

Studies on Mechanical Properties of Calcium Carbonate Filled PPO Composite with Coupling Agent

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ABSTRACT

Polyphenylene oxide (PPO) is an engineering polymer with high good dimension stability and widely used in the automotive and electrical industry. Calcium carbonate (CaCO_3) is one of the most popular mineral fillers used in the polymer composite. It is widely available around the world, easy to grind or reduce to a specific particle size, compatible with a wide range of polymer resins and economical. In the present research work calcium carbonate filled PPO composite of different concentration loading of filler which is 5% to 25%, were prepared by using untreated and surface treated of calcium carbonate with silane coupling agent. Calcium carbonate filled PPO composite with silane coupling agent and without coupling agent was compounded in twin screw counter rotating, having L/D ratio 25:1 and 16mm diameter Extruder, for various compositions and test samples were prepared from the compression moulded sheet. These samples were tested for mechanical properties. The result shows decrease in the Melt flow index, impact strength and elongation at break. There is increase in Flexural modulus with filler loading. There is increase in Tensile strength and Flexural strength, initially with filler loading, followed by decrease in it at higher loading. The improvement in the mechanical properties are seen when calcium carbonate is treated with 3- aminopropyl triethoxy silane as compared to untreated calcium carbonate filled PPO composite.

Key words- PPO, Calcium carbonate, silane coupling agent .

Introductions

W.C.J. Zuiderduin et al. [1] Studied Toughening of polypropylene with calcium carbonate particles. Polypropylene- CaCO_3 composites were prepared on a twin screw extruder with a particle content of 0–32 vol%. The influence of particle size (0.07–1.9 μm) and surface treatment of the particles (with and without stearic acid) on the toughening properties were studied. The matrix molecular weight of the polypropylene was also varied (MFI 0.3–24 dg/min). The modulus of the composites increased, while the yield stress was lowered with filler content. This lowering of yield stress was connected to the debonding of the particles from the polypropylene matrix. From DSC experiments it was shown that the particle content had no influence on the melting temperature or crystallinity of the PP phase, also particle size showed no effect on the thermal properties. The impact resistance showed large improvement with particle content. The stearic acid coating on the particle surface showed a large positive effect on the impact strength. Nhol Kao et al. [2] investigated that the extensional rheology (through melt strength measurement) of calcium carbonate (CaCO_3) filled polypropylene (PP) melts. Different concentrations of CaCO_3 filled PP were produced by mixing two master batches of pure PP and 70wt% CaCO_3 filled PP in required proportions in a counter-rotating twin-screw extruder. It has reported that the melt strength of

the CaCO₃-PP melts was independent of CaCO₃ concentrations up to 25vol%. Further increase in CaCO₃ concentration led to a severe reduction of melt strength. Melt strength was found to be independent of the CaCO₃ filler concentration over the range 0–25vol%, after which it decreased significantly with further increase of CaCO₃ filler concentration. Melt strength was found to decrease with an increase in temperature. S.M. Zebarjad et al. [3] Studied on thermal behavior of HDPE/ CaCO₃ nanocomposites. Thermal behaviour of high density polyethylene and its nanocomposites reinforced with both uncoated and coated calcium carbonate were investigated. They found that addition of 10vol% calcium carbonate to HDPE causes a slightly rise in its melting point but stearic acid content has no significant effect on the melting temperature of HDPE nanocomposites. Samson Oluropo Adeosun et al. [4] Studied physical and mechanical characteristics of polypropylene (PP) and calcium trioxocarbonate (CaCO₃) composites prepared by melt blending. The mechanical properties like tensile strength and impact energy resistance and physical like density and water absorption capacity properties of the composites were evaluated using 0% - 40% of the filler. The results showed that 20%- CaCO₃ addition improved the ultimate tensile stress by 58%, and the UTS is 84% better when 25%- CaCO₃ addition is made while the impact resistance decline by 8 and 12% respectively at these two compositions. In addition, the density only differ from that of pure PP at 25% CaCO₃ addition by 18% increment, however, water absorption increased by 400% at 10%-CaCO₃ addition. Fouzia Zoukrami et al. [5] Studied Elongational and shear flow behavior of calcium carbonate filled low density polyethylene. calcium carbonate filled low density polyethylene (LDPE) was prepared and the influence of filler content, particle size, and surface treatment with stearic acid on the strain hardening and viscoelastic properties of the composites were investigated. They found that the effect of filler content and particle size are negligible on strain hardening behavior. Also the filler surface treatment has a less important effect on the nonlinear elongational tests in comparison with low frequency range measurements. However in shear rheology, they observed the absence of yield stress and network structure at different filler contents, and the presence of shear thinning behavior. Chi- Ming Chan et al. [6] Studied Calcium carbonate filled polypropylene nanocomposite. Composites were prepared by melt blending. The average particle size of the calcium carbonate is 44nm. The dispersion of the particles in PP is good for filler content below 9.2 vol%. DSC result indicated that the calcium carbonate nanoparticles are very effective nucleating agent for PP. Tensile modulus of the composites increased by approximately 85%, while the ultimate stress and strain, as well as yield stress and strain were not much affected by the presence of Calcium carbonate nanocopolites. B.S.Tuenetal.[7]studied Mechanical properties of talc- and (calcium carbonate)-filled poly(vinyl chloride) hybrid composites. composites filled with calcium carbonate (CaCO₃), talc, and talc/CaCO₃ were prepared. Talc-filled composite showed the highest flexural modulus and the lowest impact strength, whereas uncoated, ground, 1- μ m CaCO₃ (SM 90) showed optimum properties in terms of impact strength and flexural modulus among all grades of CaCO₃. Kazuta Mitsuishi et al.[8] studied mechanical properties calcium carbonate filled polypropylene. Calcium carbonate of various particle shape (CaCO₃, sphere, cube, needle) treated with alkyl dihydrogen phosphate ester (APEN, C_nH_{2n+1}OPO(OH)₂, n = 1, 4, 8, 10, 12) and poly(propylene) (PP) were mixed on a two roll mill. The effect of carbon number of APEN on the mechanical properties (tensile elongation, tensile strength, impact strength, yield stress) and adhesion between PP matrix and various CaCO₃ particles and the effect of CaCO₃ shape on the storage modulus of elongated PP/CaCO₃ has been investigated. The tensile elongation, impact strength and adhesion of PP-CaCO₃ interface increased with carbon number of APEN (n \leq 10) for needle and cube type, but the dependence of tensile properties on APEN carbon number is not clearly recognized for the sphere type Sahai et al. [9] Studied the effect of the coupling agent on fly ash filled polyphenylene oxide composites with different filler concentration (5 to 25% by weight) on the mechanical and rheological properties of the polyphenylene oxide composites (PPO). It was found that with the addition of fly ash as filler in PPO showed improvement in flexural strength and modulus with the increase in fly ash concentration, whereas tensile strength, melt flow index and impact strength are found to decrease with increase in fly ash. Addition of fly ash as filler into the Polyphenylene oxide with coupling agent increased the mechanical properties such as tensile strength, Impact strength, elongation at break, flexural strength and flexural modulus as compare to untreated filler filled.

Experimental work

Materials

Polyphenylene oxide grade Dpnr UF-M-010 was obtained from Dhara Petrochemicals Private Limited Mumbai. Calcium carbonate obtained from Jai Vardhman Khaniz Private Limited. Calcium carbonate particles are generally spherical in shape and range in size from 30 μm to 50 μm . Silane coupling agent (3-Aminopropyl) triethoxysilane (APTES) was obtained from sigma Aldrich. Calcium carbonate was preheated in an air circulated oven at the temperature of 100⁰C for one hour. A solution ethanol/ water (95/5 %) adjust to the pH 4.5 to 5.5 with acetic acid. Silane is added with stirring to yield 2 % final concentration. Five minutes were allowed for hydrolysis and silanol formation. Filler added to the solution agitated gently and after 12 minutes, they rinsed free of excess materials. And then cure of the mixture was done at 100⁰ C for one hour. Mixing was done in tumbler mixer at different proportion of calcium carbonate (treated and untreated) with PPO for 5 minutes. The pre-dried raw materials are dry blended in the require ratio (5, 10,15,20,25 wt % of talc) in twine screw extruder which is counter rotating with 16 mm diameter and L/D ratio 25:1. The processing parameter and temperature of extrusion molding are given in table.

Zone I	Zone II	Zone III	Zone IV	Die	Screw rpm
200 ⁰ C	230 ⁰ C	260 ⁰ C	280 ⁰ C	270 ⁰ C	60

Table : The processing parameter and temperature of extrusion molding.

The extrudate material which is calcium carbonate filled PPO composite is pelletized using Boolani pelletizer. The rpm of the pelletizer is maintained between the ranges of 40-50 rpm. Compression moulding was done in to make a sheet of composite which is (180x180x2). The test specimens were cut for the tensile as per the ASTM D638, for flexural test as per the ASTM D790 M 92, and for the impact testing as per the ASTM D256.

Result and discussion

Melt Flow Index of Calcium Carbonate filled PPO Composite.

Melt flow index of untreated Calcium Carbonate filled Polyphenylene Oxide composite.

Table 1 Presents variations in melt flow index of Calcium Carbonate filled PPO composite. It can be seen that melt flow index decreases with increase in concentration of Calcium Carbonate filled PPO. The decrease in melt flow index is due to agglomeration of the particles results in restriction of flow. The trend of variation in melt flow index is presented in the **figure 1**

Melt Flow Index of (3-Aminopropyl) triethoxysilane coupling agent treated Calcium Carbonate filled PPO composite.

Table 1 shown variation in melt flow index of (3-Aminopropyl) triethoxysilane coupling agent treated Calcium Carbonate filled PPO composite. It has been seen that there is slight reduction in value of MFI of coupling agent treated at 5% and 10% Calcium carbonate filled PPO composite. It may be due to good adhesion between treated Calcium carbonate with coupling agent and PPO polymer, lowering the agglomeration particles formed. The trend of variation in melt flow index is presented in the **figure1**.

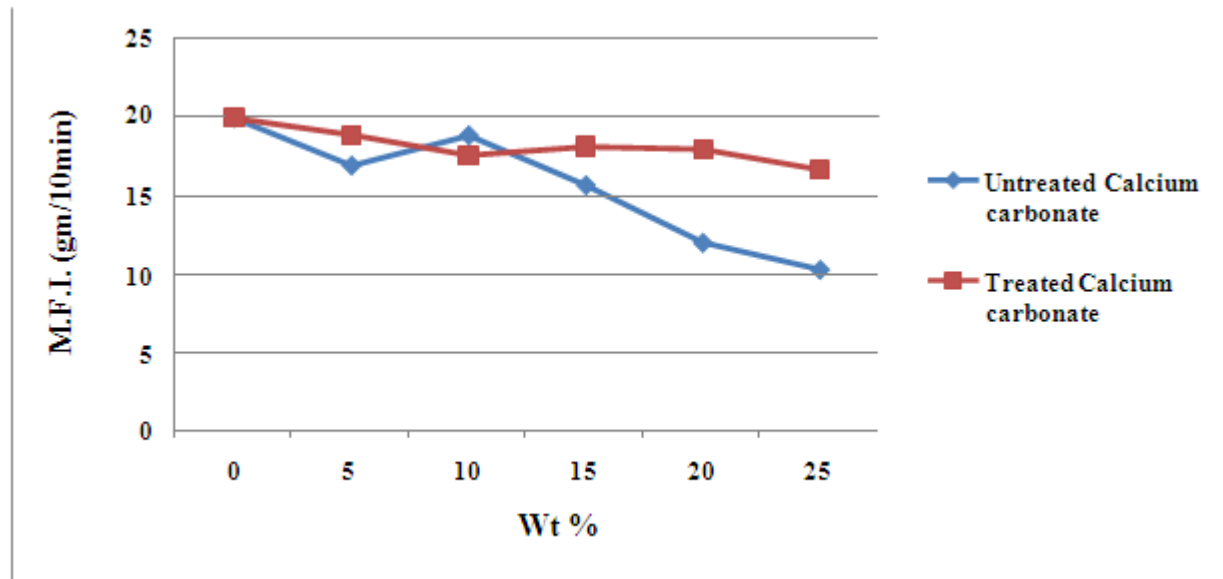


Figure 1 Variation of M.F.I of untreated and treated calcium carbonate filled

Poly phenyleneoxide composite

Impact strength of Calcium carbonate filled PPO composite.

Impact strength untreated Calcium Carbonate filled PPO composite.

Table 2 shows that the value of impact strength of untreated Calcium Carbonate filled polyphenylene oxide. It can be seen that the impact strength decreases with increase in filler loading. The trend in impact strength supports the phenomenon of agglomeration of particles. Decrease in impact strength is may be due to reduction of elasticity of material due to filler addition and thereby reducing the deformability of matrix and turn the ductility, so that composite trend to form a weak structure, an increase in concentration of untreated Calcium carbonate reduces the ability of PPO matrix to absorb energy and thereby reducing the toughness, and impact strength. The trend in variation in impact strength of untreated Calcium carbonate filled polyphenylene oxide composite shown in figure 2.

Impact strength of (3-Aminopropyl) triethoxysilane coupling agent treated Calcium Carbonate filled PPO composite.

Table 2 shows the variation in impact strength of (3-Aminopropyl) triethoxysilane coupling agent treated Calcium carbonate filled polyphenylene oxide composite. It has seen that the value of impact strength at 5% treated Calcium carbonate filled PPO composite is higher, but further increase in concentration of the Calcium carbonate, impact strength decreases. It can be concluded that the impact strength of the silane coupling agent treated Calcium carbonate is higher as compare to untreated Calcium carbonate filled PPO composite. Improvement in impact strength is may be due to proper dispersion, therefore good adhesion between Calcium carbonate and PPO which improve the impact strength of the composite. The trend in variation in impact strength of coupling agent treated Calcium carbonate filled polyphenylene oxide composite shown in figure 2.

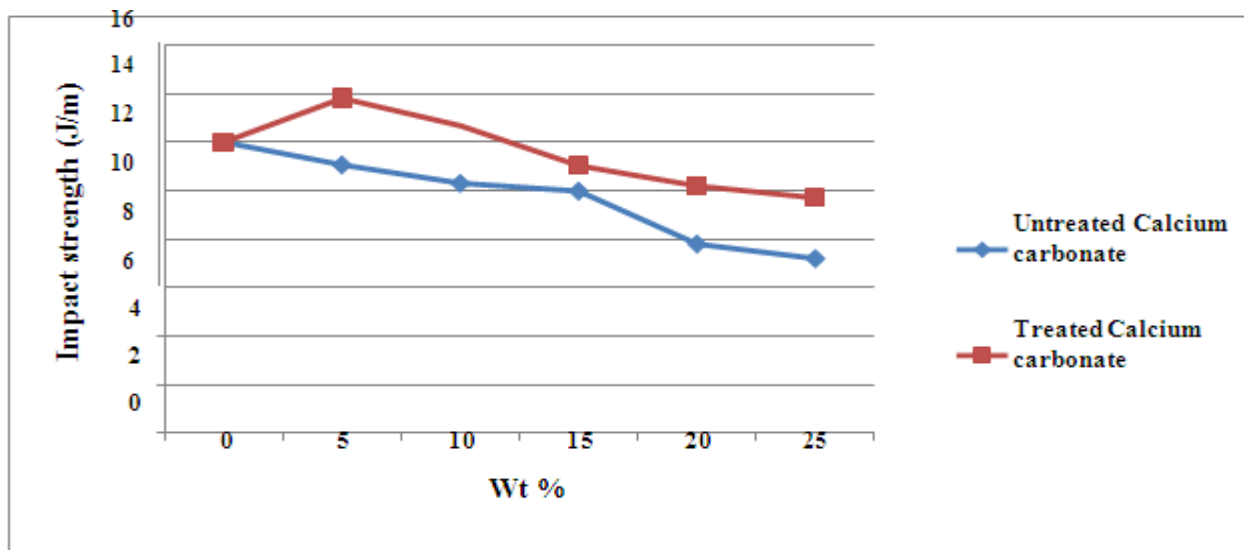


Figure 2 variation of the Impact strength of calcium carbonate filled Polyphenylene Oxide composite.

Flexural strength of Calcium carbonate filled PPO composite.

Flexural strength of untreated Calcium carbonate filled PPO composite.

Table 3 presents the variation in flexural strength of Calcium Carbonate filled polyphenylene oxide composite. It can be seen that the value of flexural strength is higher at 10% loading of filler filled PPO composite, but the value of flexural strength at 15% loading of filler almost same virgin PPO. It can be concluded that the value of flexural strength slightly decrease at 5% loading of filler, and slightly increase at 10% loading of filler, but further slowly decreases the value of flexural strength up to 20% loading of untreated Calcium Carbonate, and drastically decrease at 25% loading of Calcium Carbonate filled PPO composite. At lower concentration the value of flexural strength is comparable to untreated Caco3 which may be due the proper dispersion of the Calcium Carbonate with sufficient matrix quantity of PPO which predominates the effect of filler, but at higher concentration of Calcium Carbonate dispersion is poor as well as insufficient matrix t which is at 25%. Thereby reduction in effective total surface area for responding the applied stress and, hence the value of flexural strength drastically decreases. The trend in variation in flexural strength of untreated Calcium carbonate filled PPO shown in **figure 3**.

Flexural strength of (3-Aminopropyl) triethoxysilane coupling agent treated Calcium carbonate filled polyphenylene oxide composite.

Table 3 presents the flexural strength of (3-Aminopropyl) triethoxysilane coupling agent treated Calcium carbonate filled polyphenylene oxide composite. It can be seen that value of flexural strength increases as percent loading of increase up to 10% of treated Calcium carbonate, but further decreases in flexural strength with increase in loading of treated Calcium carbonate. The value of flexural strength is higher at 5% loading of treated Calcium carbonate, improvement in flexural strength of treated coupling calcium carbonate filled PPO composite is due to increase in adhesion between filler and polymer and proper dispersion. The trend in variation in flexural strength of treated Calcium carbonate filled PPO shown in **figure 3**.

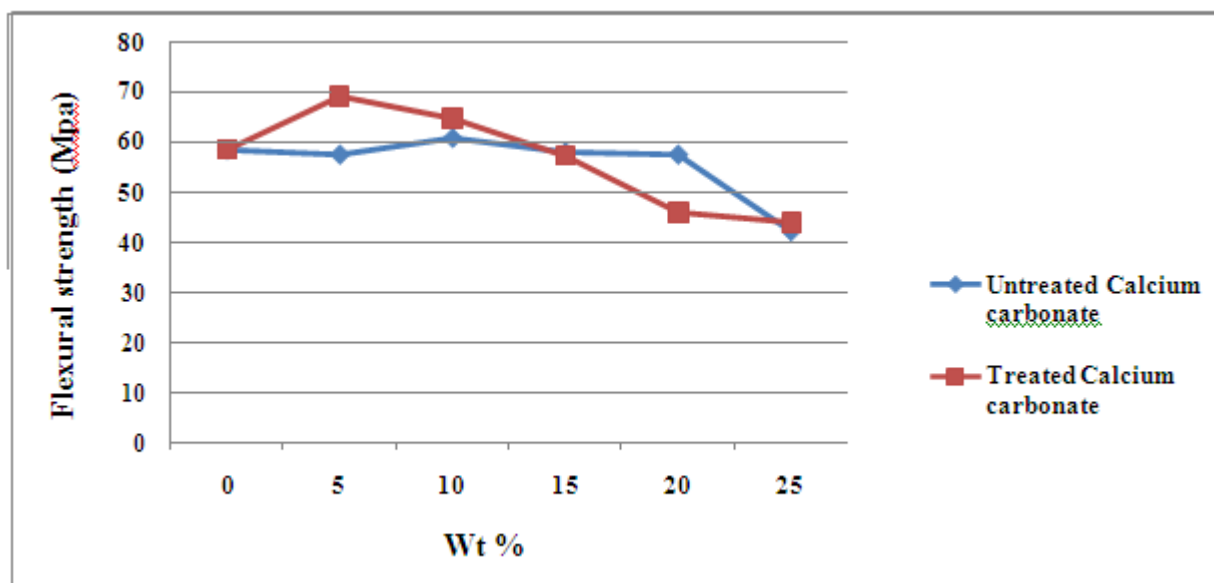


Figure 3 variation of flexural strength of calcium carbonate filled PPO composite

Flexural modulus of untreated Calcium carbonate filled PPO composite.

Table 4 presents the variation in flexural modulus of Calcium carbonate filled PPO composite. It can be seen that the flexural modulus increases with increases in loading of untreated Calcium carbonate. The trend of variation of flexural modulus of Calcium carbonate filled PPO composite is shown in **figure 4**

Flexural modulus of (3-Aminopropyl) triethoxysilane coupling agent treated Calcium carbonate filled PPO composite.

Table 4 indicates that the variation in flexural modulus of (3-Aminopropyl) triethoxysilane coupling agent treated Calcium carbonate filled PPO composite. It can be seen that flexural modulus of composite, increases as the concentration of the filler increases in composite, where as there is an improvement in flexural modulus when Calcium carbonate is treated with coupling agent. The increase in flexural modulus may be due to proper adhesion between Calcium carbonate and PPO polymer, which improves the strength of the polymer chains. The trend of variation of flexural modulus of Calcium carbonate filled PPO composite is shown in **figure 4**.

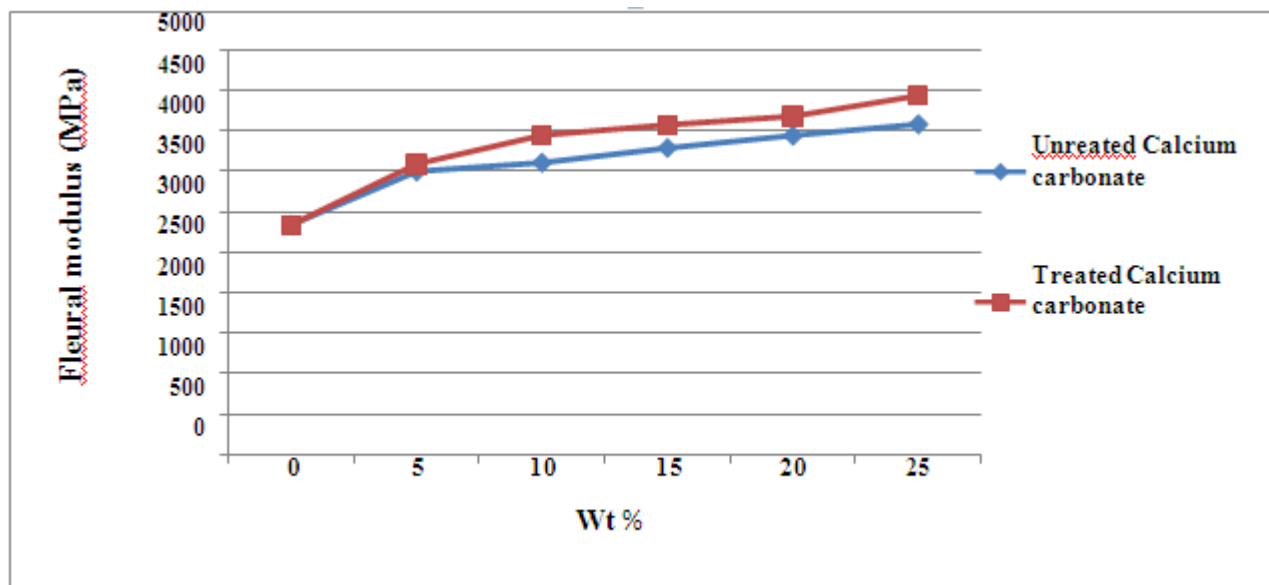


Figure 4 variation of flexural modulus of calcium carbonate filled PPO composite

Tensile strength of Calcium carbonate filled PPO composite.

Tensile strength of untreated Calcium Carbonate filled PPO composite.

Table 5 presents variation in the tensile strength of untreated Calcium Carbonate filled polyphenylene oxide composite. It can be seen that the tensile strength increases at 5% loading of untreated Calcium carbonate due to addition strengthening of polymer chains by restricted chain moments but with further increase in filler loading at 10% of untreated Calcium carbonate it decreases. But increase in loading of filler at 15% to 20% again increase in tensile strength and decreases at 25% loading of filler. It can be concluded that higher value of tensile strength at 20% and lower at 25% of loading of untreated Calcium carbonate filled PPO composite indicates that at 25% loading of filler agglomeration is more thereby interaction of individual filler particles reduces thereby reduction in total effective adhesion between filler and polymer is not good and affected the tensile strength of the composite. Increase in tensile strength is may be due to strong adhesion between filler and polymer thereby effective stress transfer between filler and polymer. The trend in variation in the tensile strength of treated with silane coupling calcium carbonate filled PPO composite is shown in **figure 5**.

Tensile strength of (3-Aminopropyl) triethoxysilane coupling agent treated Calcium Carbonate filled PPO composite.

Table 5 shows variation in the tensile strength of (3-Aminopropyl) triethoxysilane coupling agent treated Calcium Carbonate filled polyphenylene oxide composite. It can be seen that there is increase in tensile strength with increase in filler loading up to 15%. However it decreases at 25% filler loading. There is an improvement in tensile strength when Calcium carbonate is treated with silane coupling agent as compare to untreated calcium carbonate filled PPO composite. Increase in tensile strength is may be due to treated Calcium carbonate providing good reinforcement, thereby good adhesion between filler and polymer and effective stress transfer ability between polymer and filler. The trend in variation in the tensile strength of treated with silane coupling Calcium carbonate filled PPO composite is shown in **figure 5**.

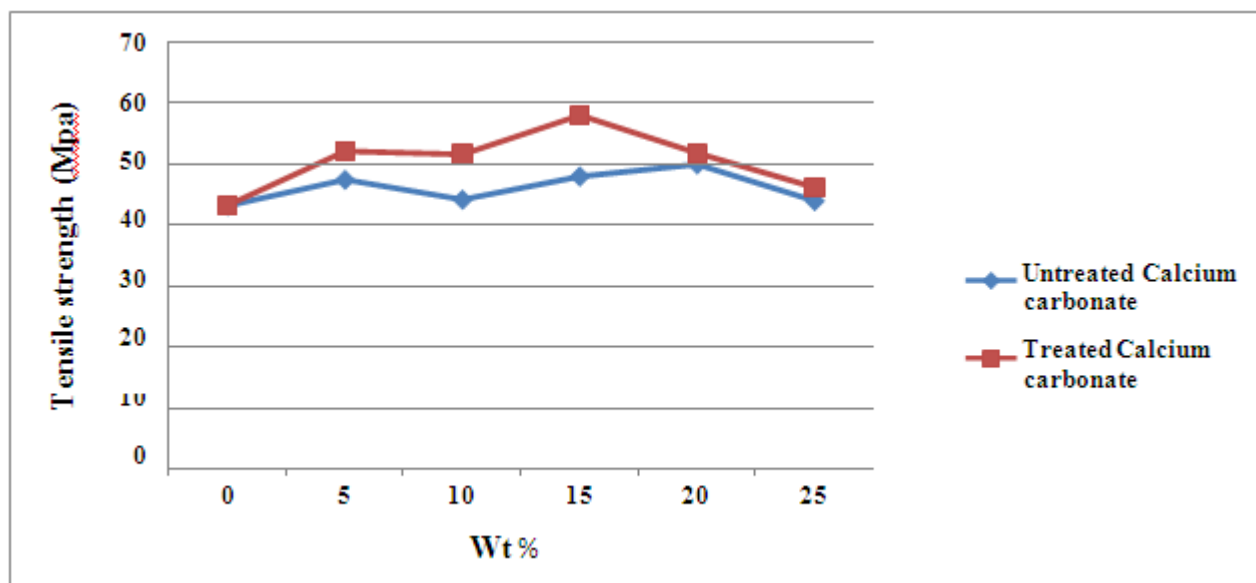


Figure 5 variation of Tensile strength of calcium carbonate filled polyphenylene oxide composite

Elongation at break of Calcium carbonate filled PPO composite.

Elongation at break of untreated Calcium Carbonate filled PPO composite.

Table 6 shows the variation in elongation at break of untreated Calcium carbonate filled Polyphenylene oxide composite. It can be seen that the elongation at break decreases drastically to at lower concentration which is 5% of untreated Calcium carbonate filled PPO composite. It can be seen that increase in filler concentration, decreases the elongation at break. This decrease in elongation is attributed to restriction of PPO polymer chain movements as well as restricted chain entanglements. The extent of filler dispersion plays an important role in changing properties of untreated Calcium Carbonate filled PPO composite. Even though, there was proper filler and matrix bonding, this bonding appeared unable to withstand shear strain and elongations at rupture of untreated Calcium Carbonate filled PPO composite. The concentration of filler increases the polymer chain movement and displacement due to applied force reduces. The trend in variation in elongation at break of untreated Calcium carbonate filled PPO composite shown in **figure 6**.

Elongation at break of (3-Aminopropyl) triethoxysilane coupling agent treated Calcium Carbonate filled PPO composite.

Table 6 presents the variation in elongation at break of (3-Aminopropyl) triethoxysilane coupling agent treated Calcium Carbonate filled PPO composite. It can be seen that elongation at break decreases with increase in filler loading. However it is slightly higher, when Calcium Carbonate is treated with silane coupling agent as compare to untreated Calcium carbonate filled PPO composite. It indicates that good dispersion of filler into the matrix as silane improve the adhesion between filler and matrix, the improvement has seen more when PPO is filled with silane coupling agent treated Calcium Carbonate, thereafter the decrease rate of elongation at break is slow. The trend in variation in elongation at break of treated Calcium carbonate filled PPO composite shown in **figure 6**.

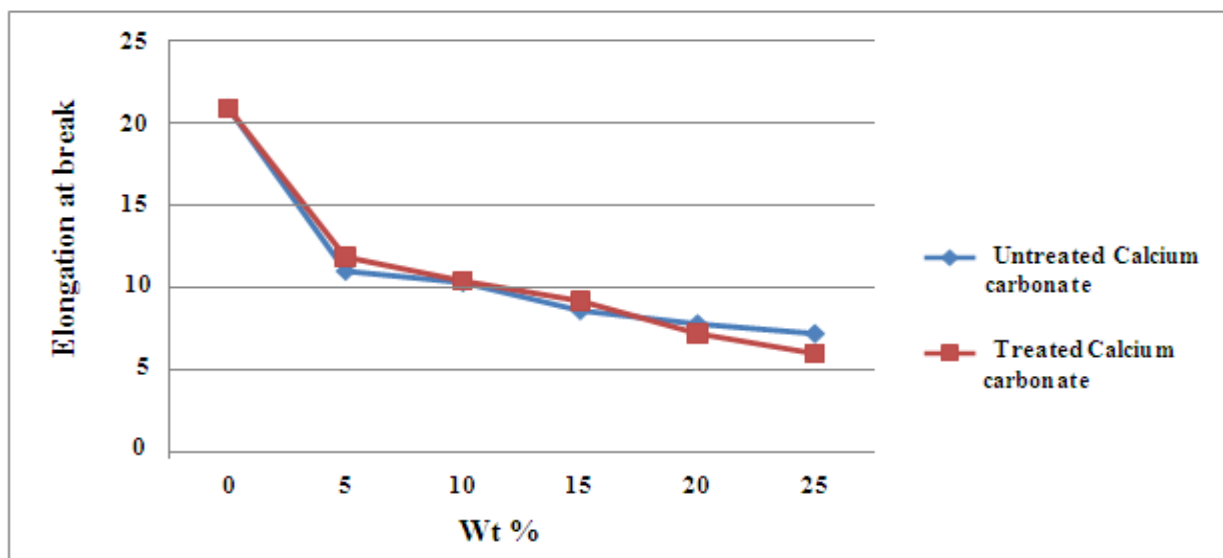


Figure 6 values Elongation at break of calcium carbonate filled PPO composite

TABLES

Wt %	M.F.I. (gm/10 min)	
	Untreated Calcium carbonate filled PPO	Coupling agent treated Calcium carbonate filled PPO
0	19.93	19.93
5	16.92	18.86
10	18.83	17.56
15	15.67	18.12
20	12.02	17.95
25	10.31	16.64

Table 1 Values of M.F.I. of Calcium carbonate filled PPO composite.

Wt %	Impact strength (J/m)	
	Calcium carbonate filled PPO	Coupling agent treated Calcium carbonate filled PPO
0	12	12
5	11.06	13.8
10	10.3	12.67
15	9.98	11.03
20	7.8	10.2
25	7.2	9.71

Table 2 Values of Impact strength of Calcium carbonate filled PPO composite.

Wt %	Flexural strength (Mpa)	
	Untreated Calcium carbonate filled PPO	Coupling agent treated Calcium carbonate filled PPO
0	58.56	58.56
5	57.6	69.2
10	60.9	64.8
15	58.1	57.31
20	57.6	46.1
25	42.3	44.09

Table 3 Values of Flexural strength of Calcium carbonate filled PPO composite.

Wt %	Flexural modulus (Mpa)	
	Untreated Calcium carbonate filled PPO	Coupling agent treated Calcium carbonate filled PPO
0	2839.26	2839.26
5	3498.34	3590.17
10	3607.18	3947.43
15	3789.47	4076.01
20	3941.34	4182.1
25	4081.21	4435.62

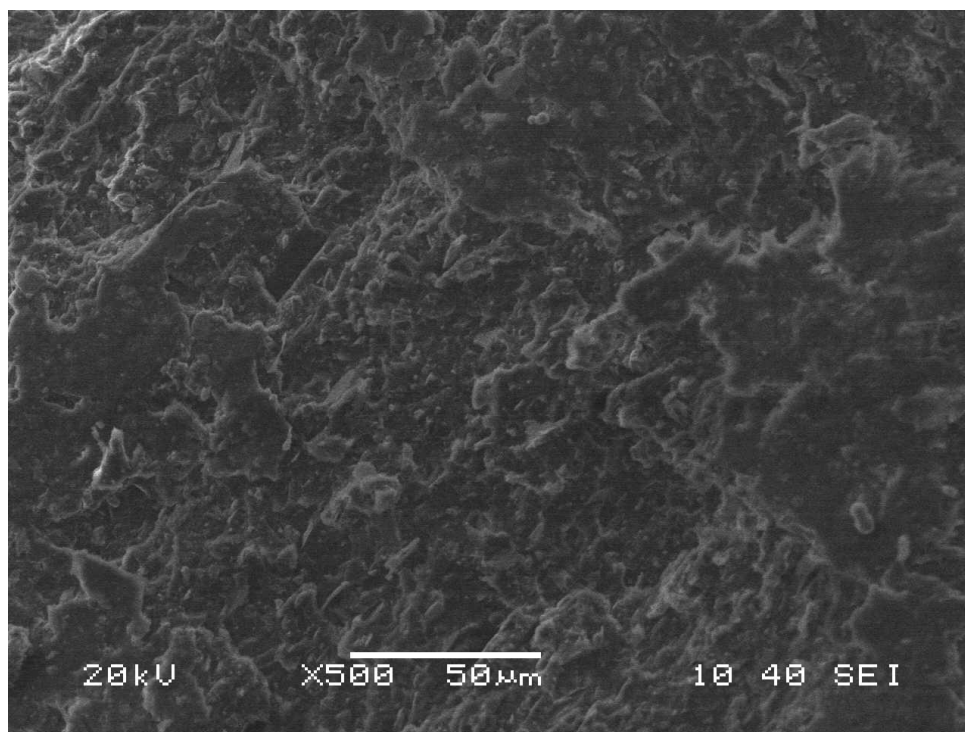
Table 4 Values of Flexural modulus of Calcium carbonate filled PPO composite.

	Tensile strength (Mpa)	
Wt %	Untreated Calcium carbonate filled PPO	Coupling agent treated Calcium carbonate filled PPO
0	43.19	43.29
5	47.46	52.13
10	44.2	51.6
15	48.02	58
20	50	51.8
25	44	46.2

Table 5 Values of Tensile strength of Calcium carbonate filled PPO composite

	Elongation at break	
Wt %	Untreated Calcium carbonate filled PPO	Coupling agent treated Calcium carbonate filled PPO
0	20.9	20.9
5	11	11.85
10	10.3	10.4
15	8.6	9.2
20	7.8	7.2
25	7.2	6

Table 6 Values of Elongation at break of Calcium carbonate filled PPO composite.



SEM 15% CaCO₃ (untreated)

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