JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

Dynamic mechanical analysis, time dependent behaviour of polyester based polymer nanocomposite under constant load

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Abstract: This work focuses on the study of dynamic mechanical behavior of polymer nanocomposite under varying load conditions and also the creep performance under tensile loading. Wide acceptability and applications of the polymer nanocomposite initiated the study. Technique of Time Temperature superposition (TTS) used to predict the long term creep behavior. Time-dependent reversible stress-strain behavior of the viscoelastic materials under the influence of nanoparticle is analysed. Creep compliance indicated a steady nature of variation. Storage modulus, loss modulus and damping properties within the temperature limit 0^{O}C to 140^{O}C analysed. With the increase of frequency the stiffness value increased but the presence of nanoclay causes to decrease.

Key words: nanoclay, creep compliance, viscoelastic

I. INTRODUCTION

Polymer nanocomposites, have gained wide acceptability as an alternative to conventional polymer composites in many applications. Polymer systems are widely used because of their light weight, design flexibility, easy processability and other desirable features [8]. Polymer materials exhibit time dependent behavior, which is critical in many applications. The strain induced; when a load applied and the stress induced when a strain is applied are functions of time. The stress-strain-time relationship, or constitutive law, can be determined by loading a polymer specimen with constant stress (creep) or constant strain (stress relaxation). When polymer material is subjected to a constant load, it deforms continuously. The initial strain is roughly predicted by its stress-strain modulus. The material will continue to deform slowly with time indefinitely or until rupture. The primary region is the early stage of loading when the creep rate decreases rapidly with time. This phenomenon of deformation under load with time is called creep. High loads and high temperatures will accelerate the creep process. Creep is often regarded as one of the life-limiting factors when materials are required to service for long periods under stress at elevated temperatures. Hence it is very significant in material for application in aviation purpose.

Creep resistance is an important proper0ty for polymeric materials for many applications such as aerospace, biomedical and civil engineering [9]. However, it is often impractical to test long-term creep behavior directly with experiment because of the extremely long time required. Thus, predicting the creep behavior of polymers using short-term testing has gained considerable attention. One of the most useful extrapolation techniques is time-temperature superposition (TTS). It can be used to predict long-term creep behavior of certain polymers by shifting the curves from tests at different temperatures horizontally along a logarithmic time axis to generate a single curve known as the master curve. Thus, a long-term experiment can be replaced by shorter tests at higher temperatures. The shifting distance is called shift factor. The materials for which TTS holds are called thermorheologically simple materials and the rest are called thermorheologically complex materials. The influence of high temperature and long time has similar effect on the polymer material. With shifting the single creep curves (measured at different testing temperatures) together to a selected reference temperature, a master curve can be created. This time-temperature superposition method is able to predict the long-term properties of the material from short time creep tests at higher temperature [3][10][11]. The relation between temperature and the shift factor can generally be described by the Arrhenius Equation. Long term creep estimations, based on master curves and heuristic relations are used to provide information on the given small loads and help designers to a limited extent in dimensioning a given product to its whole life span knowing the forces, environment and in estimating the expected failure time of the part even though it does not provide information on failure deformation or life span.

There are two superposition principles, which are important in predicting creep behavior of plastic materials under various test conditions. The Boltzmann Superposition Principle describes the response of a material to different loading. It states that the response of a material to a given load is independent of the response of the material to any load, which is already on the material. It is only valid in linear viscoelastic region. The Time Temperature superposition Principle, which describes the equivalence of time and temperature. It used Williams-Landel-Ferry (WLF) equation in glass transition region and Arrhenius model outside the glass transition region.

The creep behavior of fiber reinforced composites depends strongly on stress, temperature, void content, and fiber loading [2]. It was concluded, that creep resistance decreases if temperature or stress rises. Several investigations on the influence of adhesion and density of composites on the creep behavior have already been done and found that with the increase in consolidation (lower void content), the resistance to creep increases [10][12]. The decrease in Tg can lead to an increase in voids and cracks as well as deboning between fiber and matrix. Indeed, water and temperature can substantially affect the initial stiffness and viscoelastic behavior of a composite. Plasticization and hydrolysis are more pronounced when the samples are under both wet and hot environment, reflecting in a reduction of mechanical properties. Simultaneous loading and harsh environments on fiber-reinforced composite structures with off-axis layers also reported.

The specimens loaded under the interrupted fatigue pattern sustained significantly more cycles than those loaded continuously until failure. At high stress level, by applying interrupted loading, the stiffness at failure decreased considerably more than in specimens subjected to continuous loading. Under both loading patterns, failure was observed in the form of fiber pull-out; however, in specimens loaded continuously failure occurred with considerable necking. At low stress levels, failure with predominant fiber breakage under both loading patterns were observed [13]

Here in this study, the dynamic mechanical behavior of polymer nanocomposites on frequency sweep mode i.e. at constant temperature for different frequencies and the tensile creep behaviour are analysed. Storage modulus, loss modulus and tandelta are taken for analysis.

II. METHODOLOGY

Raw materials used for the preparation of nanocomposite were, isophthalic polyester resin as the matrix material, cobalt naphthenate as the accelerator and methyl ethyl ketone peroxide (MEKP) as the catalyst. The clay was made into dispersion with styrene and then the dispersion was added to the polyester resin for modification. Cloisite15A, quaternary ammonium modified montmorrillonite was used as the nanofiller. Specimen prepared from the blend in the preferred size as per, machine standard used for the experimental purposes. The experiment on DMA carried out in frequency sweep mode.

Tensile creep behavior of the material has been studied by using the DMA Q800 apparatus (TA Instruments, New Castle, USA). The specimen of PNC prepared as per the machine specification in a size of 25 mm X 4 mm and thickness 2 mm. The experiment was conducted for the samples with 0 wt%, 1wt% and 2 wt% Cloisite15A as filler. The test was conducted at constant stress of 1MPa at a reference temperature 30 ^{o}C (approximated to room temperature).

The creep performance is commonly represented by creep compliance $J(t) = \varepsilon(t)/\sigma$, where $\varepsilon(t)$ is creep strain and σ is applied stress [5]. In order to investigate the dynamic mechanical behavior of the material at constant temperature for different frequency it has been analyzed by the method of frequency sweep. The experiment was conducted for frequencies 0.5 Hz, 1.1 Hz, 2.3 Hz, 5.5 Hz, 12 Hz, 23 Hz and 50 Hz by the method of frequency sweep in the temperature ramp mode for the temperature range from room temperature to 140^{o}C at an increment of 5^{o}C. The different frequency conditions mentioned were applied for 5 minutes at isothermal condition. The experiment was conducted for 0%, 1% and 2% nanoclay filled samples. This experiment is helpful to determine the variation in the viscoelastic properties of the material due to the change in frequency of applied stress.

III. RESULTS AND DISCUSSION

3.1 Dynamic Mechanical Analysis in frequency sweep

The dynamic mechanical behavior of PNCs obtained experimentally for the frequencies: 0.5, 1.1, 2.3, 5, 10.8, 23.2 and 50 Hz. The variation of storage modulus with temperature is plotted in figure 1 to 3, which describes the decrease of storage modulus with temperature and increase of storage modulus with frequency. The plot indicates also that the storage modulus for different frequency converge to a single curve as temperature approaches to 140^{o}C. When the temperature reaches to about 100 ^{o}C the storage modulus reduced to zero.

The loss modulus for 0%, 1% and 2% nanofilled PNCs are plotted in figure 4 to 6. The loss modulus peak is observed around 70 to 80 ^{o}C for various frequencies. The curves for various frequencies converge to a single point for temperature at around 40 ^{o}C. The loss modulus initially increases with temperature following the general trend for the nanocomposite with 1% and 2% filler, where as for pure polyester, the increase is not as much as for nanocomposite. A similar trend of variation as that of loss modulus is indicated by Tanδ (Figure 7 to 9). The peak is obtained at around 100 to 120 ºC. There is a shift of peak towards higher temperature for 1% nanoclay filled sample which may be due to the slight change in glass transition temperature. Also a clear peak is observed for 1% nanoclay filled PNC.

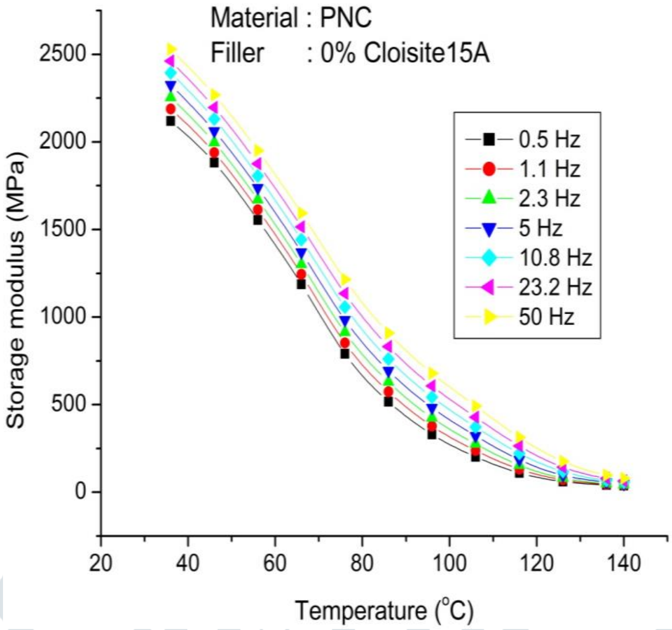

Figure 1 Variation of storage modulus with temperature, filler content 0%

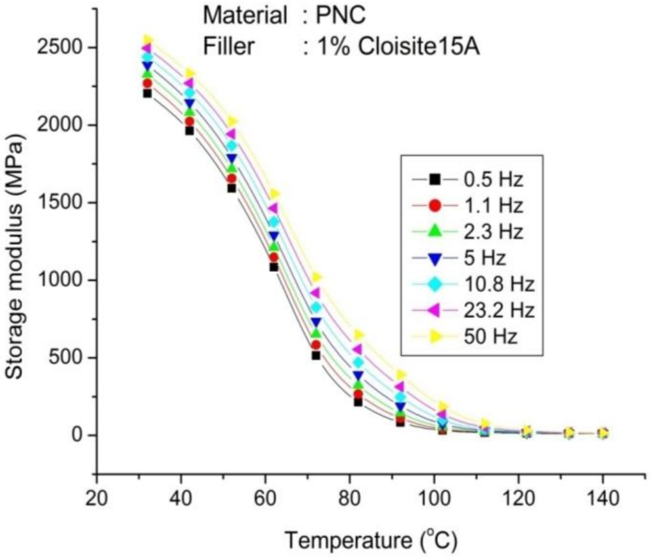

Figure 2 Variation of storage modulus with temperature, filler content 1%

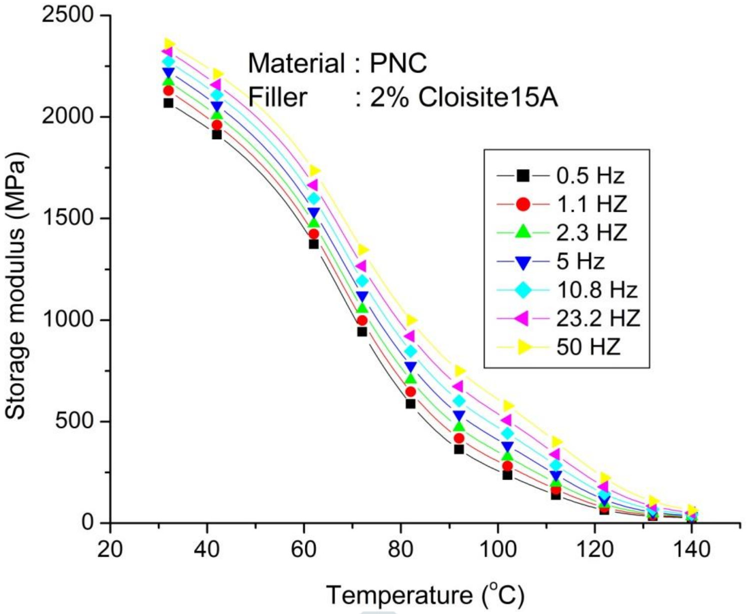

Figure 3 Variation of storage modulus with temperature, filler content 2%

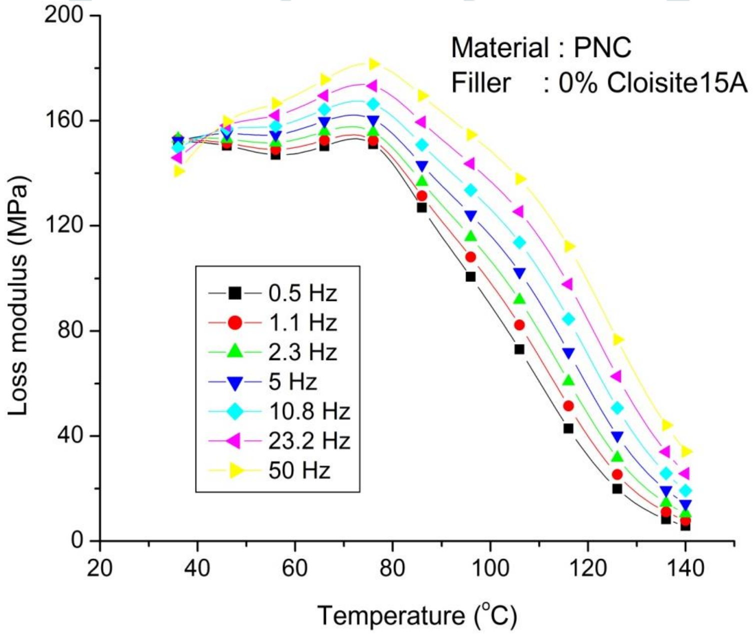

Figure 4 Variation of loss modulus with temperature, filler content 0%

Above glass transition range there is large drop of loss modulus value for low frequency lines and comparatively small drop observed for high frequency lines. The trend is more clear and gradual for 1% nanoclay filled sample. On the other hand a systematic variation of loss modulus as well as storage modulus is evident in 1% nanoclay filled sample. A similar trend as that of loss modulus is followed for damping factor tandelta (tanδ). An increase in stiffness at lower weight percentage of filler can be concluded from the trend of these curves. At a lower percentage level of filler the stiffness of the material increase/es with increase of filler content. However it is not obtained for the samples with high filler content. For high percentage of filler, the agglomeration of clay particles leads to non uniform mixing, which will contribute to the decrease of stiffness.

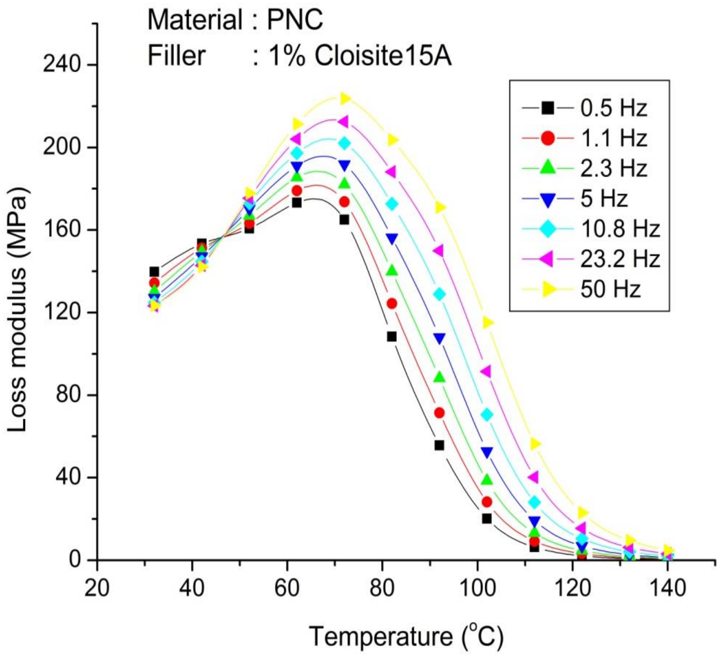

Figure 5 Variation of loss modulus with temperature, filler content 1%

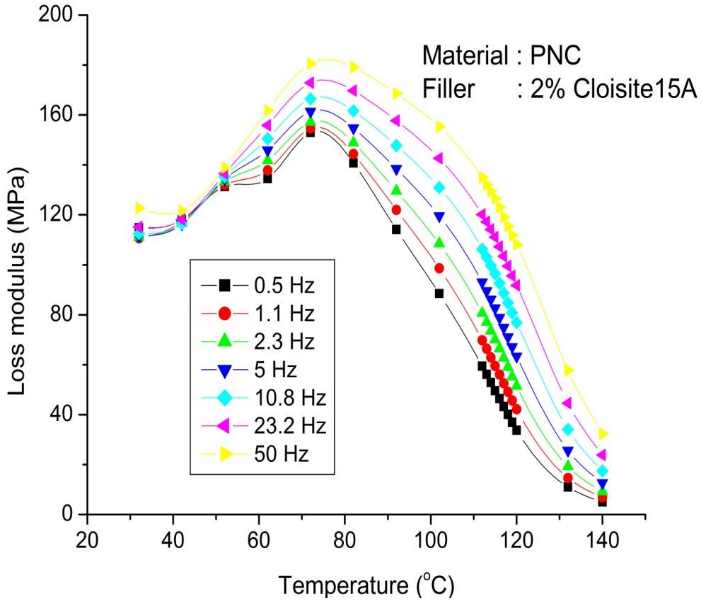

Figure 6 Variation of loss modulus with temperature, filler content 2%

The reduced value of loss modulus for the nanocomposite at low frequency is an indication of reduced energy dissipation. The average value of glass transition temperature, Tg for different wt. % of Cloisite15A is in the range 100 – 120 ºC. There is a markedly high increment in the Tg value with 1% filler. For the nanocomposite with 1% filler, due to complete exfoliation of the clay in to resin, the molecular mobility may be restricted at high temperature and hence the increase in Tg. whereas for 2% filled samples the Tg is low as compared to 1% filled samples. Here due to the increased percentage of clay the absence of entanglement surrounding the nanoclay, the effect due to surface modifiers, un reacted resin plasticization, and a lower cross-link density have been attributed to the decrease in Tg [1].

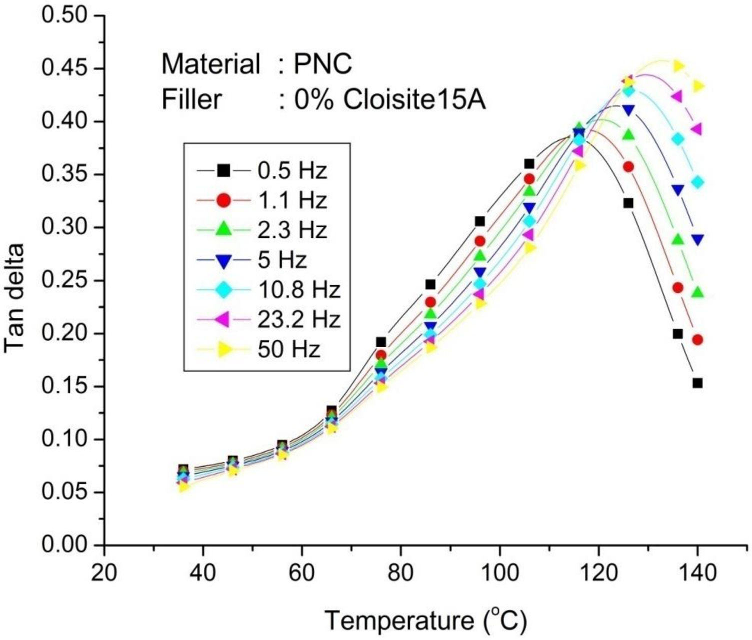

Figure 7 Variation of tandelta with temperature, filler content 0%

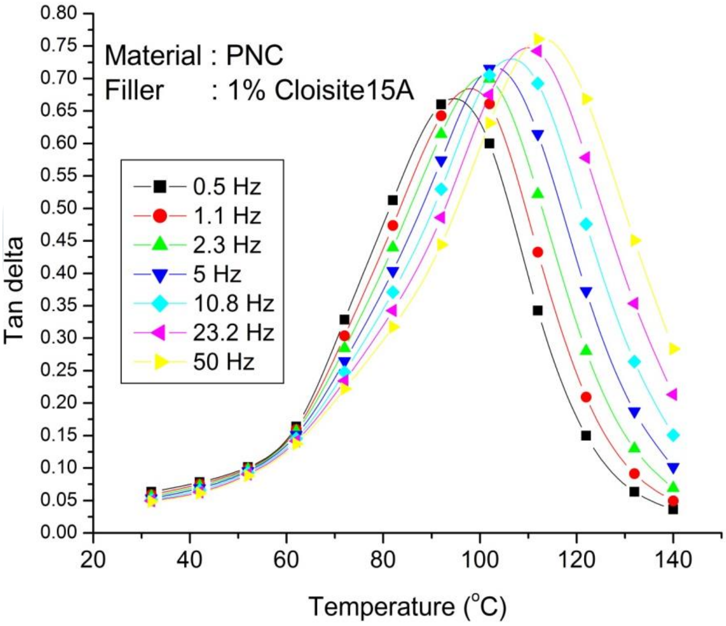

Figure 8 Variation of Tan delta with temperature, filler content 1%

Tanδ increases with the increase of filler weight percentage as per variation indicated in curves for 0% and 1% nanoclay filled samples. Various mechanisms like matrix viscoelasticity, filler/filler interfacial friction, etc., could increase the damping capacity of the polymer composite materials. However, the molecular motion at room temperature is frozen, and this may not contribute to the damping mechanisms. At Tg, the Tanδ value is higher for nanocomposite with 1% filler at 10 Hz frequency indicating the viscous damping because of the segmental motion in the polymer. This increase in the damping factor can be attributed to the restriction to the molecular movements of nanofiller, which caused reduction in the matrix viscoelasticity. However, this did not agree with the samples with 1% and 2 % nanofiller [1][6].

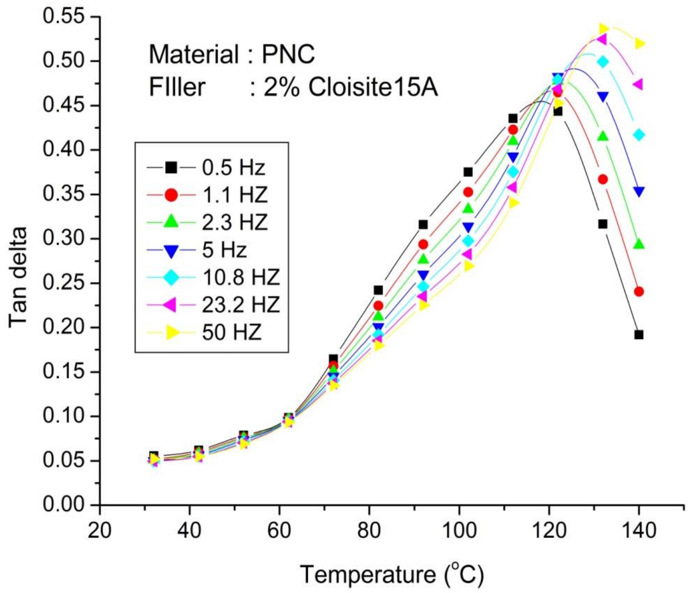

Figure 9 Variation of Tandelta with temperature, filler content 2%

The curves plotted with experimental results from frequency sweep mode at frequencies 0.5 Hz, 1.1 Hz, 2.3 Hz, 5 Hz, 10.8 Hz, 23.2 Hz and 50 Hz , shown in figure 1 to 9 for polyester nanocomposites, i.e. plots in general describe the effect of nanofiller under continuous loading. It is observed that the storage modulus increases first and reaches a stable condition with the increase of frequency. The change in the nature of curve reaches the limiting value corresponding to the peak of loss modulus curve as well as tanδ. The peak of damping coefficient curve shifts slightly to higher frequency range with the addition of nanofiller. This is a clear indication of the damping nature of nanocomposite.

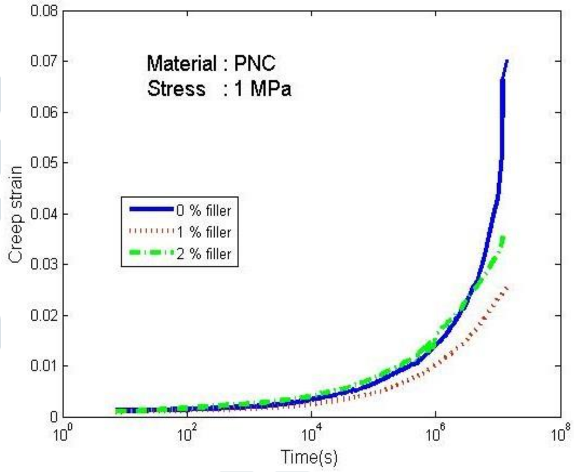

Figure 10 Variation of tensile creep strain with time for different filler (Cloisite15A) content at stress 1MPa for PNC

3.2 Creep data Analysis

The numerical value obtained by simulating the experimental results of tensile creep behaviour analysis of polyester based polymer nanocomposite(PNC) conductd at constant stress 1 MPa. Figure 10 and 11 respectively display the variation of creep strain and creep complaince of polyester nanocomposite at stress 1 MPa, which are the master curves [7] obtained at stress 1 MPa with referene temperture 30°C. Tensile creep properties of polyester nanocomposite(PNC) with 1% and 2% cloisite15A as nano filler as well as pure polyester (0% filler) is indicated by the curves. The creep strain as well as creep compliance is almost constant up to 100000 seconds of loading. After that the creep compliance and creep strain increase with time. The rate of increase of creep compliance as well as creep strain for pure polyester (0% filler) is high. The creep compliance and strain is low for 1% nanoclay filled specimen. Thus the creep resistance of nanocomposite is high as compared to pure polyester. Also the nanocomposite with 1% nanoclay has showed high creep resistance compared to 2% nanoclay. The improved intercalation of nanoclay in to polyester at 1% filler content reported by previous studies may be the reason for high creep resistance.

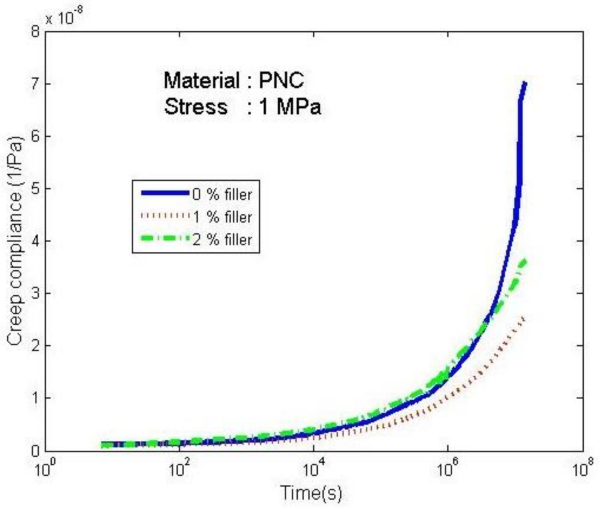

Figure 11 Variation of tensile creep compliance with time for different filler (Cloisite15A) content at stress 1MPa for PNC

These curves can also be obtained by extrapolating the experimental results for a short period to long period by WLF equation. The plots clearly demonstrating the increase of creep resistance with the addition of nanoclay. Thus the addition of nanoclay (Cloisite15A) enhances the creep resistance. The creep strain as well as creep compliance is almost constant up to 100000 seconds of loading. After that the creep compliance and creep strain increase with time. This may be attributed to the restricted motion of the polymer chain by the addition of nanofiller which occupies the interface. The nanoplatelets also help to establish a good bonding between the fiber and polymer matrix, which also restricts the motion of the polymer matrix. For the 2% filled nanocomposite the possibility for the agglomeration of the clay particles is high which may result in improper mixing [4]. With the creep deformation of nanocomposites with 1 wt% Cloisite15A shows the minimum value and which also shows improved creep resistance from nanofiller.

IV. CONCLUSIONS

Dynamic mechanical behaviors at frequency sweep mode and creep resistance were determined for PNCs. The following conclusions can be drawn from the studies:

1. The storage modulus of PNC increased with increase of frequency. However, it decreased with increase of nanoclay content for PNC.
2. Peaks of loss modulus and tanδ curves shifted to higher values with increase of frequency.
3. 1% nanoclay recorded maximum storage modulus for nanocomposites.
4. Creep compliance of the nanocomposite (PNC) was lowest at 1% nanoclay content and remained almost steady for a long period of time. The creep resistance was maximum at filler content 1%.

REFERENCES

[1] **Shahryar Pashaei, Siddaramaiah** and **Akheel Ahmed Syed** (2010), Investigation on Thermal, Mechanical and Morphological behaviours of Organo Nanoclay incorporated Epoxy Nanocomposites, *ARPN journal of engineering and applied sciences*, 5(12), 1-11

[2] **A.Greco, Claudio Musardo** and **Alfonso Maffezzoli** (2007), Flexural creep behaviour of PP matrix woven composite, *Composites Science and Technology*, 67, 1148-58.

[3] **K.Banik, J.Karger-Kocsis** and **T. Abraham** (2008), Flexural creep of all-polypropylene composites: Model analysis, *Polymer Engineering and Science*,48, 941-948.

[4] **C.Z. Chen, Y.Li** and **J. Xu**(2011), Creep and Dynamic Mechanical Behavior of Natural Fiber/Functionalized Carbon Nanotubes Modified Epoxy Composites, *proc. of 18th ICCM, School of Aerospace Engineering and Applied Mechanics, Tongji University, Shanghai, China, 1-6*

[5] **Catherine, A. Tweedie** and **Krystyn J. Van Vlieta** (2006), Contact creep compliance of viscoelastic materials via nanoindentation, *Journal of Mater. Res*., 21(6), 1576-89.

[6] **Jayita Bandyopadhyay, Suprakas Sinha Ray** and **Mosto Bousmina** (2007), Thermal and Thermo-mechanical Properties of ` Poly(ethylene terephthalate) Nanocomposites , *Journal of Ind. Eng. Chem.*, 13(4), 614-623

[7] **Yu Jia, Ke Peng, Xing-long Gong** and **Zhong Zhang** (2011), Creep and recovery of polypropylene/carbon nanotube composites, *International Journal of Plasticity*, 27(8), 1239-51.

[8] **Wu, C.L., Zhang, M.Q., Rong, M.Z.** and **Friedrich, K.**(2002), Tensile Performance Improvement of Low Nanoparticles Filled- Polypropylene Composites, *Composites Science and Technology*, 62 ,1327-40.

[9] **S.Y. Lee, H. S. Yang, H.J. Kim, C.S. Jeong, B.S. Lim** and **J.N. Lee** (2004), Creep behavior and manufacturing parameters of wood flour filled polypropylene composites, *Composite Structures*, 65, 459-469

[10] **Banik K., Abraham T. N.** and **Karger-Kocsis J.**(2007), Flexural creep behavior of unidirectional and cross-ply all poly (propylene) (PURE) composites, *Macromolecular Materials and Engineering*, 292, 1280–88.

[11] **Venkata S. Chevali, Derrick R. Dean** and **Gregg M Janowski** (2009), Flexural creep behavior of discontinuous thermoplastic composites: Non-linear viscoelastic modeling and time temperature- stress superposition. *Composites Part A: Applied Science and Manufacturing*, 40, 870–877.

[12] **Kim KJ., Yu WR.** and **Harrison P**. (2008), Optimum consolidation of self-reinforced polypropylene composite and its time-dependent deformation behavior. *Composites Part A: Applied Science and Manufacturing*, 39, 1597–1605.

[13] **Abdolvahid Movahedi-Rad, Thomas Keller** and **Anastasios P. Vassilopoulos** (2018), Effect of Loading Pattern on Fatigue Behavior of Laminated Composites, *ICEM18, 2, 438; doi:10.3390/ICEM18-05321*