

August 7, 2006

Dr. Christopher C Ibeh, Director
2006 PSU-CNCMM REU/RET
Professor, Plastics Engineering Technology
Pittsburg State University

RE: Mechanical properties of nanoclay based nanocomposites: a review

Dear Dr. Ibeh:

I am very pleased to inform you that I have completed the above stated project.

The main objective of this report is to review different published articles in regard to the mechanical properties of nanoclay based nanocomposites.

I hope this report will meet with your approval. If you have any other information about my review, I'll supply it for you upon your request. If you have any questions or comments, I can be reached at bhanubhattarai@hotmail.com

Sincerely,

Bhanu Bhattarai
Cc: Stefano Bietto

Mechanical properties of nanoclay based nanocomposites: a review

**August 7, 2006
PSU-CNCMM REU/RET**

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Mechanical properties of nanoclay based nanocomposites: a review

Abstract

In this study a review of different properties of nanocomposites containing nanoclay is made. The study will be focused sharply on the mechanical properties, like Tensile strength, Stress strain, Flexural properties, Young Modulus of different nanocomposites with an intention to create an online data-base system. Different scientific journals and articles will be reviewed, different graphs and tables will be analyzed and interpreted and structure for data base will be developed in this study. From all the articles reviewed, it can be concluded that with the right amount of nanoclay mechanical properties of nanocomposites will be enhanced. It's not only the amount of nanoclay but also the kind of epoxy used, sample preparation technique, pre and post curing of samples contribute equally on the mechanical properties of nanocomposites.

Introduction

In the past decade, the research on nanocomposites has shown some promising results. With the right amount of nano clay, nanocomposites have shown positive result in mechanical properties. Though the experiments are in primitive stage and yet more to investigate, it is already heading towards positive direction.

The change in mechanical properties in nanocomposites after filling nano clay has tremendous impact in the field of material science. This paper will investigate the change in mechanical properties in nanocomposite after mixing nano particles. Different scientific articles,

journals, and publications will be reviewed, analyzed and interpreted. The study will be limited to previously published articles, journals and reports.

The possible outcome will be very helpful for the researchers, industries and academicians, who are working in the field of nanocomposite. Numbers of article will be reviewed, analyzed and structured in such a way that even novice in the field of nanotechnology can easily comprehend the report.

Literature Review

In Huang et al. [1], a comprehensive review is presented on the researches and developments related to electrospun polymer nanofibers including processing, structure and property characterization, applications, and modeling and simulations. Information of those polymers together with their processing conditions for electrospinning of ultrafine fibers has been summarized. Other issues regarding the technology limitations, research challenges, and future trends are also discussed. In his paper he had concluded that electrospinning is an efficient technique for the fabrication of polymer nanofibers. Various polymers have been successfully electrospun into ultrafine fibers in recent years mostly in solvent solution and some in melt form.

In a study conducted at University of Oxford [2], Structural ceramic nanocomposites are reviewed with emphasis on the $\text{Al}_2\text{O}_3/\text{SiC}$ and $\text{Si}_3\text{N}_4/\text{SiC}$ systems. The review was divided into three parts. First, basic processing routes for nanocomposites, namely conventional powder processing, sol-gel processing and polymer pyrolysis and presented in detail. Second, the mechanical properties of different nanocomposites are compared. Finally, models which attempt to explain the improvements in these properties are explored. And it was shown that the strength increase can best be related to a reduction in processing defect size.

In Ray et al. [3], a wide range of polymer matrices is reviewed, with special emphasis on biodegradable polymers. In the paper it was concluded that, in general, polymer/layer silicate nanocomposites are of three different types, namely (1) intercalated nanocomposited, (2) flocculated nanocomposited, (3) exfoliated nanocomposites. This new family of composites materials frequently exhibits remarkable improvements of material properties when compared with the matrix polymers alone or conventional micro-and macro-composite materials. Improvements can include a high storage modulus, both in solid and melt state, increased tensile and flexural properties, a decrease in gas permeability and flammability, increased heat distortion temperature, and increases in the biodegradability rate of biodegradable polymers, and so forth.

References

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- [2] Martin Sternitzke, "*Structural ceramic nanocomposites*", Journal of the European Ceramic Society, Volume 17, Issue 9, 1997, Pages 1061-1082
- [3] Suprakas Sinha Ray, Masami Okamoto, "*Polymer/layered silicate nanocomposites: a review from preparation to processing*", Prog.Polym. Sci.28 (2003) 1539-1641

Mechanical properties of nanoclay based nanocomposites

In a research conducted at Tuskegee University, Alabama [4], a novel technique to fabricate nanocomposite materials was developed. The resin used in this study is a commercially available SC-15 epoxy (obtained from Applied Poleramic, Inc). It is a low-viscosity two-phase toughened epoxy resin system consisting of part A (resin mixture of diglycidylether of bisphenol-A (DGEBA), aliphatic diglycidylether epoxy toughener) and part B (hardener mixture of

cycloaliphatic amine and polyoxylalkylamine). The inorganic clay used in this study was K-10 grade montmorillonite (obtained from Sigma-Aldrich Co.,USA) with a surface area 220-270 m²/g. The weight fraction of clay are range from 0 wt.% to 4 wt.% to identify an optimal loading giving the best thermal and mechanical properties.

Firstly, clay was dried in oven at a temperature of 80⁰ C for 24 hours. Then pre-calculated amount of clay and part A resin were carefully weighted and mixed together in a suitable beaker. The mixing was carried out through a high-intensity ultrasonic irradiation for 1.5 hours with pulse mode. To avoid a temperature rise during the sonication process, external cooling was employed by submerging the beaker containing the mixture in an ice bath. Once the irradiation was completed, part B was added to the modified part A then mixed using high speed mechanical stirrer for about 10 minutes. A high vacuum was accordingly applied using Brand Tech Vacuum system for about 30 minutes. After the bubbles were completely removed, the mixture was transferred into a plastic and Tefloncoated material rectangular molds and kept for 24 hours at room temperature. All as-prepared panels were postcured at 100⁰ C for 5 hours in a Lindberg/Blue Mechanical Convection Oven.

Dynamic Mechanical analysis (DMA), Thermogravimetric analysis (TGA) and three-point bending tests were performed on unfilled, 1 wt.%, 2 wt.%, 3 wt.%, 4 wt.% clay-filled SC-15 epoxy to identify the loading effect on thermal and mechanical properties of the composites. From the DMA and three-point bending test, it was observed that the mechanical properties change with respect to the clay content, however, the TGA results showed that the thermal stability of composite is insensitive to the clay content. The three-point bending test results indicate that 2 wt.% loading of clay in epoxy showed the highest improvement in flexural

strength as compared to others and likewise, DMA studies also revealed that 2.0 wt.% doped system exhibit the highest storage modulus which can be seen in the table below.

Material	Modulus (GPa)	Improvement in modulus (%)	Strength (MPa)	Improvement in strength (%)
Neat Epoxy	2.25 ± 0.11	-----	85 ± 4.3	-----
1 wt. % clay	2.58 ± 0.12	14.7	94 ± 5.9	10.6
2 wt. % clay	2.96 ± 0.14	31.6	108 ± 5.6	27.1
3 wt. % clay	2.70 ± 0.14	20.0	105 ± 4.6	23.5
4 wt. % clay	2.43 ± 0.11	8.0	104 ± 4.1	23.5

Table 1: effects of clay content on the mechanical and thermal properties of epoxy and its nanocomposites

In Wang et al [5], a novel approach assisted with solvent was developed to disperse clay into epoxy matrix. The dispersion of clay was examined by means of optical microscope (OM), wide angle X-ray scattering (WAXS) and transmission electron microscope (TME). Batches of cured samples containing 1-3 wt% silane-modified clay (SMC) were prepared and their thermal/mechanical properties were studied by dynamic mechanical analysis (DMA), tensile and fracture tests. The objective of this study is to prepare epoxy/clay nanocomposites with highly exfoliation morphology using organic solvent as processing aid and dispersing media, and study the effectiveness of exfoliated clay on the resin cement of high performance system.

In order to obtain materials with high T_g , an aromatic epoxy, diglycidyl ether of bisphenol A (DGEBA) was chosen for the study. The pristine clay, Nanomer PGW and 3-aminopropyl-trimethoxysilane were used to chemically modify the clay surface. Acetone was selected as the inactive solvent to facilitate clay modification and dispersion.

Pristine clay (4g) was dissolved in 120 ml deionized water and stirred vigorously overnight to form uniformly dispersed slurry. Acetone (800 ml) was then introduced into slurry slowly, precipitating a white cotton-like product, which was assumed to be acetone-expanded clay. After filtered and washed with acetone for several times, the precipitation was transferred to an acetone for several times, the precipitation was transferred to an acetone solution of γ -

aminopropyl-trimethoxysilane. The amount of silane is 10 wt. % of pristine clay. The mixture solution was further stirred overnight to facilitate the reaction between silane and clay surface to achieve silane-modified clay (SMC). The SMC solution was dispersed in the epoxy resin at a room temperature using a homogenizer at 10,000 rotation per minute (rpm). After mixed for one hour, the acetone was removed by evaporation in a rotary evaporator and further dried in a vacuum oven. Then the curing agent Ethacure 100LC was added and thoroughly mixed with the epoxy/clay mixture. The mixture were then degassed and poured into a preheated and vertically mounted glass mold in an oven and cured for two hours at 100⁰ C followed by a post curing for 5 hours at 180⁰ C. After that, the oven was switched off and the cured resin was allowed to cool slowly to room temperature in the oven. The resulted nanocomposite plates with thickness of 3 mm and 6.25 mm were then machined for thermal/ mechanical test. SMC dry samples were also prepared for characterization by evaporating the SMC acetone before addition of epoxy resin.

The storage modulus of the nanocomposites was measured using DMA 2980 dynamic mechanical analyzer (DMA) in single cantilever mode. At least six specimens of each composition were tested. The mode I fracture toughness, as quantified by the critical stress intensity factor (K_{IC}), was determined using three-point bending (3PB) test. The 3 PB experiments were performed at room temperature using a computer-controlled Instron machine (Mode 5567) at a crosshead speed of 2 mm/min with a span of 50 mm.

OM, WAXS and TEM characterizations reveal clay is highly exfoliated and uniformly dispersed in the matrix. The storage modulus increased monotonically with clay content. The T_g exhibits a maximum value at 1 wt.% clay concentration, which can be attributed to the complex interactions between the matrix and clay layers. In the study of the dependences of Young's modulus and fracture toughness on clay concentration, it was observed that both stiffness and

toughness of the materials were improved through the incorporation of SMC clay. Change of dominant toughening mechanisms was proposed in low and high clay content composites. Data gathered in the experiment are tabulated as below.

Clay concentration (%)	Storage Modulus (MPa)	Glass Transition Temperature T_g (°C)
0	1775	217.5
1	1800	227.5
2	2050	215
3	2300	206

Table 2: Dependence of storage modulus and glass transition temperature on clay concentration

Clay concentration (wt%)	Tensile Module, E (GPa)	Strength (MPa)
0	2.95-3.05	40-51
1	3.0-3.15	50-60
2	3.18-3.38	52.5-62.5
3	3.28-3.5	45-60

Table 3: Dependence of tensile modulus and tensile strength on clay concentration.

Clay concentration (wt %)	Fracture Toughness, K_{IC} , (MP a.m ^{1.2})	Critical Strain energy release rate, G_{IC} (J.m ⁻²)
0	0.55-0.65	110
1	0.89-1.05	275
2	0.99-1.20	310
3	0.85-1.05	225

Table 4: Dependence of fracture toughness on clay concentration.

In Wang et al. [6], positron annihilation lifetimes have been measured for epoxy resin/organic montmorillonite (OMMT) nanocomposites. Effects of different dispersion states of nano-layered OMMT on the positron annihilation parameters and the mechanical properties were studied.

Epoxy resin (DGEBA) CYD-128, OMMT and methyl four phthalic anhydride (MeTPHTA), 2-ethy-4mehtyl imidazole as a curing agent and accelerator were used to make the epoxy resin nanocomposites using the melting blend technology. The dispersibility of the OMMT layer in samples was evaluated by X-ray diffraction (XRD) measurement. The impact

and flexural strength measurements were carried out using an impact tester (XCJ-400) according to the ASTM-D256 and universal test machine.

In the experiment, a significant increase in the flexural and impact strengths when compared to that of unfilled epoxy is observed. Further, we can see that they increase up to an OMMT content of 2 wt%, followed by a decrease with increasing the OMMT content. This observation suggests that the interfacial interaction plays an important role in determining flexural and impact strengths. When the OMMT content is $\leq 2\text{wt}\%$, nano-scale layered OMMT are well dispersed in the epoxy matrix, which brings about the formation of the exfoliated structure. Exfoliated structure is more desirable in enhancing the mechanical properties due to a stronger interfacial interaction. For OMMT content $>2\text{ wt}\%$, the exfoliation and intercalation structures coexist, the interfacial interaction between OMMT and matrix is reduced, resulting in poorer mechanical properties. Thus it can be concluded that exfoliated structure enhances the flexural and impact strengths of nanocomposites due to the stronger interfacial interaction between OMMT and epoxy matrix.

OMMT content (wt%)	Impact Strength (KJ/m ²)	Flexural Strength (MPa)
0	4	63
1	4.3	69
2	15	110
3	13	105
4	11	100
5	10.5	97
6	10.2	90

Table 5: Variations of mechanical properties versus OMMT content (wt%)

In Wu et al. [7], the structure of several rubber-clay nanocomposites, including styrene butadiene rubber (SBR)- clay, natural rubber (NR)- clay, nitrile butadiene rubber (NBR)- clay, carboxyllated acrylonitrile butadiene rubber (CNBR)- clay nanocomposites, prepared by direct co-coagulating the rubber latex and clay aqueous suspension, were investigated.

About 3% clay aqueous suspension and the rubber latex were mixed and vigorously stirred for a given period of time. After that, the mixture was co-coagulated in the electrolyte solution (2% dilute triethylenetetrammonium chloride solution for the NR and SBR systems and 1% calcium chloride aqueous solution for the NBR and CNBR systems), washed with water and dried in an oven at 80⁰ C for 18 hours, and then the rubber-clay nano compound (uncured nanocomposite) was obtained. The vulcanizing ingredients and other additives were mixed into the nanocompound with a 6-in. two-roll mill; then, the compound was vulcanized in a standard mold. The vulcanized are referred to as rubber-clay nanocomposites. Vulcanizates filled with carbon black (M330), silica or clay was prepared using the same processing procedure as references.

X-ray diffraction (XRD) patterns and transmission electron microscope (TEM) micrographs showed that these nanocomposites possessed a unique structure, in which the rubber molecules “separated” the clay particles into either individual layers or just silicate layer aggregates of nanometer thickness without the intercalation of rubber molecules into clay galleries, different from intercalated and exfoliated clay nanocomposites. Such a structure resulted from the competition between separation of rubber latex particles and re-aggregation of single silicate layers during the co-coagulating process. The content of bound rubber of SBR-clay nanocompound is more than that of the corresponding rubber filled with micrometer clay or silica because of the increased networking of silicate layers with the nano-meter dispersion and the high aspect ratio.

The mechanical properties of the three rubber-clay nano-composites: SBR-clay, NR clay and CNBR-clay, are listed in the table 6 below. Compared to the corresponding conventional rubber-clay composites containing the equivalent amount of clay (20phr), all of the three

nanocomposites exhibit substantially higher 300% stress, shore A hardness, tensile strength and tear strength. Of particular notice is that the tensile strength of SBR-clay nanocomposite exhibited 6.0 times higher value than that of conventional SBR-clay composites. Compared to the corresponding gum vulcanizates, the nitrogen permeability of SBR-clay, NR-clay, and NBR-clay nanocomposites reduced by 54.1%, 46.7% and 47.8%, respectively, and the decrease amplitude is about 50% for all the three nanocomposites. This implies that the dispersion of silicate layers in SBR, NR and NBR matrix is almost the same, which is consistent with the above resulted presented by XRD and TEM.

Samples	SBR- Clay		NR- Clay		CNBR – clay	
	MC	NC	MC	NC	MC	NC
Stress at 300% strain (MPa)	2.1	7.4	2.7	12.3	5.2	----
Tensile strength (MPa)	2.4	14.5	11.6	26.8	9.0	18.0
Elongation at break (%)	400	548	568	644	444	228
Shore A hardness	52	60	41	54	60	82
Tear strength (KN/m)	16.5	45.3	22.8	44.1	24.4	46.5

Table 6: Mechanical properties of rubber –clay nanocomposites (NC samples) and conventional rubber-clay composites (MC samples) with 20 phr clay

Materials	Pure SBR	SBR-clay	Pure NR	NR-clay	Pure NBR	NBR-clay
Permeability	7.4	3.4	13.7	7.3	2.3	1.2

Table 7 : Nitrogen permeabilities of clay/rubber nanocomposites with 20 phr clay

In Lepoittevin et al.[8], Nano composites of poly(ϵ -caprolactone) (PCL) were prepared by melt blending the polymer with natural Na^+ montmorillonite and montmorillonite modified by hydrogenated tallowalkyl (HTA)-based quaternary ammonium cation, such as dimethyl 2-ethylhexyl HTA ammonium and methyl bis (2-hydroxyethyl) HTA ammonium. Microcomposites or nanocomposites were prepared depending on whether neat or modified montmorillonites was used, as assessed by X-ray diffraction and transmission electron microscope. Mechanical and thermal properties were studied as a function of the filler content by

tensile testing, Izod impact testing, thermogravimetric analysis and differential scanning calorimetry.

The PCL-layered silicate composites were prepared by mechanical kneading with at 130⁰ C for 10 minutes. The collected molten materials were compression-molded into 3 mm-thick plates by hot-pressing at 100⁰ C under 150 bar for 10 seconds, then under 30 bar for 10 additional seconds, followed by clod pressing at 15⁰ C under 30 bar for 5 minutes. Composites containing 1,3,5 and 10 wt % of montmorillonite were prepared. The inorganic content of each composite was analyzed by TGA under air flow and calculated from the residue left at 600⁰ C.

An intercalated/exfoliated structure was observed by both XRD and TEM analyses. In contrast, natural sodium montmorillonite formed conventional composite, with micron-sized particles dispersed in PCL. Tensile properties of the nanocomposites, particularly stiffness, increased continuously with the filler content, at least until a content of 5 wt%, beyond which the mechanical properties leveled off and/or decreased. A significant improvement in thermal stability of PCL was noted especially at very low clay content (1wt %). A solid-like rheological response was observed for PCL modified by 3 wt% and more of organo-modified MMT. Storage and loss moduli in the terminal region were substantially increased for all the studied nanocomposites compared with unfilled PCL and or PCL-based microcomposites.

Samples	Filler content (wt%)	Melting enthalpy ΔH_m (J/g)	Degree of crystallinity
Commercial PCLC	0	71.2	52.4
PCLC 1	1	64.8	47.2
PCLC 2	3	58.6	41.5
PCLC 3	5	55.7	38.4
PCLC 4	10	40.6	25.5

Table 8: Calorimetric data for nanocomposite prepared with MMT – (OH₂)

Samples	Filler content (wt%)	Young's modulus (MPa)	Elongation at break (%)	Tensile strength (MPa)
Commercial PCL	0	216 ± 5	746 ± 43	37 ± 2
PCLC 5	1	210 ± 9	715 ± 61	35 ± 3
PCLC 6	2	197 ± 9	714.5 ± 44	35 ± 3
PCLC 7	5	207 ± 7	666 ± 29	32.5 ± 2
PCLC 8	10	238 ± 15	569 ± 26	28 ± 1

Table 9: Tensile properties of neat poly (ε-caprolactone) and composite containing 1,3,5 and 10 wt% of natural montmorillonite MMT – Na

Samples	Filler content (wt%)	Young's modulus (MPa)	Elongation at break (%)	Tensile strength (MPa)
PCLC 9	1	262 ± 13	659 ± 27	33 ± 1
PCLC 10	3	282 ± 9	528 ± 58	26 ± 3
PCLC 11	5	307 ± 18	598 ± 43	28 ± 1
PCLC 12	10	371 ± 15	9 ± 1	18 ± 1

Table 10: Tensile properties of poly (ε-caprolactone) nanocomposite containing 1, 3,5 and 10 wt% of organo-modified montmorillonite MMT – Alk

Samples	Filler content (wt%)	Young's modulus (MPa)	Elongation at break (%)	Tensile strength (MPa)
PCLC 1	1	259 ± 11	705 ± 47	36 ± 2
PCLC 2	3	272 ± 16	563 ± 62	25 ± 4
PCLC 3	5	313 ± 23	560 ± 46	24 ± 3
PCLC 4	10	399 ± 23	7 ± 1	17 ± 0.5

Table 11: Tensile properties of poly (ε-caprolactone) nanocomposites containing 1,3,5,10 wt% of organo-modified montmorillonite MMT – (OH)₂

Filler content (wt%)	Izod impact strength (J/m)			Remark
	MMT –Na	MMT-Alk	MMT-(OH) ₂	
1	33 ± 5	28 ± 6	33 ± 3	
3	22 ± 2	22 ± 2	18 ± 3	
5	19 ± 1	15 ± 1	13 ± 1	
10	15 ± 1	16 ± 3	13 ± 2	

Table 12: Izod-impact properties of composites containing MMT-Na, MMT – Alk and MMT – (OH)₂ clays

In an experiment conducted at Donghua University, Shanghai, China [9], a new type of stimuli-responsive organic/inorganic nano-composite hydrogel was prepared by introducing fibrillar attapulgite into poly (2-hydroxyethyl methacrylate-co poly(ethylene glycol) methyl ether methacrylate-co-methacrylic acid) network, in which the nanosized attapulgite fibril worked as the cross-linker instead of conventional chemical cross-linker. In the preparation

process, a prepolymerization route was adopted to effectively stabilize the dispersion of attapulgite.

2-Hydroxyethyl methacrylate (HEMA), methacrylic acid (MAA) were purified by vacuum-distillation and stored at -5°C before used. Attapulgite (AT) was refined before used. Poly (ethylene glycol) methyl ether methacrylate (PEGMA) was used as received. N, N'-methylenebisacrylamide (MBA), ammonium persulfate (APS) and N,N,N,N'-tetramethylethylenediamine (TEMED) were analytical grade and used as received.

Poly (HEMA-PEGMA-MAA)/AT NC hydrogels were prepared by free radical polymerization in deionized water/methanol solution. Before polymerization in the deionized water/methanol (volume ratio 1:1) solution at 20°C for 2 hours and dispersed under the ultrasonic vibration for 30 minutes. Then, the monomers of HEMA, PEGMA and MAA were added into the solution and mixed by the ultrasonic vibration for 10 minutes. Nitrogen was used to remove dissolved oxygen from the reactive solution. To initiate the polymerization, 50 μL APS solution (5 wt.% in deionized water) and 30 μL TEMED were added into the reactive system as an initiator and accelerator, respectively. The reactive solution was first prepolymerized at 65°C for 30 minutes under stirring, and then poured into glass mould quickly. The post polymerized at 65°C for 30 minutes under stirring, and then poured into glass mould quickly. The post polymerization was carried out at 45°C for 15 hours. When the reaction completed, the hydrogel was cut into same size and immersed in repeatedly changed deionized water for 72 hours to remove the residual monomers. The sample codes NC1, NC2, and NC3 corresponded to the attapulgite contents of 0.05, 0.1 and 0.2 wt.%, respectively. For comparison, chemically cross-linked poly (HEMA-PEGMA-MAA) hydrogel (CR hydrogel) was also prepared by free radical polymerization, using MBA as the organic cross-linker (0.1 wt.%)

From the experiment, it was observed that all the NC hydrogels exhibit much higher toughness than that of the corresponding CR hydrogel. The tensile strength and elongation at break of NC and CR hydrogel samples are listed in the table 13 below. The elongation at break of CR hydrogel is very low. This situation can be much improved by introducing AT in the hydrogel network. The NC1 samples can reach a value of elongation at break up to 100%. This obvious improvement in mechanical property may be attributed to the different network nature between the two types of hydrogels. The polymer chain in CR hydrogel have broad distribution in length between the cross-link points and are restricted due to the random nature of cross-linking reaction. Moreover, the friction between the chain is small in CR hydrogel. These two factors result in the inhomogeneous distribution of tension among the polymers. The scission of the polymer chains occurs when the ample is under tension. However, the situation is different in the NC hydrogel. Network of NC hydrogel is composed of rigid AT fibril and flexible polymer chains, which increases the friction between the chains by sliding of rigid AT fibril under the extern tensile force. Furthermore, it was observed that the stress to deform NC hydrogels increases with increasing AT content. Since NC hydrogels show extraordinarily large reversible deformation, and the polymer chains in the swollen state at ambient temperature could be regarded as flexible polymer chains just like those in the rubber state of solid polymer above glass transition temperature.

Sample	Tensile Strength (kPa)	Elongation (%)	σ at $\lambda = 2$ (kPa)	v_c (mol/m ³)	$10^4 M_c$ (g/mol)
NC1	36.5	655	26.5	6.1	19.6
NC2	79.1	731	42.0	9.8	12.3
NC3	136.9	1064	96.9	22.5	5.3
CR	12.1	61	-----	-----	-----

Table 13: Mechanical properties of synthesized nano-composite (NC) and cross-linked hydrogel (CR) and the structure parameters

In an study conducted at University of Washington [10], the matrices of carbon fiber/epoxy composite were modified with layered inorganic clays and a traditional filler to determine the effects of particle reinforcement, both micro and nano scale, on the response of these materials of cryogenic cycle.

A mixture of commercial epoxy resins was used as the base resin for the polymer matrix. The resins used were EPON 828 from Resolution Performance Products and Araldite MY 9512. Cloisite 25A and 5 μ m alumina particles were used to modify the base matrix formulation. The epoxy resins were combined in a 60:40 ratio by weight of MY 9512:EPON 828 in an oil bath at 120⁰ C and stirred until they were completely mixed. At this point the appropriate amount of modifier was added and the material was stirred for two hours. It should be noted that the unmodified resin was also stirred for two hours at 120⁰ C even though no modifier was present. A stoichiometric amount of DDS was melted and added to the epoxy mixture in the oil bath. The epoxy/modifier/DDS mixture was blended for 2 minutes in the oil bath at 120⁰ C after which the resin was quenched to room temperature and stored at -10⁰ C until it was prepregged.

A small increase in interlaminar shear strength (ILSS) was observed at 2 and 5 phr 25A. This was most likely due to reinforcement of the matrix by the nanoparticles. The largest increase in ILSS was seen when the laminates contained alumina particles. This increase may have resulted from the alumina particles reinforcing the interlayer regions. When 8 phr 25A was used the ILSS decreased slightly. In the case of flexural strength, when 2 and 5 phr 25A were present in the laminates the flexural strength decreased slightly; however, at 8 phr 25 A the strength was the same as unmodified laminate. When alumina particles were present the strength increased when compared with the control. However, transverse flexural modulus showed no statical change when the nanoparticles modifiers were incorporated into the matrix at

concentrations of 5 and 8 phr. Very decreases were observed when alumina and 2 phr 25 A were used as modifiers. Similarly, in the case of transverse CTE of a unidirectional lamination a small initial increase was seen at a nanoclay concentration of 2 phr 25A. after this increase the CTE decreased steadily with increasing nanoclay concentration.

Therefore, it can be concluded that the mechanical properties of the laminates studies were not significantly altered through nanoclay modification of the matrix. The incorporation of nanoclay reinforcement in the proper concentration resulted in laminates with microcrack densities lower than those seen in the unmodified or macro-reinforced materials as a response to cryogenic cycling. Lower nanoclay concentrations resulted in a relatively insignificant reduction in microcracking and higher concentrations displayed a traditional filler effect.

	ILSS (MPa)
5phr Alumina	75
8phr 25 A	59
5phr 25 A	70
2phr 25 A	72
Control	65

Table 14: Interlaminar shear strength variation with particle modification

	Transverse Flexural Stress at Yield (MPa)
5phr Alumina	72
8phr 25A	68
5phr 25A	50
2phr 25A	49
Control	55

Table 15: Transverse flexural strength variation with particle modification

	Transverse Flexural Modulus (GPa)
5phr Alumina	6.8
8phr 25A	7.1
5phr 25 A	7.2
2phr 25 A	6.7
Control	7.3

Table 16: Transverse flexural modulus variation with particle modification

	Transverse CTE ($\mu\text{m}/\text{m}^0\text{C}$)
5phr Alumina	38
8phr 25A	34
5phr 25A	41
2phr 25A	42
Control	37

Table 17: Transverse CTE variation with particle modification

In Wang et al. [11], the effect of the chemistry and shear on the dispersion of clay in polymer matrix via dynamic packing injection molding (DPIM) was studied.

A commercial powdered isotactic PP with an average diameter about 100 μm was used as the basal polymer. PP-MA (MA content = 0.9 wt%, MI=6.74) was used as compatibilizer. 50 g sodium montmorillonite was dispersed into 1000 ml hot water using stirrer. The dioctadecyl dimethylammonium bromide (2C-18) (25 g) was dissolved into hot water (300 ml) and then poured into the montmorillonite-water solution under vigorous stirring for two hours. The product was washed three times and filtered, then dried in vacuum at 100⁰ C for several hours. The pristine MMT is termed as MMT, while treated as MMT as OMMT. Without a of 68.8 mmol/100g clay was originally modified obeying a procedure described in one conventional extrusion step. The premixing PP/clay blend were compounded directly in DPIM, in which the melt is firstly injected into the mold then forced to move repeatedly in a chamber by two pistons that moved reversibly with the same frequency as the solidification progressively occurred from the mold wall to the molding core part, and a special orientation region is produced via imposing the reversible shear effect during the cooling of composite melt. Two types of specimens were prepared using two different injection molding techniques, dynamic packing injection molding and static packing injection molding. Both injection molding were carried out using the same processing parameters. Three PP/clay composite were chosen to inspect the influence of chemical modification (thermodynamic factor) on the dispersion of MMT particles and nano-scale morphology. The one is a compatibilized PP/PP-MA/OMMT (85/10/5 wt %), abbreviated

as PPCN3. The other two are iPP/MMT (95/5 wt%, abbreviated as PPCN1) and iPP/OMMT (95/5 wt%, abbreviated as PPCN2)

The interplay of thermodynamics and shear on the dispersion of clay in PP matrix has been clearly demonstrated via dynamic packing injection molding. Without shear, an improved dispersion is observed by chemical modification of clay. Adding compatibilizer results in a good dispersion of clay with partially intercalated structure. By combination of chemistry with shear, a much better dispersion is obtained, with intercalated morphology at oriented zone and completely exfoliated morphology at the core. Both the chemistry and shear are important to determine the dispersion of clay in polymer matrix. PP/clay nanocomposites with excellent impact strength can be prepared via simple one step, direct injection molding without a conventional pre-extrusion, by dynamic packing injection molding. The observed improvement of impact strength could be related to the local hierarchical structure of dynamic sample.

	Pure PP	PPCN1	PPCN2	PPCN3
Static	2.9 ± 1.0	1.9 ± 0.2	3.2 ± 0.3	3.3 ± 0.5
Dynamic	4.6 ± 1.1	8.3 ± 2.3	15.3 ± 1.0	13.6 ± 2.1

Table 18: The Notched Izod impact strengths (KJ/m²) of as-prepared PP/MMT nanocomposites via DPIM process

In the study conducted at Purdue University [12], morphology of nanoclay dispersed in resin and suspended in acetone was studied using scanning electron microscope (SEM) and transmission electron microscope (TEM) and a vacuum assisted wet lay-up (VAWL) process was used for the inclusion of nano-clay in conventional fiber reinforced composition.

A weighed amount of nanoclay was mixed with un-catalyzed resin using a shear blender. Even though the nanoclay is surface treated, it does not readily blend with the resin. Hence, shear mixing was done at different head speeds to produce through mixing. This shear blending introduced a lot of air into the mixture and hence the resulting mixture was rather foamy. The

foamy mixture was allowed to degas for 10 minutes. Then, an ultrasonic sonicator was used to further degas the solution and to disperse the nanoclay platelets uniformly. The ultrasonic sonicator send an ultrahigh frequency pulse into the mixture and was operated at a power of 50-70 W. In order to maintain constant temperature, the ultrasonic sonicator was programmed to operate continuously for two minutes, then stopped for two minutes. This cycle was repeated for a sonication time of 30 minutes. Catalyst, promoter and gel-time retarder were added to the mixture and stirred well. This catalyzed resin was poured into a mold and allowed to cure. Two different cure cycles were studied : (i) room temperature cure for 24 hours and (ii) curing at elevated temperature (100⁰ C) for 3 hours followed by a 24 hours room temperature cure. After the initial curing process, part of the specimen is subjected to a high temperature post-cure cycle to investigate the effect of post – cure on the resin. Specimen with 0 %, 3 %, 5 % and 8 % clay loading (by weight) were fabricated following the above procedure. Fiber reinforced composites were fabricated using two different processes, namely, vacuum assisted resin transfer molding (VARTM) and vacuum assisted wet lay-up (VAWL). In the VARTM process, conventional procedures were followed for lay-up and arrangement of 16 fiber layers. To maintain repeatability of the process, a fixed vacuum pressure 30 kPa for all laminates. The laminate was allowed to cure under vacuum pressure ate room temperature for 24 hours and then post-cured using the same post-cure cycle as above.

From the observation, sonication was found to be an effective mixing method to separate nanoclay stacks. TEM image clearly indicate intercalation of resin in the gallery space of nanoclay and some areas of exfoliated nanoclay with random orientation. Initial elastic modulus of resin increases with addition of nanoclay and improvement increases with increase in nanoclay loading. Compressive strength (off-axis) increases substantially with addition of

nanoclay for specimens extracted from off-axis tests show an increase of 22% and 36% with 3% and 5% nanoclay, respectively. The prediction results of the elastic-plastic model also confirm the enhancement in compressive strength resulting from addition of nanoclay. Hence it can be concluded that the proposed approach of enhancing compressive strength of fiber reinforced composites with addition of nanoclay is indeed feasible.

Fiber Volume Fraction in Composite (C_f)	Type	Off-axis angle (degree)	Misalignment angle (degree)	Compressive strength	
				Test (average) (MPa)	Prediction (MPa)
22%	0% Nano	10	1.1	196	200
		15		166	164
	5% Nano	10	3.2	232	227
		15		182	186
36%	0% Nano	0	1.5	423 (extracted)	438
		5		302	308
		10		233	220
		15		199	192
	3% Nano	0	1.3	518 (extracted)	527
		5		349	353
		10		268	257
		15		197	202
	5% Nano	0	3.1	575 (extracted)	562
		5		347	339
		10		250	249
		15		188	197

Table 19: Summary of the theoretical strength prediction results and tested results.

In Siddiqui et al. [13], the mechanical properties and fractural behavior of nanocomposites and carbon fiber composites (CFRPs) containing organ clay in the epoxy matrix have been investigate.

The laminate composites were fabricated from carbon fiber plain woven fabric and organoclay-filled epoxy resin. The epoxy resin was a DGEBA epoxy. A eutectic mixture of 1,3-phenylenediamine (mPDA) and 4,4-methylenedianaline (MDA) at a ratio of 40:60 by weight was used as curing agent. The addition of MDA was aimed to reduce the viscosity of the epoxy – hardener mixture without affecting the resultant composite properties. Plain woven carbon fiber

with a unit weight of 200 g/m² was used as the main reinforcement for composite laminates. The liquid epoxy was drawn into a beaker, which was heated to 75 ° C to lower the resin viscosity, and a desired amount of I30.P organoclay was added into resin. The I30P clay content was varied between 0,3,5,7 wt% of epoxy resin. The resin and clay mixture was subjected to sonication using an ultrasonicator at an ultrahigh frequency for 12 hours, while maintaining the resin temperature at 75⁰ C using an oil bath. The details of sonication power and duration were chosen after an extensive preliminary trial and error. the mixture was outgassed in a vacuum oven, followed by addition of curing agent in 23 wt% of epoxy and stirring for 3 minutes.

Ten ply laminates of 30 cm square were prepared by hand lay-up with all warp tows in the same direction on a steel mould plate. Necessary precautions were taken to keep fabrics well aligned. A 25 µm thick Teflon release film was inserted in the mid-plane of the laminate at right angle to the warp direction as an initial crack for the mode I interlaminar fracture toughness test. The moulded laminates were wrapped with bleeders and peel plies within a Teflon dam all around, which was cured in vacuum hot press. The laminates were cured at 80⁰ C for two hours and at 150⁰ C for 10 hours, followed by post cure at 160⁰ C for 2 hours. The high curing temperature excursions for long durations were applied to make sure the resin was completely cured. A low pressure of 0.3 MPa was applied for the first 10 hours to maintain a constant fiber volume fraction of 21% ± 1% and a uniform laminate thickness of 5.2 ± 0.5mm. The laminates were cooled to room temperature before removal from the hot press.

From this experiment, it was concluded that the organoclay brought about a significant improvement in flexural modulus: an increase of 26% was registered with the addition of 3 wt% clay. The flexural strength gradually decreased with increase in clay content. There was a direct or inverse relationship between the fracture toughness and clay concentration, depending on the

loading rate. The quasi-static fracture toughness increased about 60% with the addition of 3 wt% clay, and further increase in clay content was not beneficial to fracture toughness. There was a large drop of nearly 45% in impact fracture toughness with only 1 wt% clay, followed by little variation with further increasing the clay content. The flexural properties of CFRP composites generally followed the trends against clay concentration, similar to the matrix nanocomposites. The modulus increased while the strength decreased marginally with increase in clay content. The organoclay modified epoxy gave rise to significant improvements in both crack growth resistance and fracture toughness of mode I interlaminar fracture of CFRP composites. Both the initiation and propagation values of CFRP composites increased with increasing clay content: in particular, the propagation fracture toughness almost doubled with 7 wt% clay loading. There was a strong correlation found between the static fracture toughness of organoclay-modified epoxy and the interlaminar fracture toughness of CFRP composites. The data obtained in this study also fell within the well-established general trend for other CFRP composites, partly confirming the validity of test results.

Matrix (clay content)	Carbon fiber content (vol%)	Flexural Strength (MPa)	Normalized Strength (MPa)	Flexural modulus (GPa)	Normalized modulus (GPa)
0%	22.1	401.2±23	363.0±21.3	19.0±.9	17.2±0.7
3%	22.3	385.1±22.8	345.4±21.4	19.4±1.2	17.5±1.1
5%	20.5	330.9±44	323.9±43.8	18.5±1.1	18.1±1.1
7%	21.2	365.4±20.5	344.7±19.4	20.0±1.5	18.9±1.4

Table 20: Flexural properties of CFRP without and with organoclay reinforcements.

In Miyagawa et al. [14], the mechanical and thermophysical properties of biobase epoxy nanocomposite reinforced with organo-montmorillonite clay and PAN-based carbon fibers are investigated.

DGEBF (50 wt %) was substituted by the same weight of epoxidized linseed oil (ELO). The mixture of DGEBF epoxy and ELO was processed with an anhydride curing agent methyltetrahydrophthalicanhydride (MTHPA) and 1-methylimidazole accelerator. Organo-

montmorillonite clay, modified with methyl, tallow, bis (2-hydroxyethyl) quaternary ammonium (MT2EtOH) ion, was used as nano-reinforcements. To fabricate the anhydride-cured epoxy nanocomposites reinforced by exfoliated clay nano-platelets, the 2.5 – 5.0 wt% of organo-clay was sonicated in acetone for two hours using a solution concentration of more than 301 of acetone of 1 kg of clay, while being constantly stirred. The DGEBF and ELO were then added and mixed for an additional hour. The acetone was removed by vacuum extraction at approximately 100⁰ C for 24 hours, after which time the anhydride curing agent MTHPA and the accelerator were blended in solution together. After mixing all components, the specimens were cured at 80⁰ C for 4 hours followed by 160⁰C for 2 hours. Intercalated clay (5.0 wt%) nanocomposites were processed without the sonication process; organo-clay particles were directly added to the mixture of DGEBF, ELO, and MTHPA, and mixed together for 30 minutes. The same cure profile clay was used for the intercalated clay nanocomposites.

In the case of Carbon Fiber Reinforced Plastics (CFRP), unidirectional carbon fiber fabric was employed as the reinforcement. The processing of CFRP using four different anhydride-cured epoxy matrix is as follow. They are: (a) pure DGEBF, (b) neat biobased epoxy in which 50 wt% DGEBF was replaced by the same weight of ELO, (c) 2.5 wt% exfoliated clay nanocomposites with 50 wt% of ELO, and (d) 5.0 wt% intercalated clay nanocomposites with 50 wt% of ELO. Exfoliated clay (2.5 wt%) nanocomposites and intercalated clay (5.0 wt%) nanocomposites were processed. Because of the difficulties of processability due to higher viscosity, 5.0 wt% exfoliated clay nanocomposites were not applied for CFRP process. These epoxy resin matrices were painted on 50 X 150 mm unidirectional carbon fiber fabrics, and stacked to produce 10 layers. Finally, CFRP wee processed by compression molding. To avoid resin flow out during the compression molding process, different cure conditions were employed.

The CFRP specimens were cured at 100⁰C under 17.6 kPa (25 psi) for 45 min followed by 58.6 kPa (83.3 psi) for 75 minutes, then followed by 160⁰ C under 58.6 kPa for 2 hours. The heating rate was 2.8⁰ C/min.

Dynamic mechanical analysis (DMA) was conducted and that yielded an increased of 0.9 GPa for the storage modulus of biobased epoxy at 30⁰ C with the addition of 5.0 wt % exfoliated clay nanoplatelets. The glass transition temperature, however, decreased with addition of the organo-clay nanoplates. To completely understand the role of clay nanoplatelets in biobased epoxy nanocomposites, the microstructure of clay nanoplatelets were observed using transmission electron microscope (TEM). Carbon fiber reinforced plastics (CFRP) were processed using the new biobased epoxy/clay nanocomposites as the matrices. Flexural modulus and strength values did not change regardless of the use of different epoxy matrices. This response is normal for a fiber dominated mechanical test. It was, however, observed that the interlaminar shear strength (ILSS) of CFRP improved by adding 5.0 wt% intercalated clay nanoplatelets.

	Flexural modulus (GPa)
DGEBF	131
ELO 50	131
ELO50/2.5 wt% exfoliated clay	129
ELO50/5.0 wt% intercalate clay	124

Table 21: Elastic modulus of unidirectional CFRP containing different epoxy matrix.

	Flexural strength (GPa)
DGEBF	1.32
ELO 50	1.28
ELO50/2.5 wt% exfoliated clay	1.28
ELO50/5.0 wt% intercalate clay	1.29

Table 22: Flexural strength of unidirectional CFRP containing different epoxy matrix.

	Interlaminar shear strength (MPa)
DGEBF	71.6
ELO 50	60.8
ELO50/2.5 wt% exfoliated clay	56.5
ELO50/5.0 wt% intercalated clay	64.1

Table 23: Interlaminar shear strength of unidirectional CFRP containing different epoxy matrix.

In Chang et al. [15], a study was conducted to clarify the intercalation of polymer chains to organoclays and to improve the thermo-mechanical properties.

Dispersion of Na^+ - MMT and Na^+ - Mica were added to solution of ammonium salts of hexadecylamine (C_{16}^-). Organophilic clays were obtained through multi-step process and were called C_{16} - MMT and C_{16} - Mica respectively. In a 500 ml beaker, 4.0 g of hexadecylamine, 2.5 ml of concentrated HCL, and 200 ml of water were placed. This solution was heated at 80°C . In 400ml of water, 10 g of clay was dispersed at 80°C . This dispersion of clay was added to the ammonium salt of the hexadecylamine solution, and the mixture was stirred vigorously for one hour. The precipitate was isolated by filtration, placed in a 250 ml beaker with 300 ml of hot water, and stirred for one hour. The product was then filtrated and freeze-dried. C_{16} - Mica was made using the same procedure of that used for C_{16} - MMT. A mixture of 50.0 g of a DMAc was stirred vigorously at room temperature for four hours. The solution was spread onto a $10 \times 10 \text{ cm}^2$ glass plate, and the solvent was evaporated in a vacuum at 70°C for one day. The films were then cleaned in an ultrasonic cleaner three time for 5 minutes each. These films, with the solvent removed, were dried again in a vacuum oven at 70°C for one day. The thickness of the film were 10-15 μm .

The maximum ultimate tensile strength was observed for blends containing 4 wt% of either of the two organo clays and decreased with further increase in the organoclay content. The initial modulus increased with increasing organoclay content up to 4 wt% for C_{16} -MMT. When

the C₁₆- MMT content was greater than this critical wt%, the modulus of the hybrids started to decrease. In contrast, the initial modulus of the hybrids using C₁₆ – Mica increased continually with increasing clay content from 2 to 8%. The tensile properties of the C₁₆ –Mica hybrids were higher than those of the hybrids containing C₁₆ – MM. The optical translucency was not affected by the organoclay content up to 6 wt%; however, the films containing 8 wt % organoclays were slightly more cloudy.

Clay (wt%)	C ₁₆ –MMT			C ₁₆ - Mica		
	Utl. Str. (MPa)	Ini. Mod (MPa)	Elong. at Break (%)	Utl. Str. (MPa)	Ini. Mod (MPa)	Elong. at Break (%)
0 (pure PLA)	19	208	845	19	208	845
2	27	254	981	41	252	1272
4	28	285	1146	44	270	1150
6	26	276	1054	38	311	1100
8	25	274	1060	31	633	569

Table 24: Tensile properties of PLA/organoclay hybrids films

In a study conducted at University of Akron [16], epoxy- aided dispersion of nanoclay particles in a glassy polymer, polymethylmethacrylate (PMMA), was studied using melt-blending technique. Organically treated nanoclay particles were dispersed in PMMA using mixtures of aromatic and aliphatic epoxies to yield three-phase composite materials, the mechanical properties of which were evaluated and compared with PMMA – nanoclay, epoxy-nanoclay, and PMMA-epoxy composite systems as function of nano- and micro- dispersed domains of phase separated epoxy and nanoparticles.

The epoxy components were mixed in a beaker at room temperature (25⁰ C) in the weight ratio of 90/10, 80/20, and 70/30, respectively, and cured with stoichiometric quantities of DDS at 200⁰ C for three hours. Cloisite[®] 30B clay particles were mixed with the epoxy mixtures by stirring at 80⁰ C for 72 hours to produce epoxy-intercalated clay mixtures containing 10, 20, and 30 wt% clay. The clay-epoxy mixtures thus produced were dried at 80⁰ C for 12 hours in vacuum

oven to remove the traces of moisture. Such large excess of clay were mixed with epoxies primarily to obtain PMMA – epoxy – clay composites with 1-5 wt% clay.

Ground PMMA pellets, dried for 24 hours at 80⁰ C in vacuum oven, were lightly mixed with clay-epoxy mixtures using a spatula to produce a paste, which was dried in vacuum oven for 6 hours at 80⁰ C before mixing in an internal mixer, Brabender Plasticorder at 200⁰ C for 12 minutes. A homogeneous material was produced, to which stoichiometric amount (in relation to the epoxy content) of curing agent DDS was added and mixed further for 4 minutes. PMMA-epoxy blends, without the clay, were prepared in the same manner. PMMA-clay blends, without the epoxy, were prepared by mixing dried clay particles, and PMMA pellets at 200⁰ C for 16 minutes in Brabender Plasticorder. The PMMA- epoxy ratio in blends with and without clay particles was varied between 90:10, 80:20, and 70:30 by weight.

From the study, it was observed that the microscale structures of clay tactoids in melt-blended PMMA – clay composites deteriorated the mechanical strengths, while the nanoscale exfoliated structure of clay particles in epoxy – clay composites improved their mechanical properties. The phase separated epoxy domains in three-phase PMMA – epoxy –clay systems were microscale and contained clay particles either in exfoliated – therefore, nanodispersed inside the epoxy domains – or in intercalated states. These three-phase composites showed the properties with two parts of clay content with fully exfoliated clay structures.

In Wang et al. [17], biopolymer chitosan/montmorillonite nanocomposites have been prepared in which montmorillonite (MMT) is used as nanofiller and diluted acetic acid is used as solvent for dissolving and dispersing chitosan (CS) and montmorillonite. The thermal stability and the mechanical properties of the nanocomposites are characterized by TGA and nanoindentation.

Glacial acetic acid (HAc)- CS/MMT nanocomposites: chitosan solution was prepared by dissolving CS in 2% (v/v) aqueous acetic acid solution at a concentration of 2 wt% followed by centrifuging to remove the insoluble material. MMT was first swelled by 50 ml distilled water and then added to 50 ml chitosan solution with MMT contents of 2.5 wt%, 5 wt%, 10 wt%, followed by stirring at 60 °C for 6 hours. After that, MMT/CS solutions were cast on a plastic dish at 60 °C for 48 hours. The dry films still contained a small quantity of the solvent (HAc), which formed chitosonium acetate, and they were termed HAc-CS-x (x is concentration of MMT). CS/MMT nanocomposites were prepared by the same procedure as HAc-CS/MMT nanocomposites. After drying, the film were soaked in 1 M aqueous NaOH for 5 hours to neutralize the acid followed by rinsing in distilled water to neutral and then dried at 60 °C for 24 hours. They were termed CS-x (x is the content of MMT). All the nanocomposite films were dried at 80 °C for overnight before testing and the neat HAc-CS and CS films were made in the same conditions as their nanocomposites.

From the study, it was observed that, with addition of 2.5 wt% of clay, the moduli of CS 2.5 and HAc-CS-2.5 nanocomposites have increased by approximately 6.8% and 9.8%, respectively, comparing with their neat counter parts. With addition of 10 wt% of clay, the moduli of CS-10 and HAc-CS-10 dramatically increased for about 12% and 26.1%, respectively, indicating that clay addition has effectively enhanced the stiffness of the chitosan system. Therefore it can be concluded that the hardness and the elastic modulus are gradually enhanced with increasing clay concentration. Furthermore, compared to the CS and its nanocomposites and HAc-CS and its nanocomposites, the former have superior thermal stability and modulus as well as hardness to the later ones.

Samples	Modulus (GPa)	Hardness (GPa)
	(500-1000nm)	(1000-2000nm)
With HAc		
HAc-CS	3.76±0.15	0.119±0.006
HAc-CS-2.5	4.13±0.09	0.136±0.002
HAc-CS-5	4.39±0.20	0.147±0.008
HAc-CS-10	4.74±0.34	0.164±0.009
Without HAc		
CS	4.39±0.06	0.176±0.004
CS-2.5	4.69±0.15	0.195±0.008
CS-5	4.71±0.47	0.195±0.022
CS-10	4.92±0.41	0.199±0.023

Table 25 : Summary of the average values of elastic modulus and hardness of chitosan and its nanocomposites as a function of clay concentration.

In Yasmin et al. [18], a three-roll mill was used to disperse/exfoliate the clay nanoparticles in and epoxy matrix and the morphology and mechanical properties were studied.

A three-roll mill was used to disperse and exfoliate the clay nanoparticles in the epoxy matrix. First, the epoxy resin (DGEBA) was placed between the feed and the center rolls. Once the rolls started moving, the clay particles were spread gradually on the resin to get direct and maximum contact with the rolls. The dispersion was achieved by the shear forces generated between the adjacent rolls. Compounding was carried out at room temperature for three hours, with a rotation speed of 500 rpm and a feed rate of 120 g/h. it was observed that the solution became viscous and opaque as the silicate layers dispersed and expanded with time. However, when the dispersion was completed, it produced a clear and transparent solution. The final product from the mill was then collected and mixed with the hardener at 60⁰ C for one hour on a hot plate. After adding accelerator and mixing for a few minutes, the solution was left overnight for degassing. After degassing, the solution was cast in an aluminum mold following ASTM standard D638-99 and cured in an oven at 148⁰ C for an hour. Nanocomposites were prepared with clay contents from 1 to 10 wt %.

The elastic modulus of the nanocomposites is found to increase with increasing concentration of clay and a maximum of 80% improvement is observed from an addition of 10 wt% of clay. However, the decreasing rate of elastic modulus improvement with higher clay content can be attributed to the inevitable aggregation of clay particles. In case of tensile strength a very low improvement was observed and it may be because of the clustering of nanoparticles and/or to the occasional occurrence of nano- to micro-size voids in the microstructure. The observed higher tensile strength with better degassing also confirms the importance of degassing in reducing the number of nano- to micro- size voids.

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Methodology

As mentioned above, the study was limited to the previously published articles, journals and reports. So, initially the number of previous papers were gathered from different data base like Science Direct (paper published by Elsevier) , Compendex (A Complete Scientific Article Database), ABI/INFORM and from the different libraries. After collecting papers, reviews were made, articles will be summarized and tables and graphs will be interpreted and structure in such a manner that anyone can obtain information very easily. Ultimately, the online data base will be developed from the finding of this study.

The will be reviewed in a certain standard format. First the materials used in the experiments will be specified, followed by the sample preparation procedure. Procedure for sample preparation will be reviewed thoroughly as it is one of the important part of the

experiment. After the procedure, the equipment use in experiment and the procedure of the experiment will be discussed. Some of the experiment procedure are so common that they will be discussed in detail in the paper. After the experiment procedure, the data and result will be discussed. Graphs and tables presented in the article will be interpreted and will be organized in a structural manner. From all of those articles review one conclusion will be drawn.

Results/ Evidence

Article	Epoxy used	Clay used	Other material used	Major achievement/ conclusion
1	Part A- resin mixture of DGEBA Part B- hardener mixture of cycloaliphatic amine and polyoxyalkylamine	Inorganic clay K-10 grade montmorillonite	aliphatic diglycidylether epoxy toughener	<ul style="list-style-type: none"> • Increase in flexural strength, highest level of flexural strength at 2 wt % • Highest level of storage modulus at 2 wt%
2	DGEBA in the form of DER 332		Pristine clay- to chemically modify the clay surface Acetone- to facilitate clay modification and dispersion	<ul style="list-style-type: none"> • Both stiffness and toughness of the material were improved through the incorporation of silane-modified clay (SMC)
3	DGEBA CYD-128, OMMT and methyl four phthalic anhydride (MeTPHTA)		2-ethyl-4methyl imidazole as curing agent	<ul style="list-style-type: none"> • Flexural and impact strengths increased. Further these properties increased up to an OMMT content of 2 wt% , followed by a decrease with increasing the OMMT content
4		<ul style="list-style-type: none"> • Styrene Butadiene Rubber (SBR) • Natural Rubber (NR) • Nitrile Butadiene Rubber (NBR) 	Carboxylated acrylonitrile Butadiene Rubber (CNBR)- clay nanocomposites	<ul style="list-style-type: none"> • all of the three nanocomposites exhibit substantially higher 300% stress, shore A hardness, tensile strength and tear strength. • The tensile strength of SBR-clay nano composite exhibited 6.0 times higher
5			Nano composites of poly (ϵ -caprolactone) (PCL) were prepared by melt blending the polymer with natural Na^+ montmorillonite and montmorillonite modified by hydrogenated talloalkyl (HTA) – based quaternary ammonium cation	<ul style="list-style-type: none"> • Tensile properties of the nanocomposites, particularly stiffness, increased continuously with the filler content, at least until a content of 5 wt%, beyond which the mechanical properties leveled off and/or decreased.
6			2-Hydroxyethyl methacrylate, methacrylic acid, Attapulgit, Poly methyl ether methacrylate, $\text{N,N}'$ -methylenebisacrylamide, ammonium persulfate, $\text{N,N,N,N}'$ -tetramethylenediamine	<ul style="list-style-type: none"> • NC hydrogels exhibits much higher toughness than that of corresponding CR hydrogel • The elongation at break of CR hydrogel is very low • The stress to deform NC hydrogels increases with increasing Attapulgit

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7	EPON 828 from Resolution Performance Products and Araldite MY 9512		Cloisite 25 A and 5 µm alumina particles were used to modify the base matrix formulation	<p>content.</p> <ul style="list-style-type: none"> The mechanical properties of the laminates studies were not significantly altered through nanoclay modification of the matrix Lower nanoclay concentrations resulted in a relatively insignificant reduction in microcracking and higher concentrations displayed a traditional filler effect PP/clay nanocomposites with excellent impact strength can be prepared via simple one step, direct injection molding without a conventional pre-extrusion, by dynamic packing injection molding.
8			Isotactic PP with an average diameter about 100 µm was used as basal polymer PP-MA(MA content =0.9 wt %, MI = 6.74) was used as a compatibilizer	<ul style="list-style-type: none"> Initial elastic modulus of resin increases with addition of nanoclay and improvement increase with increase in nanoclay loading Compressive strength increases substantially with addition of nanoclay for specimens extracted from off-axis test show an increase of 22% and 36% with 3% and 5% nanoclay loading respectively
9	Epoxy vinyl resin	Montmorillonite clay (Nanomer I.30 E)	Unidirectional E-glass fiber cloth (E-LR 0908-14) was used to fabricate fiber reinforced laminates	
10	DGEBA	I30P clay	1,3-phenylenediamine; 4,4-methylenedianiline Carbon fiber composites	<ul style="list-style-type: none"> The organoclay brought about a significant improvement in flexural modulus: an increase of 26% was registered with the addition of 3 wt % clay then gradually decreased with increase in clay content There was a direct or inverse relationship between the failure toughness and clay concentration, depending on the loading rate. The quasi-static failure toughness increased about 60% with the addition of 3 wt% clay, and further increase in clay content was not beneficial to failure toughness. There was a large drop of

				<p>nearly 45% in impact fracture toughness with only 1 wt% clay, followed by little variation with further increasing the clay content</p> <ul style="list-style-type: none"> • The modulus increase while the strength decrease marginally with increase in clay content • The organoclay modified epoxy gave rise to significant improvements in both crack growth resistance and fracture toughness of mode I interlaminar fracture of CFRP composites. Both the initiation and propagation values of CFRP composites increased with increasing clay content: in particular, the propagation fracture toughness almost doubled with 7 wt% clay loading • Strong correlation found between the static fracture toughness of organoclay-modified epoxy and the interlaminar fracture toughness of CFRP composites.
11	DGEBF, Epoxidized linseed oil (ELO)	Organo-montmorillonite clay (cloisite® 30B), modified with methyl, tallow, bis (2-hydroxyethyl) quaternary ammonium (MT@EtOH)		<ul style="list-style-type: none"> • Increase of 0.9 GPa for the storage modulus of biobased epoxy at 30°C with the addition of 5.0 wt % exfoliated clay nanoplatelets • In case of CFRP, flexural modulus and strength values did not change, however ILSS improved by adding 5.0wt. % intercalated clay nanoplatelets
12		C ₁₆ -Mica, C ₁₆ -MMT	N,N',-dimethylacetamide (DMAc), poly (lactic acid) (PLA)	<ul style="list-style-type: none"> • The maximum ultimate tensile strength was observed for blends containing 4 wt% of either of the two organo clays and decreased with further increase in the organoclay content. • The tensile properties of the C₁₆-Mica hybrids were higher than those of the hybrids containing C₁₆- MMT
13	DGEBA- aromatic epoxy, Polypropylene glycol glycidyl ether	Cloisite®30B with methyl, tallow, bis-2-hydroxyethyl	Polymethylmethacrylate (PMMA)	<ul style="list-style-type: none"> • The microscale structures of clay tactoids in melt-blended PMMA – clay

14		quaternary ammonium ion as the cation exchange resin	Chitosan	<p>composites deteriorated the mechanical strengths, while the nanoscale exfoliated structure of clay particle in epoxy- clay composites improved their mechanical properties</p> <ul style="list-style-type: none"> • With addition of 2.5 wt% of clay, the moduli of CS 2.5 and HAC-CS-2.5 nanocomposites have increased by approximately 6.8% and 9.8% respectively • With addition of 10% of clay, the moduli of CS-10 and HAC-CS-10 increased for about 12% and 26.1% respectively
15	DGEBA	Unmodified pristine montmorillonite (MMT) Cloisite® 30B	Anhydride hardner (Aradur 917), accelerator (DY070)	<ul style="list-style-type: none"> • Elastic modulus of the nanocomposites increased with increasing concentration of clay and a maximum of 80% improvement is observed from an addition of 10 wt% of clay • Very low improvement on tensile strength

Discussion of Results

From the table above, it can be derived that different kind of mechanical properties, like Tensile strength, Stress strain, Flexural properties, Young Modulus, of nanocomposites will be improve with the mixture of nanoclay. It is always necessary to find the right amount of nanoclay needed because after reaching certain point the mechanical properties tends to decrease even with the additional loading of nanoclay.

It can also be concluded from that it's not only the amount of nanoclay that make difference in the mechanical properties of the nanocomposites but also the way they are prepared, kind of epoxy used, kind of other material or chemical used to accelerate the preparation of nanocomposites. Each studies were unique in a sense that they were done by different people at different circumstance using different type of material but nevertheless the are pointing the same result. All of those studies are suggesting that the enhancement of the mechanical properties of nanocomposites will be achieved by loading the right amount of nanoclay.

Conclusions

From all the articles reviewed, it can be concluded that with the right amount of nanoclay mechanical properties of nanocomposites will be enhanced. It's not only the amount of nanoclay but also the kind of epoxy used, sample preparation technique, pre and post curing of samples contribute equally on the mechanical properties of nanocomposites. Most of the studies were based on Tensile strength, Stress strain, Flexural properties, Young Modulus and it can be said that these properties generally improved with the right amount of nanoclay.

Recommendations

Though this review gave some information about the mechanical properties of nanoclay based nanocomposites, there are lots of things that need to be answer. Since, this field is very wide and numbers of experiments are going around, more articles should be reviewed before to have complete knowledge on nanocomposites. In addition to nano clay, there are other nano fillers too and it's would be very interesting to compare results of nano clay and other nano fillers.

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