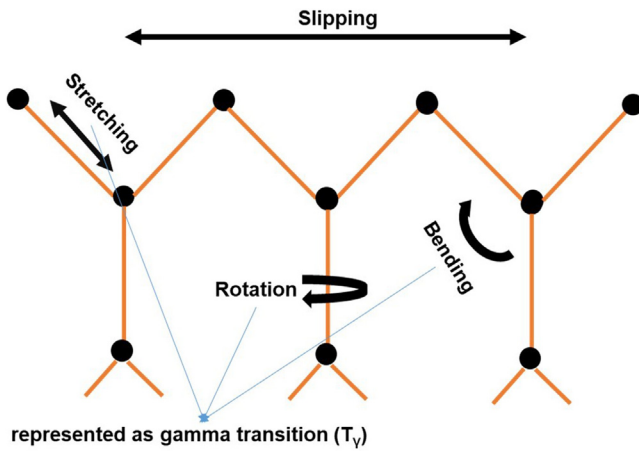


Figure 13.4 Various motions in a polymer chain.

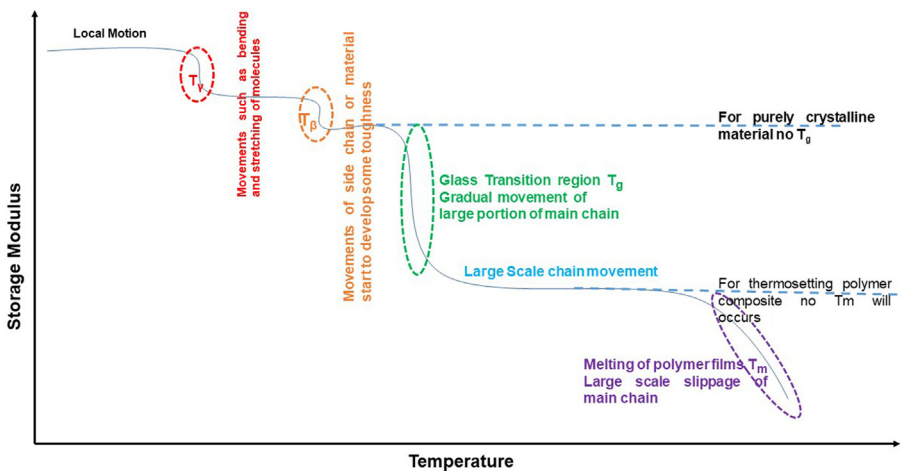


Figure 13.5 Generalized DMA curve (storage modulus) shows different phases.

movement of main chains one over the other, also known as large-scale movement. This transition is known as glass transition or alpha transition (T_α). For 100% crystalline material, this transition is not seen. Further increases in temperature result in melting of the composite; the temperature at which this occurs is known as the melting temperature (T_m).

13.4.1 Measurement of glass transition temperature

For a polymeric material, glass transition temperature becomes an important characteristic. It is a point where the polymer changes its state from glassy to rubbery. Glass transition temperature depends upon the type of polymer chain, blending agent used, amount of cross-linking, or molecular mass. The polymer in general changes its state over a period of temperature, that is, T_g is not a discrete temperature, but it is reported as a single temperature for convenience. As it is closely related to strength and flexibility, it becomes an important parameter for polymer-based composites. As per modern thermal analysis, there are three standard testing techniques available: these are DMA, DSC, and thermomechanical analysis (TMA).

In DMA, cyclic load is applied to a specimen over a predefined range of temperatures at a certain heating rate. In each cycle, three mechanical properties are calculated, loss modulus, storage modulus, and damping coefficient, over a predefined range of temperatures. According to the result, the obtained glass transition temperature can be measured as the intersecting point of the slope lines, where the storage modulus begins to drop, that is, one from glassy plateau and other from sudden drop in storage modulus. It gives the lowest measure for glass transition temperature. It is the highest peak temperature of the damping curve, as shown in Fig. 13.6. In DSC thermal analysis, a small amount of sample is heated over a predefined range of temperature. A curve is plotted between the amount of heat required, that is, heat capacity and temperature. During the transition phase, a sudden change in heat capacity is measured, as shown in Fig. 13.6. Three tangent lines are drawn, and three points are calculated from the data representing start point (starting of transition phase), middle point (reported as the glass transition temperature), and endpoint (ending of transition phase). In TMA analysis, a specimen is heated over a range of temperatures and change in dimension (length) is measured. A graph is plotted between change in dimension and temperature. After the point of glass transition temperature, the change in the slope of curve is seen. The intersection point of a line tangent to the initial and final slope gives the value of glass transition temperature, as shown in Fig. 13.6.

13.5 Effect of plasticizer on glass transition temperature of polymer composites

Many researchers have been employing plasticizers to enhance the properties of polymer-based composites. Plasticizers in general have lower glass transition

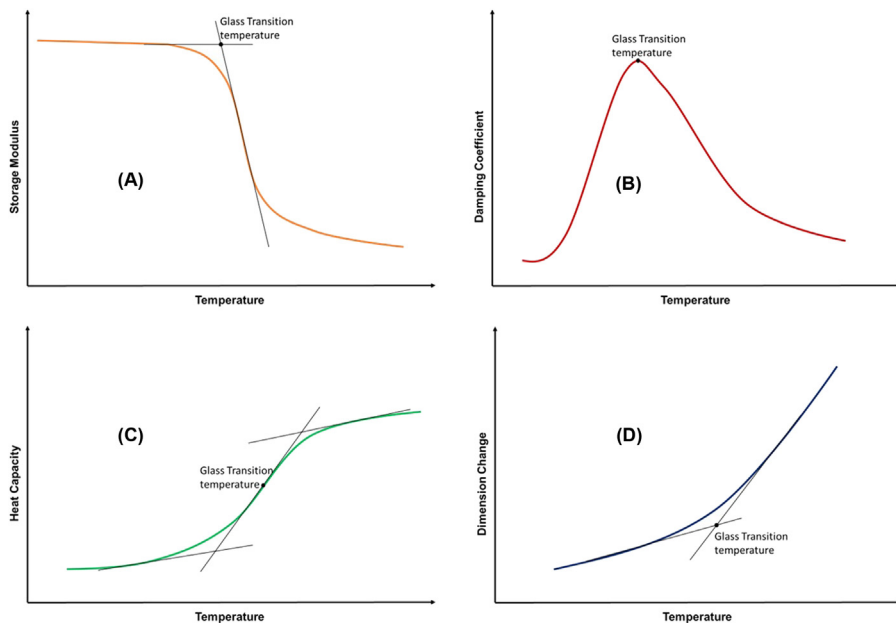


Figure 13.6 Measurement of glass transition temperature using (A) storage modulus and damping coefficient in dynamic mechanical analysis (DMA), (C) differential scanning calorimetry (DSC), and (D) thermomechanical analysis (TMA).

temperatures, as compared to the main polymer chain, which results in lower glass transition temperature with increase in ductility. Pradhan et al. (2011) studied the effect of plasticizers on polymer nanocomposite electrolytes. The plasticizer used is polyethylene glycol having a molecular weight of about 200. X-ray diffraction analysis shows that there was shift in polyethylene oxide peaks toward a lower angle when a plasticizer was added. This signifies increase in interplanar spacing. DSC results show that with increase in plasticizer content (polyethylene glycol), glass transition temperature (midpoint value of step) and crystalline melting temperature (peak point of melting endotherm) of composite material decrease. This decrease in T_g enhances the conductivity by facilitating the polymer chain motion at low temperatures. A similar type of results has also been obtained by other researchers, which use ethylene carbonate, polyethylene glycol, propylene carbonate, and so forth as plasticizers to enhance the conductivity of polymer electrolytes (Kumar & Sekhon, 2002; Tsutsumi et al., 1998). The main aim of using a plasticizer is to decrease the T_g , which signifies increase in amorphous content and a tendency of dissociating ion pairs into free cations and anions, which enhances the overall conductivity.

With growing environmental issues, researchers also shift toward the use of bio-based plasticizers such as vegetable oils (Hosney et al., 2018; Siqueira et al., 2009). In 2021, Ferreira et al. (2021) studied the rheology of ethylene-vinyl acetate

and styrene-butadiene-styrene blend with a cashew nutshell liquid plasticizer. As per the morphology study, the addition of a plasticizer results in a decrease in the domain size because of the interfacial action of the plasticizer. On the other hand, a bioplasticizer does not have any significant effect on storage modulus. Alamri et al. (2020) enhanced the ductility of poly (L-lactic acid) (PLLA) with the help of triacetin (TA) and glycerol monostearate (GMS) as plasticizers. Sample preparation was done with the help of the solution casting method at different weight percentage ratios of GMS/TA (25%:75%). As per DSC results, the T_g of neat PLLA is about 61°C, whereas with increase in GMA/TA content from 15 to 30 wt.% T_g of the blend decreases from 61°C (neat PLLA) to 23°C (30% GMA/TA). There is no such significant change in T_m temperature of the bioplastic. The ratio of crystallinity of bioplastic also increases with increase in the plasticizer content from 8% to 39%. All these results indicate that plasticizers increase the free space, which also improves the % elongation of bioplastic to 40 times that of neat PLLA.

Song et al. (2021) studied the effect of polyphosphoric acid (PPA) and plasticizers on asphalt. Different plasticizers were used to improve the low-temperature flexibility in asphalt such as dioctyl maleate. At the temperature of about 76°C, the storage and complex modulus of virgin asphalt was nearly zero. On the other hand, addition of PPA increases the thermal stability (both storage and complex modulus) of the asphalt by 405% and 536% at temperature of about 58°C. Thermal stability increases with increase in PPA content up to 2%, which is because protonic acid in PPA reacts with asphalt and converts it to asphaltene (i.e., from gel-solution structure to higher macromolecular content and strong interactions). In contrast, addition of a plasticizer reduces the complex and storage modulus of asphalt by 67.92% and 62.26% at 58°C for dioctyl phthalate and trioctyl trimellitate, respectively. The addition of PPA improves the thermal stability of plasticizer-modified asphalt. These results conclude that high temperature performance of asphalts in the presence of PPA transformed the resin into asphaltene, which results in function group reaction in asphalt.

Kawai and Hagura (2012) studied the rheology behavior of plasticized carbohydrate (dextrin) polymer systems by investigating heterogeneous and discontinuous glass transition temperatures. In this investigation, glucose and maltose were taken as the plasticizer and their effect on glass transition temperature on low molecular weight carbohydrate (dextrin) was studied. The DSC result of dextrin shows the endothermic peak at 198°C (T_g). Plasticizing of dextrin with glucose results in lowering the glass transition temperature. Moreover, as the content of glucose increases and reaches an equal content of dextrin, the glass transition temperature range becomes broader, which signifies the multiple T_g . When the content of glucose further increases, then a sudden drop in DSC graphs was observed, that is, shift from broad T_g to distinctive T_g . A similar type of behavior was observed when dextrin was plasticized with maltose. As per the DSC thermograph, the T_g behavior of carbohydrate-glucose and carbohydrate-maltose was divided into three regions: Region A, where the plasticizer has been trapped between polymer chains, resulting in lower glass transition temperature of the plasticizer carbohydrate system; Region B, where two phases were formed that are plasticizer-polymer phase and

plasticizer-rich phase. Firstly, T_g occurs in the plasticizer-rich phase and then in plasticizer–polymer phase, resulting in a broad range of glass transition temperatures; and Region C, where the plasticizer surrounds the polymer–plasticizer phase completely such that the polymer is embedded into the plasticizer. Therefore, a distinctive T_g has been observed, which is similar to T_g of a pure plasticizer.

13.6 Effect of molecular weight on glass transition temperature

The work of [Fox and Flory \(1950\)](#) states that glass transition temperature is a second order transition that does not come under thermodynamic transition. T_g originated from kinetic limitations that occurred due to internal adjustments of the polymer chain due to temperature change. Another important factor that affects the glass transition temperature of polymer composites is molecular weight. With increase in molecular weight, the amount of free space available is less as compared to low molecular weight polymer composites. Therefore, T_g increases with increase in molecular weight. Mathematically, the relation between glass transition temperature and molecular weight of a polymer, as given by the Fox–Flory equation, is

$$T_g = T_{g\infty} - K/M_n$$

where

T_g is the glass transition temperature of the polymer in Kelvin

M_n is the molecular weight of the polymer

$T_{g\infty}$ is the glass transition temperature for an infinite molecular chain composite in Kelvin

K is a constant

This mathematical model shows a linear increment in T_g with increase in molecular weight. This relation may not hold well for low molecular weight ([Clarson et al., 1985](#)) such as polydimethylsiloxane, which shows a slightly higher T_g with decrease in molecular weight.

[Beevers and White \(1960\)](#) studied the effect of the molecular weight of polymethylmethacrylate on its glass transition temperature. The average molecular weight of polymethylmethacrylate is found to vary between 3000 and 76,000 through the free radical polymerization technique. The refractometric technique has been employed to determine the glass transition temperature of polymethylmethacrylate. The result shows that the abovementioned linear relation shows optimum fit for infinite molecular weight glass transition temperature of about 387K and constant value of 2.1×10^5 K.mol/g for molecular weight above 10^4 mol/g. The mathematical expression is represented as

$$T_g(K) = 378 - 2.1 \times 10^5 / M_n$$

Blanchard et al. (1974) investigated the influence of molecular weight on glass transition temperature of polystyrene. Molecular weight of polystyrene varied from 900 to 1.8×10^6 mol/g. The DSC technique was employed to determine the glass transition temperature. After plotting the curve between T_g and $1/M_n$, it was found that the best fit was obtained for the $T_{g\infty}$ value of 106°C and K of $0.1 \times 10^5^\circ\text{C}$. mol/g. The final empirical relation obtained is

$$T_g(^{\circ}\text{C}) = 106 - 2.1 \times 10^5 / M_n$$

As per Blanchard et al. (1974), other than molecular weight, the heating rate also plays an important role in determining the glass transition temperature. In their experiment, the heating rate has been varied from 5°C to $80^\circ\text{C}/\text{min}$. Results show that T_g was higher for the higher heating rate. The mathematical relation is represented as

$$\log q = A - B/T_g$$

where q is the heating rate and A and B are constants.

Oguz et al. (2017) studied the effect of molecular weight on polyethylene oxide-based polyurethane–urea copolymers (PUUs). PUUs were synthesized by the pre-polymer method, and polymer films were prepared through the solution casting method. Three samples consisting of PEO-200, 4600, and 8000 with urethane at 30 wt.% were prepared. Three films have 100000 (PU-2), 232000 (PU-5), and 309000 (PU-8) g/mol^{-1} average molecular weights. Results show that with increase in molecular weight, glass transition temperature of films increases. PU-2 has T_g of about -57.2°C , PU-5 has -51.9°C , and PU-8 has -48.9°C .

Novikov and Rossler (2013) studied the correlation of molecular mass and glass transition temperature of the polymer and nonpolymeric glass formers. Their studies focus on the glass transition of molecular glasses and their correlation with molecular mass (M). Previous studies show that $T_g \cong 2T_m/3$, where T_m depends upon Debye frequency, intermolecular distance, and molecular mass. As per their investigation one parameter, that is, molecular mass, is a major notable factor for molecular glasses. In the case of a polymer, the relation between molecular mass and T_g mathematically is represented by the Fox–Flory equation, but it fails at low molecular masses. The end free group introduces free volume, which tends to decrease the T_g and saturation of T_g at a larger value of M , as shown in Fig. 13.7, where the free volume effect is ignored. After conducting different experiments, T_g vs M plots for molecular and nonpolymeric glass are plotted. A correlation between T_g and M was obtained and described by power law $T_g(M) \propto M^\alpha$, where $\alpha = 0.51$. A similar correlation was found for the melting point where $\alpha = 0.43$. Similar types of experiments were also performed on mono- and polyalcohols, alkanes (the number of C atoms not greater than 10), and aromatics. Correlation between T_g and T_m (scale down to $2/3$ factor) with molecular mass shows a similar power-law exponent of about 0.54 – 0.8 . In next analysis, they compare the dependence of T_g with M , at higher values of M for molecular glasses and some linear polymers. At a higher value of

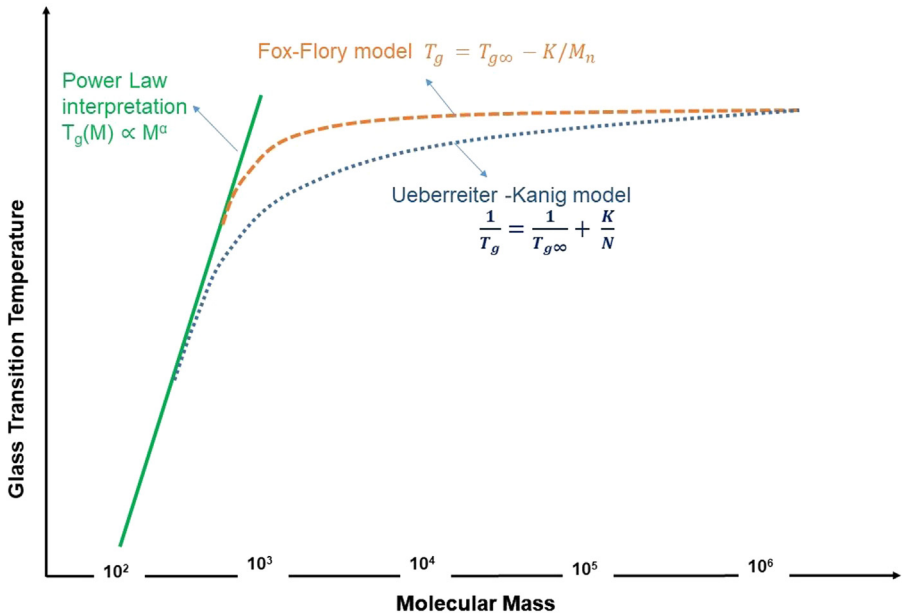


Figure 13.7 T_g vs M plot and fitting of various mathematical models.

molecular mass, the value of glass transition temperature becomes constant for most of the linear polymers. However, some linear polymers such as polydimethyl siloxane and polystyrene show almost similar behavior as compared molecular glass. Moreover, experiment data obtained has been fitted into the Fox–Flory model and Ueberreiter–Kanig model for polystyrene. The Ueberreiter–Kanig equation is

$$\frac{1}{T_g} = \frac{1}{T_{g\infty}} + \frac{K}{N}$$

where K is a constant, and N is the polymeric index.

The Fox–Flory model is not able to fit the data at lower molecular mass and best suited for intermediate value of M . The Ueberreiter–Kanig model shows optimal fit for all ranges of molecular mass.

13.7 Effect of a cross-linking agent on glass transition temperature

Cross-linking of the polymer chain also affects the glass transition temperature of polymer composites. The main reason behind the cross-linking of a polymer is the enhancement of the mechanical thermal and physical properties of polymer composites. The cross-linking of the main polymer chain is restricted, which increases

glass transition temperature, makes the damping peak wider, and leads to decrease in the peak value, as shown in Fig. 13.8, and increase in storage modulus of polymer composites. Other than that, in the case of thermoplastic composites, cross-linking agents may act as plasticizers by coming up in between the main polymer chain. This results in two transitions: one is associated with the moment of a side chain, also known as beta transition ($T\beta$); a cross-linking agent acts as a plasticizer, and a peak-related large-scale movement of the main polymer chain is observed.

Gadhave et al. (2019b) studied the effect of an epoxy silane cross-linker on the thermal-mechanical properties of starch/polyvinyl alcohol (PVA) blend films. -Si-OH groups of silica do not easily react with -OH groups of starch and PVA even at higher temperature (Hill et al., 2004). Therefore, hydrolyzing of alkoxy groups is done to activate the -Si-OH group to improve interaction with -OH groups of starch and PVA. The DMA result shows that the $\tan \delta$ peak, which represents the glass transition temperature, shifted toward higher temperature for those blends which were cross-linked with epoxy silane. Jain et al. in 2019 characterized the polyvinyl-based biocomposites cross-linked with hydrochloric acid. The reason behind the cross-linking is to restrict the solubility of PVA (due to presence of the -OH group). Cross-linking is done through dehydration, where the -OH group of PVA is replaced with Cl of hydrochloric acid, and esterification, where C-OH bonds of the same and different PVA chains react with two HCl to form -C-O-C- bonds. DMA results show two peaks in the $\tan \delta$ curve. The intensity of the second peak, which represents the glass temperature, decreases, and due to cross-linking, it is shifted toward a higher temperature side.

Gandhave et al. (2019a) improved the thermal and mechanical properties of different PVA grades (PVA-PH 88%–89% degree of hydrolysis), PVA-FH

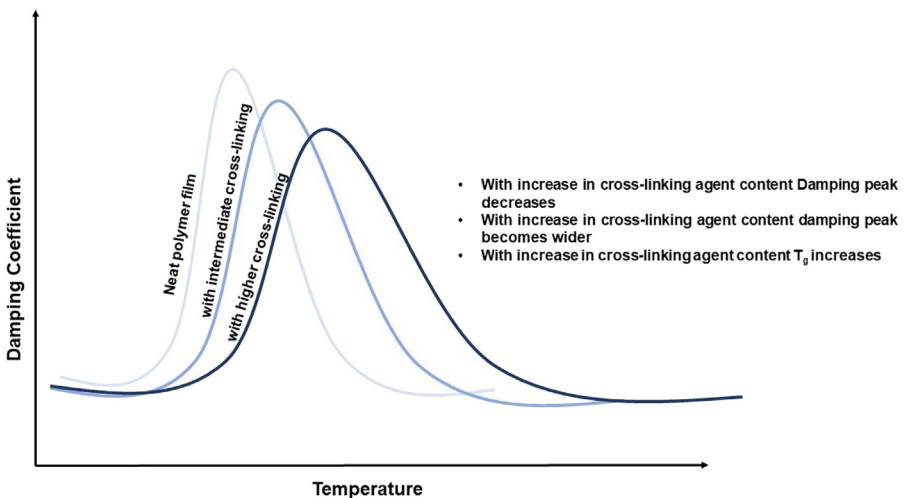


Figure 13.8 Effect of cross-linking agents on the damping coefficient measured in DMA analysis.

(97%–99% degree of hydrolysis), and modified PVA-M (97%–99% degree of hydrolysis) through cross-linking by boric acid. The DSC technique is employed to determine the glass transition temperature. PVA-FH has higher T_g as compared to PVA-PH and PVA-M due to a high degree of hydrolysis, which results in a high crystalline structure. With increase in the cross-linking agent content in PVA films, T_g values increase for all three cases. Moreover, with increase in cross-linking, the molecular weight of the films also increased. Therefore, cross-linking results in a larger chain structure, as compared to the precross-linked structure.

[Bandzierz et al. \(2016\)](#) studied the glass transition temperature of different cured elastomers to investigate the effect of cross-linking on polymer networks. In their work, different cross-linking agents such as tetramethylthiuram (TMTD), dicumyl peroxide (DCP), tetrabenzylthiuram disulfide (TBzTD), N-cyclohexyl-1-benzothiazyl sulfenamide (CBS)/rhombic sulfur (S_8), ZDT (2-ethylhexyl zinc)/ S_8 , DPG (1,3-diphenylguanidine)/ S_8 , MBTS (2,2'-dibenzothiazyl disulfide)/ S_8 , and vulcuren were used to cure styrene-butadiene rubber (SBR). A cross-linking agent results in different types of intermolecular cross-links such as C-C cross-links; cyclic sulfur structure; sulfidic cross-links; and pendent groups. Results show that curing through different agents results in a diversified cross-linked structure. Curing with DCP results in C-C cross-links; curing with TMTD results in C-C and monosulfidic cross-linking; curing with TBzTD results in monosulfidic cross-links; curing with vulcuren results in C-C and disulfidic cross-links; and curing with DPG, CBS, ZDT, and MBTS with S_8 results in polysulfidic and disulfidic cross-links as a major portion. All cross-linked SBRs have higher glass transition temperatures as compared to neat ones. Moreover, with the increase in the cross-linked density value of T_g linearly due to restriction in the mobility of the main chain. For single-component curatives, the increase in the value is lower.

[Zhang et al. \(2011\)](#) studied the effect of cross-linking agents on glass transition temperature of shape memory polymers (SMPs) based on styrene thermosets. In their work, polymerization of SMP is done through free radical reaction with butylacrylate and styrene as comonomers. Divinylbenzene was used as the cross-linking agent. Results show that both storage modulus and T_g increase with increase in cross-linking content from 1 to 4 wt.%. Moreover, with increase in cross-link content, there is decrement in the peak value; the peak becomes wider and relaxation activation energy also increased by 48.6%. The authors have a notable experience in the polymer composites field and computational mechanics ([Arpitha et al., 2021, 2022](#), [Bharath et al., 2020, 2021](#); [Bisht et al., 2021](#); [Chaturvedi et al., 2022, 2022a, 2022b](#), [Chaudhary et al., 2022a, 2022b](#); [Chaurasia et al., 2019](#); [Deji et al., 2022a,b,c,d](#); [Homer et al., 2022](#); [Jain et al., 2019](#); [Kataria et al., 2022a, 2022b](#); [Lila et al., 2022](#); [Prabhakaran et al., 2022](#); [Raja et al., 2022](#); [Rastogi et al., 2020](#); [Sethi et al., 2022](#); [Shankar et al., 2022a, 2022b](#); [Singh et al., 2020](#); [Thimmaiah et al., 2022](#); [Verma, 2022](#); [Verma et al., 2017, 2018, 2019a, 2019b, 2019c, 2019a, 2019b, 2019d, 2020a, 2020b, 2020a, 2020b, 2020c, 2020d, 2020e, 2021a, 2021b, 2022a, 2022b, 2022c, 2022d](#), [Verma & Parashar, 2017, 2018a, 2018b, 2018, 2020](#); [Verma & Sharma, 2022](#); [Verma & Singh, 2016a, 2016b, 2016](#)).

References

- Alamri, H. R., El-hadi, A. M., Al-Qahtani, S. M., Assaedi, H. S., & Alotaibi, A. S. (2020). Role of lubricant with a plasticizer to change the glass transition temperature as a result improving the mechanical properties of poly(lactic acid) PLLA. *Materials Research Express*, 7(2)025306. Available from <https://doi.org/10.1088/2053-1591/ab715a>.
- Altenhofen Da Silva, M., Adeodato Vieira, M. G., Gomes Maumoto, A. C., & Beppu, M. M. (2011). Polyvinylchloride (PVC) and natural rubber films plasticized with a natural polymeric plasticizer obtained through polyesterification of rice fatty acid. *Polymer Testing*, 30(5), 478–484. Available from <https://doi.org/10.1016/j.polymertesting.2011.03.008>.
- Arpitha, G. R., Verma, A., M R, S., Gorbatyuk, S., Khan, A., Sobahi, T. R., Asiri, A. M., & Siengchin, S. (2022). Bio-composite film from corn starch based vetiver cellulose. *Journal of Natural Fibers*, 19(16), 14634–14644. Available from <https://doi.org/10.1080/15440478.2022.2068174>.
- Arpitha, G. R., Verma, A., Sanjay, M. R., & Siengchin, S. (2021). Preparation and experimental investigation on mechanical and tribological performance of hemp-glass fiber reinforced laminated composites for lightweight applications. *Advances in Civil Engineering Materials*, 10(1), 427–439. Available from <https://doi.org/10.1520/ACEM20200187>, http://www.astm.org/DIGITAL_LIBRARY/JOURNALS/ACEM/acem_about.html.
- Bandeira, C. F., Montoro, S. R., Espindola, E. L., Botelho, E. C., Costa, M. L., & Cioffi, M. O. H. (2015). Comparison of glass transition temperature values of composite polymer obtained by TMA and DSC. *Applied Mechanics and Materials*, 719–720, 91–95. Available from <https://doi.org/10.4028/http://www.scientific.net/amm.719-720.91>.
- Bandzierz, K., Reuvekamp, L., Dryzek, J., Dierkes, W., Blume, A., & Bielinski, D. (2016). Influence of network structure on glass transition temperature of elastomers. *Materials*, 9(7), 607. Available from <https://doi.org/10.3390/ma9070607>.
- Beevers, R. B., & White, E. F. T. (1960). Physical properties of vinyl polymers: Part 1.—Dependence of the glass-transition temperature of polymethylmethacrylate on molecular weight. *Transactions of the Faraday Society*, 56, 744–752. Available from <https://doi.org/10.1039/TF9605600744>.
- Bharath, K. N., Madhu, P., Gowda, T. G. Y., Verma, A., Sanjay, M. R., & Siengchin, S. (2020). A novel approach for development of printed circuit board from biofiber based composites. *Polymer Composites*, 41(11), 4550–4558. Available from <https://doi.org/10.1002/pc.25732>, [http://onlinelibrary.wiley.com/journal/10.1002/\(ISSN\)1548-0569](http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1548-0569).
- Bharath, K. N., Madhu, P., Yashas Gowda, T. G., Verma, A., Sanjay, M. R., & Siengchin, S. (2021). Mechanical and chemical properties evaluation of sheep wool fiber-reinforced vinyl ester and polyester composites. *Materials Performance and Characterization*, 10(1), 99–109. Available from <https://doi.org/10.1520/MPC20200036>, https://www.astm.org/DIGITAL_LIBRARY/JOURNALS/MPC/index.html.
- Bisht, N., Verma, A., Chauhan, S., & Singh, V. K. (2021). Effect of functionalized silicon carbide nano-particles as additive in cross-linked PVA based composites for vibration damping application. *Journal of Vinyl and Additive Technology*, 27(4), 920–932. Available from <https://doi.org/10.1002/vnl.21865>, [http://onlinelibrary.wiley.com/journal/10.1002/\(ISSN\)1548-0585](http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1548-0585).
- Blanchard, L.-P., Hesse, J., & Malhotra, S. L. (1974). Effect of molecular weight on glass transition by differential scanning calorimetry. *Canadian Journal of Chemistry*, 52(18), 3170–3175. Available from <https://doi.org/10.1139/v74-465>.

- Bortel, K. (2008). *Auxiliaries used in the processing of polymeric plastics*. Part 2, Lukaszewicz Research Network—Institute of Polymer Materials and Dyes Engineering.
- Chanda, M., & Roy, K. S. (2006). *Plastics technology handbook*. CRC Press. Available from <https://doi.org/10.1201/9781420006360>.
- Chaturvedi, S., Verma, A., Sethi, S. K., Mavinkere Rangappa, S., & Siengchin, S. (2022). *Stalk fibers (rice, wheat, barley, etc.) composites and applications. Plant fibers, their composites, and applications* (pp. 347–362). India: Elsevier. Available from <https://www.sciencedirect.com/book/9780128245286>, <https://doi.org/10.1016/B978-0-12-824528-6.00009-6>.
- Chaturvedi, S., Verma, A., Sethi, S. K., & Ogata, S. (2022a). *Defect energy calculations of nickel, copper and aluminium (and their alloys): Molecular dynamics approach. Lecture notes in applied and computational mechanics* (pp. 157–186). India: Springer Science and Business Media Deutschland GmbH. Available from <http://www.springer.com/series/4623>, https://doi.org/10.1007/978-981-19-3092-8_8.
- Chaturvedi, S., Verma, A., Singh, S. K., & Ogata, S. (2022b). *EAM inter-atomic potential—its implication on nickel, copper, and aluminum (and their alloys). Lecture notes in applied and computational mechanics* (pp. 133–156). India: Springer Science and Business Media Deutschland GmbH. Available from <http://www.springer.com/series/4623>, https://doi.org/10.1007/978-981-19-3092-8_7.
- Chaudhary, A., Sharma, S., & Verma, A. (2022a). Optimization of WEDM process parameters for machining of heat treated ASSAB '88 tool steel using Response surface methodology (RSM). *Materials Today: Proceedings*, 50, 917–922. Available from <https://doi.org/10.1016/j.matpr.2021.06.314>.
- Chaudhary, A., Sharma, S., & Verma, A. (2022b). WEDM machining of heat treated ASSAB '88 tool steel: A comprehensive experimental analysis. *Materials Today: Proceedings*, 50, 946–951. Available from <https://doi.org/10.1016/j.matpr.2021.06.354>.
- Chaurasia, A., Verma, A., Parashar, A., & Mulik, R. S. (2019). Experimental and computational studies to analyze the effect of h-BN nanosheets on mechanical behavior of h-BN/polyethylene nanocomposites. *Journal of Physical Chemistry C*, 123(32), 20059–20070. Available from <https://doi.org/10.1021/acs.jpcc.9b05965>, <http://pubs.acs.org/journal/jpcceck>.
- Clarson, S. J., Dodgson, K., & Semlyen, J. A. (1985). Studies of cyclic and linear poly (dimethylsiloxanes): 19. Glass transition temperatures and crystallization behaviour. *Polymer*, 26(6), 930–934. Available from [https://doi.org/10.1016/0032-3861\(85\)90140-5](https://doi.org/10.1016/0032-3861(85)90140-5).
- Datta, R. (2002). Rubber curing systems. In *Rapra review reports*, (144). RAPRA Technology Ltd.
- Deji, R., Jyoti, R., Verma, A., Choudhary, B. C., & Sharma, R. K. (2022a). A theoretical study of HCN adsorption and width effect on co-doped armchair graphene nanoribbon. *Computational and Theoretical Chemistry*, 1209(ISSN 2210-271X), 113592. Available from <https://doi.org/10.1016/j.comptc.2022.113592>.
- Deji, R., Verma, A., Choudhary, B. C., & Sharma, R. K. (2022b). New insights into NO adsorption on alkali metal and transition metal doped graphene nanoribbon surface: A DFT approach. *Journal of Molecular Graphics and Modelling*, 11108109. Available from <https://doi.org/10.1016/j.jmgm.2021.108109>.
- Deji, R., Verma, A., Kaur, N., Choudhary, B. C., & Sharma, R. K. (2022c). Density functional theory study of carbon monoxide adsorption on transition metal doped armchair graphene nanoribbon. *Materials Today: Proceedings*, 54, 771–776. Available from <https://doi.org/10.1016/j.matpr.2021.11.078>, <https://www.sciencedirect.com/journal/materials-today-proceedings>.

- Deji, R., Verma, A., Kaur, N., Choudhary, B. C., & Sharma, R. K. (2022d). Adsorption chemistry of co-doped graphene nanoribbon and its derivatives towards carbon based gases for gas sensing applications: Quantum DFT investigation. *Materials Science in Semiconductor Processing*, 146106670. Available from <https://doi.org/10.1016/j.mssp.2022.106670>.
- Faruk, O., Bledzki, A. K., Fink, H. P., & Sain, M. (2012). Biocomposites reinforced with natural fibers: 2000-2010. *Progress in Polymer Science*, 37(11), 1552–1596. Available from <https://doi.org/10.1016/j.progpolymsci.2012.04.003>.
- Ferreira, I. P., Sirqueira, Ad. S., Santos, T. Ad, Naccache, M. F., & Soares, B. G. (2021). Rheological studies of SBS/EVA blends modified with bio-based cashew nut shell liquid. *Journal of Elastomers and Plastics*, 51(7), 825–840. Available from <https://doi.org/10.1177/0095244321990407>, <https://journals.sagepub.com/home/jep>.
- Fox, T. G., & Flory, P. J. (1950). Second-order transition temperatures and related properties of polystyrene. i. influence of molecular weight. *Journal of Applied Physics*, 21(6), 581–591. Available from <https://doi.org/10.1063/1.1699711>.
- Frados, J. (1976). *Plastics engineering handbook*. Van Nostrand Reinhold.
- Gadhve, R. V., Mahanwar, P. A., & Gadekar, P. T. (2019a). Study of cross-linking between boric acid and different types of polyvinyl alcohol adhesive. *Open Journal of Polymer Chemistry*, 9(01), 16–26. Available from <https://doi.org/10.4236/ojpcchem.2019.91002>.
- Gadhve, R. V., Mahanwar, P. A., & Gadekar, P. T. (2019b). Cross-linking of polyvinyl alcohol/starch blends by epoxy silane for improvement in thermal and mechanical properties. *BioResources*, 14(2), 3833–3843. Available from <https://doi.org/10.15376/biores.14.2.3833-3843>, http://www.ncsu.edu/bioresources/Back_Issues.htm.
- Godwin, A. D., & Krauskopf, L. G. (2008). *Handbook of vinyl formulating monomeric plasticizers*. Wiley. Available from <https://doi.org/10.1002/9780470253595.ch7>.
- Greener Donhowe, I., & Fennema, O. (1993). The effects of plasticizers on crystallinity, permeability, and mechanical properties of methylcellulose films. *Journal of Food Processing and Preservation*, 17(4), 247–257. Available from <https://doi.org/10.1111/j.1745-4549.1993.tb00729.x>.
- Hill, C. A. S., Farahani, M. R. M., & Hale, M. D. C. (2004). The use of organoalkoxysilane coupling agents for wood preservation. *Holzforschung*, 58(3), 316–325. Available from <https://doi.org/10.1515/HF.2004.049>.
- Homer, E. R., Verma, A., Britton, D., Johnson, O. K., & Thompson, G. B. (2022). Simulated migration behavior of metastable $\Sigma 3$ (11 8 5) incoherent twin grain boundaries. *IOP Conference Series: Materials Science and Engineering*, 1249(1)012019. Available from <https://doi.org/10.1088/1757-899x/1249/1/012019>.
- Hosney, H., Nadiem, B., Ashour, I., Mustafa, I., & El-Shibiny, A. (2018). Epoxidized vegetable oil and bio-based materials as PVC plasticizer. *Journal of Applied Polymer Science*, 135(20), 46270. Available from <https://doi.org/10.1002/app.46270>.
- Jain, N., Verma, A., & Singh, V. K. (2019). Dynamic mechanical analysis and creep-recovery behaviour of polyvinyl alcohol based cross-linked biocomposite reinforced with basalt fiber. *Materials Research Express*, 6(10)105373. Available from <https://doi.org/10.1088/2053-1591/ab4332>.
- Kataria, A., Verma, A., Sanjay, M. R., & Siengchin, S. (2022). Molecular modeling of 2D graphene grain boundaries: Mechanical and fracture aspects. *Materials Today: Proceedings*, 2404–2408. Available from <https://doi.org/10.1016/j.matpr.2021.10.416>.
- Kataria, A., Verma, A., Sethi, S. K., & Ogata, S. (2022). *Introduction to interatomic potentials/forcefields*. *Lecture notes in applied and computational mechanics* (pp. 21–49). India: Springer Science and Business Media Deutschland GmbH. Available from <http://www.springer.com/series/4623>, https://doi.org/10.1007/978-981-19-3092-8_2.

- Kawai, K., & Hagura, Y. (2012). Discontinuous and heterogeneous glass transition behavior of carbohydrate polymer–plasticizer systems. *Carbohydrate Polymers*, 89(3), 836–841. Available from <https://doi.org/10.1016/j.carbpol.2012.04.018>.
- Krauskopf, L. G., & Godwin, A. (2005). *Plasticizers. PVC Handbook*. HANSER.
- Kumar, M., & Sekhon, S. S. (2002). Role of plasticizer's dielectric constant on conductivity modification of PEO–NH4F polymer electrolytes. *European Polymer Journal*, 38. Available from [https://doi.org/10.1016/s0014-3057\(01\)00310-x](https://doi.org/10.1016/s0014-3057(01)00310-x).
- Langer, E., Bortel, K., Waskiewicz, S., & Lenartowicz-Klik, M. (2020). In E. Langer, K. Bortel, S. Waskiewicz, & M. Lenartowicz-Klik (Eds.), *Plastics design library, plasticizers derived from post-consumer PET*. William Andrew Publishing. Available from <https://doi.org/10.1016/B978-0-323-46200-6.00002-7>.
- Lila, M. K., Verma, A., & Bhurat, S. S. (2022). *Impact behaviors of epoxy/synthetic fiber composites* (pp. 1–18). Springer Science and Business Media LLC. Available from https://doi.org/10.1007/978-981-15-8141-0_55-1.
- Maitra, J., & Shukla, V. K. (2014). Cross-linking in hydrogels—A review. *American Journal of Polymer Science*, 4(2). Available from <https://doi.org/10.5923/j.ajps.20140402.01>.
- Menard, K. P., & Menard, N. R. (2020). *Dynamic mechanical analysis*. CRC Press. Available from <https://doi.org/10.1201/9780429190308>.
- Miyazaki, T., Takeda, Y., Akane, S., Itou, T., Hoshiko, A., & En, K. (2010). Role of boric acid for a poly (vinyl alcohol) film as a cross-linking agent: Melting behaviors of the films with boric acid. *Polymer*, 23, 5539–5549. Available from <https://doi.org/10.1016/j.polymer.2010.09.048>, <http://www.journals.elsevier.com/polymer/>.
- Moreno, R. (1992). The role of slip additives in tape casting technology, part II—binders and plasticizers. *Journal of the American Ceramic Society*, 71(11), 1647–1657.
- Nielsen, L. E. (1969). Cross-linking—effect on physical properties of polymers. *Journal of Macromolecular Science, Part C*, 3(1), 69–103. Available from <https://doi.org/10.1080/15583726908545897>.
- Novikov, V. N., & Rössler, E. A. (2013). Correlation between glass transition temperature and molecular mass in non-polymeric and polymer glass formers. *Polymer*, 54(26), 6987–6991. Available from <https://doi.org/10.1016/j.polymer.2013.11.002>, <http://www.journals.elsevier.com/polymer/>.
- Oguz, O., Koutsoumpis, S. A., Simsek, E., Yilgor, E., Yilgor, I., Pissis, P., & Menciloglu, Y. Z. (2017). Effect of soft segment molecular weight on the glass transition, crystallinity, molecular mobility and segmental dynamics of poly(ethylene oxide) based poly (urethane–urea) copolymers. *RSC Advances*, 7(65), 40745–40754. Available from <https://doi.org/10.1039/c7ra08007g>.
- Prabhakaran, S., Sharma, S., Verma, A., Rangappa, S. M., & Siengchin, S. (2022). Mechanical, thermal, and acoustical studies on natural alternative material for partition walls: A novel experimental investigation. *Polymer Composites*, 43(7), 4711–4720. Available from <https://doi.org/10.1002/pc.26723>, [http://onlinelibrary.wiley.com/journal/10.1002/\(ISSN\)1548-0569](http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1548-0569).
- Pradhan, D. K., Samantaray, B. K., Choudhary, R. N. P., Karan, N. K., Thomas, R., & Katiyar, R. S. (2011). Effect of plasticizer on structural and electrical properties of nano-composite solid polymer electrolytes. *Ionics*, 17(2), 127–134. Available from <https://doi.org/10.1007/s11581-010-0491-5>.
- Raja, S., Verma, A., Rangappa, S. M., & Siengchin, S. (2022). Development and experimental analysis of polymer based composite bipolar plate using Aquila Taguchi optimization: Design of experiments. *Polymer Composites*, 43(8), 5522–5533. Available from <https://doi.org/10.1002/pc.26861>, [http://onlinelibrary.wiley.com/journal/10.1002/\(ISSN\)1548-0569](http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1548-0569).

- Rastogi, S., Verma, A., & Singh, V. K. (2020). Experimental response of nonwoven waste cellulose fabric-reinforced epoxy composites for high toughness and coating applications. *Materials Performance and Characterization*, 9(1), 151–172. Available from <https://doi.org/10.1520/MPC20190251>, https://www.astm.org/DIGITAL_LIBRARY/JOURNALS/MPC/index.html.
- Sejidov, F. T., Mansoori, Y., & Goodarzi, N. (2005). Esterification reaction using solid heterogeneous acid catalysts under solvent-less condition. *Journal of Molecular Catalysis A: Chemical*, 240(1-2), 186–190. Available from <https://doi.org/10.1016/j.molcata.2005.06.048>.
- Sethi, S. K., Gogoi, R., Verma, A., & Manik, G. (2022). How can the geometry of a rough surface affect its wettability?—A coarse-grained simulation analysis. *Progress in Organic Coatings*, 172107062. Available from <https://doi.org/10.1016/j.porgcoat.2022.107062>.
- Shankar, U., Gogoi, R., Sethi, S. K., & Verma, A. (2022). *Introduction to materials studio software for the atomistic-scale simulations. Lecture notes in applied and computational mechanics* (pp. 299–313). India: Springer Science and Business Media Deutschland GmbH. Available from <http://www.springer.com/series/4623>, https://doi.org/10.1007/978-981-19-3092-8_15.
- Shankar, U., Sethi, S. K., & Verma, A. (2022). *Forcefields and modeling of polymer coatings and nanocomposites. Lecture notes in applied and computational mechanics* (pp. 81–98). India: Springer Science and Business Media Deutschland GmbH. Available from <http://www.springer.com/series/4623>, https://doi.org/10.1007/978-981-19-3092-8_4.
- Singh, K., Jain, N., Verma, A., Singh, V. K., & Chauhan, S. (2020). Functionalized graphite-reinforced cross-linked poly(vinyl alcohol) nanocomposites for vibration isolator application: Morphology, mechanical, and thermal assessment. *Materials Performance and Characterization*, 9(1). Available from <https://doi.org/10.1520/MPC20190254>, https://www.astm.org/DIGITAL_LIBRARY/JOURNALS/MPC/index.html.
- Sirqueira, A. S., Reis, R., Sirelli, L., Silva, M. V. O., & Monteiro, R. V. (2009). Nitrigreen the ecological rubber. *Polimeros.*, 19(1), 10–13. Available from <https://doi.org/10.1590/s0104-14282009000100007>, <http://www.scielo.br/pdf/po/v19n1/07.pdf>.
- Song, R., Sha, A., Shi, K., Li, J., Li, X., & Zhang, F. (2021). Polyphosphoric acid and plasticizer modified asphalt: Rheological properties and modification mechanism. *Construction and Building Materials* 125158. Available from <https://doi.org/10.1016/j.conbuildmat.2021.125158>.
- Thimmaiah, S. H., Narayanappa, K., Thyavihalli Girijappa, Y., Gulihonenahali Rajakumara, A., Hemath, M., Thiagamani, S. M. K., & Verma, A. (2022). An artificial neural network and Taguchi prediction on wear characteristics of Kenaf–Kevlar fabric reinforced hybrid polyester composites. *Polymer Composites*. Available from <https://doi.org/10.1002/pc.27043>, [http://onlinelibrary.wiley.com/journal/10.1002/\(ISSN\)1548-0569](http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1548-0569).
- Ticoalu, A., Aravinthan, T., & Cardona, F. (2010). A review of current development in natural fiber composites for structural and infrastructure applications. Southern Region Engineering Conference, Toowoomba, Australia.
- Tsutsumi, H., Matsuo, A., Onimura, K., & Oishi, T. (1998). Conductivity enhancement of a polyacrylonitrile-based polymer electrolyte containing cascade nitrile as a plasticizer. *Electrochemical and Solid-State Letters*, 1. Available from <https://doi.org/10.1149/1.1390700>.
- Verma, A., Baurai, K., Sanjay, M. R., & Siengchin, S. (2020). Mechanical, microstructural, and thermal characterization insights of pyrolyzed carbon black from waste tires

- reinforced epoxy nanocomposites for coating application. *Polymer Composites*, 41(1), 338–349. Available from <https://doi.org/10.1002/pc.25373>, [http://onlinelibrary.wiley.com/journal/10.1002/\(ISSN\)1548-0569](http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1548-0569).
- Verma, A., Budiyal, L., Sanjay, M. R., & Siengchin, S. (2019). Processing and characterization analysis of pyrolyzed oil rubber (from waste tires)-epoxy polymer blend composite for lightweight structures and coatings applications. *Polymer Engineering and Science*, 59(10), 2041–2051. Available from <https://doi.org/10.1002/pen.25204>, [http://onlinelibrary.wiley.com/journal/10.1002/\(ISSN\)1548-2634](http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1548-2634).
- Verma, A., Gaur, A., & Singh, V. K. (2017). Mechanical properties and microstructure of starch and sisal fiber biocomposite modified with epoxy resin. *Materials Performance and Characterization*, 6(1), 500–520. Available from <https://doi.org/10.1520/MPC20170069>, https://www.astm.org/DIGITAL_LIBRARY/JOURNALS/MPC/index.html.
- Verma, A., Jain, N., Kalpana., Rangappa, S. M., Siengchin, S., & Jawaid, M. (2020). *Natural fibers based bio-phenolic composites* (pp. 153–168). Springer Science and Business Media LLC. Available from https://doi.org/10.1007/978-981-15-8932-4_10.
- Verma, A., Jain, N., & Mishra, R. R. (2022). *Applications and drawbacks of epoxy/natural fiber composites* (pp. 1–15). Springer Science and Business Media LLC. Available from https://doi.org/10.1007/978-981-15-8141-0_32-1.
- Verma, A., Jain, N., Parashar, A., Gaur, A., Sanjay, M. R., & Siengchin, S. (2020). *Lifecycle assessment of thermoplastic and thermosetting bamboo composites* (pp. 235–246). Springer Science and Business Media LLC. Available from https://doi.org/10.1007/978-981-15-8489-3_13.
- Verma, A., Jain, N., Parashar, A., Singh, V. K., Sanjay, M. R., & Siengchin, S. (2020a). *Design and modeling of lightweight polymer composite structures* (pp. 193–224). Informa UK Limited. Available from <https://doi.org/10.1201/9780429244087-7>.
- Verma, A., Jain, N., Parashar, A., Singh, V. K., Sanjay, M. R., & Siengchin, S. (2020b). *Lightweight graphene composite materials* (pp. 1–20). Informa UK Limited. Available from <https://doi.org/10.1201/9780429244087-1>.
- Verma, A., Jain, N., Rastogi, S., Dogra, V., Sanjay, S. M., Siengchin, S., & Mansour, R. (2020). *Mechanism, anti-corrosion protection and components of anti-corrosion polymer coatings* (pp. 53–66). Informa UK Limited. Available from <https://doi.org/10.1201/9780429199226-4>.
- Verma, A., Jain, N., Sanjay, M. R., & Siengchin, S. (2022). *Viscoelastic properties of completely biodegradable polymer-based composites* (pp. 173–188). Informa UK Limited. Available from <https://doi.org/10.1201/9781003173625-11>.
- Verma, A., Jain, N., & Sethi, S. K. (2022). *Modeling and simulation of graphene-based composites. Innovations in Graphene-Based Polymer Composites* (pp. 167–198). India: Elsevier. Available from <https://www.sciencedirect.com/book/9780128237892>, <https://doi.org/10.1016/B978-0-12-823789-2.00001-7>.
- Verma, A., Jain, N., Singh, K., Singh, V. K., Rangappa, S. M., & Siengchin, S. (2021). *PVA-based blends and composites. Biodegradable polymers, blends and composites* (pp. 309–326). India: Elsevier. Available from <https://www.sciencedirect.com/book/9780128237915/biodegradable-polymers-blends-and-composites>, <https://doi.org/10.1016/B978-0-12-823791-5.00010-7>.
- Verma, A., Joshi, K., Gaur, A., & Singh, V. K. (2018). Starch-jute fiber hybrid biocomposite modified with an epoxy resin coating: Fabrication and experimental characterization. *Journal of the Mechanical Behavior of Materials*, 27(5–6). Available from <https://doi.org/10.1515/jmbm-2018-2006>, <http://www.degruyter.com/view/j/jmbm>.
- Verma, A., Kumar, R., & Parashar, A. (2019). Enhanced thermal transport across a bi-crystalline graphene-polymer interface: An atomistic approach. *Physical Chemistry*

- Chemical Physics*, 21(11), 6229–6237. Available from <https://doi.org/10.1039/c9cp00362b>, <http://pubs.rsc.org/en/journals/journal/cp>.
- Verma, A., Negi, P., & Singh, V. K. (2019). Experimental analysis on carbon residuum transformed epoxy resin: Chicken feather fiber hybrid composite. *Polymer Composites*, 40(7), 2690–2699. Available from <https://doi.org/10.1002/pc.25067>, [http://onlinelibrary.wiley.com/journal/10.1002/\(ISSN\)1548-0569](http://onlinelibrary.wiley.com/journal/10.1002/(ISSN)1548-0569).
- Verma, A., & Parashar, A. (2018a). Structural and chemical insights into thermal transport for strained functionalised graphene: A molecular dynamics study. *Materials Research Express*, 5(11)115605. Available from <https://doi.org/10.1088/2053-1591/aade36>.
- Verma, A., & Parashar, A. (2018b). Molecular dynamics based simulations to study failure morphology of hydroxyl and epoxide functionalised graphene. *Computational Materials Science*, 143, 15–26. Available from <https://doi.org/10.1016/j.commatsci.2017.10.048>.
- Verma, A., Parashar, A., Jain, N., Singh, V. K., Rangappa, S. M., & Siengchin, S. (2020). *Surface modification techniques for the preparation of different novel biofibers for composites. Biofibers and biopolymers for biocomposites: Synthesis, characterization and properties* (pp. 1–34). India: Springer International Publishing. Available from <http://doi.org/10.1007/978-3-030-40301-0>, https://doi.org/10.1007/978-3-030-40301-0_1.
- Verma, A., Parashar, A., & Packirisamy, M. (2019a). Role of chemical adatoms in fracture mechanics of graphene nanolayer. *Materials Today: Proceedings*, 11, 920–924. Available from <https://doi.org/10.1016/j.matpr.2018.12.019>, 1 2019/01, <https://www.sciencedirect.com/journal/materials-today-proceedings>.
- Verma, A., Parashar, A., & Packirisamy, M. (2019b). Effect of grain boundaries on the interfacial behaviour of graphene-polyethylene nanocomposite. *Applied Surface Science*, 470, 1085–1092. Available from <https://doi.org/10.1016/j.apsusc.2018.11.218>, <http://www.journals.elsevier.com/applied-surface-science/>.
- Verma, A., Parashar, A., & Packirisamy, M. (2018a). Atomistic modeling of graphene/hexagonal boron nitride polymer nanocomposites: A review. *Wiley Interdisciplinary Reviews: Computational Molecular Science*, 8(3). Available from <https://doi.org/10.1002/wcms.1346>, [http://onlinelibrary.wiley.com/journal/10.1111/\(ISSN\)1759-0884](http://onlinelibrary.wiley.com/journal/10.1111/(ISSN)1759-0884).
- Verma, A., Parashar, A., & Packirisamy, M. (2018b). Tailoring the failure morphology of 2D bicrystalline graphene oxide. *Journal of Applied Physics*, 124(1)015102. Available from <https://doi.org/10.1063/1.5033542>.
- Verma, A., Parashar, A., Singh, S. K., Jain, N., Sanjay, S. M., & Siengchin, S. (2020). *Modeling and simulation in polymer coatings* (pp. 309–324). Informa UK Limited. Available from <https://doi.org/10.1201/9780429199226-16>.
- Verma, A., Parashar, A., & Van Duin, A. C. T. (2022). *Graphene-reinforced polymeric membranes for water desalination and gas separation/barrier applications. Innovations in graphene-based polymer composites* (pp. 133–165). United States: Elsevier. Available from <https://www.sciencedirect.com/book/9780128237892>, <https://doi.org/10.1016/B978-0-12-823789-2.00009-1>.
- Verma, A., & Parashar, A. (2020). *Characterization of 2d nanomaterials for energy storage, Lecture notes in mechanical engineering* (21954364, pp. 221–226). Springer Science and Business Media Deutschland GmbH India. Available from https://doi.org/10.1007/978-981-15-1189-9_18, <http://www.springer.com/series/11236>, 1 2020/01.
- Verma, A., & Parashar, A. (2017). The effect of STW defects on the mechanical properties and fracture toughness of pristine and hydrogenated graphene. *Physical Chemistry Chemical Physics*, 19(24), 16023–16037. Available from <https://doi.org/10.1039/c7cp02366a>, <http://www.rsc.org/Publishing/Journals/CP/index.asp>.

- Verma, A., & Parashar, A. (2018). Reactive force field based atomistic simulations to study fracture toughness of bicrystalline graphene functionalised with oxide groups. *Diamond and Related Materials*, 88, 193–203. Available from <https://doi.org/10.1016/j.diamond.2018.07.014>.
- Verma, A., & Sharma, S. (2022). *Atomistic simulations to study thermal effects and strain rate on mechanical and fracture properties of graphene like BC3*. *Lecture notes in applied and computational mechanics* (pp. 237–252). India: Springer Science and Business Media Deutschland GmbH. Available from <http://www.springer.com/series/4623>, https://doi.org/10.1007/978-981-19-3092-8_12.
- Verma, A., & Singh, V. K. (2016a). Human hair: A biodegradable composite fiber—a review. *International Journal of Waste Resources*, 6(2). Available from <https://doi.org/10.4172/2252-5211.1000206>.
- Verma, A., & Singh, V. K. (2016b). Experimental investigations on thermal properties of coconut shell particles in DAP solution for use in green composite applications. *Journal of Material Sciences and Engineering*, 5(3).
- Verma, A., & Singh, V. K. (2016). Experimental characterization of modified epoxy resin assorted with almond shell particles. *ESSENCE-International Journal for Environmental Rehabilitation and Conservation*, 7(1), 36–44.
- Verma, A., & Singh, V. K. (2019). Mechanical, microstructural and thermal characterization of epoxy-based human hair-reinforced composites. *Journal of Testing and Evaluation*, 47(2), 1193–1215. Available from <https://doi.org/10.1520/JTE20170063>, https://www.astm.org/DIGITAL_LIBRARY/JOURNALS/TESTEVAL/jote_issues.html.
- Verma, A., Singh, C., Singh, V. K., & Jain, N. (2019). Fabrication and characterization of chitosan-coated sisal fiber—Phytigel modified soy protein-based green composite. *Journal of Composite Materials*, 53(18), 2481–2504. Available from <https://doi.org/10.1177/0021998319831748>, <http://jcm.sagepub.com/content/by/year>.
- Verma, A., Zhang, W., & Van Duin, A. C. T. (2021). ReaxFF reactive molecular dynamics simulations to study the interfacial dynamics between defective h-BN nanosheets and water nanodroplets. *Physical Chemistry Chemical Physics*, 23(18), 10822–10834. Available from <https://doi.org/10.1039/d1cp00546d>, <http://pubs.rsc.org/en/journals/journal/cp>.
- Verma, A. (2022). A perspective on the potential material candidate for railway sector applications: PVA based functionalized graphene reinforced composite. *Applied Science and Engineering Progress*, 15(2). Available from <https://doi.org/10.14416/j.asep.2022.03.009>, <https://ojs.kmutnb.ac.th/index.php/ijst/article/view/5727>.
- Vieira, M. G. A., Da Silva, M. A., Dos Santos, L. O., & Beppu, M. M. (2011). Natural-based plasticizers and biopolymer films: A review. *European Polymer Journal*, 47(3), 254–263. Available from <https://doi.org/10.1016/j.eurpolymj.2010.12.011>.
- Wilson, A. S. (1995). *Plasticizers principles and practice*. Cambridge: The Institute of Materials.
- Wypych, G. (2017). *Handbook of plasticizers*. ChemTec Publishing.
- Yesid, O. (2014). *Encyclopedia of polymers and composites*. <https://doi.org/10.1007/978-3-642-37179-0>.
- Zhang, D., Liu, Y., Yu, K., & Leng, J. (2011). Influence of cross-linking agent on thermomechanical properties and shape memory effect of styrene shape memory polymer. *Journal of Intelligent Material Systems and Structures*, 22(18), 2147–2154. Available from <https://doi.org/10.1177/1045389X11425282>.