

## 7. DISCUSSION

Surface area and structure from DBP (Dibutyl Phthalate ) adsorption of china clay (kaolin) is far below to the precipitated silica and reinforcing carbon black.(20) Therefore kaolin is less significant in rubber compounding as a reinforcing filler. To increase the significance as a reinforcing filler, the kaolin surface was modified by calcination, oxination and acetate/acrylate (polymer) treatments. Reduced the particle size by ball milling and also discarded the coarser particles by incremental sedimentation method.

Compound No.(2) shows lower hardness than compound No.(1) due to the kaolin which was added as a filler to the compound No.(2). This kaolin was calcined, ballmilled and ballmilling caused surface structure breakdown. (see table 6.3) Calcination of kaolin (at 800°C for 4 hours) leads to condense free silanol groups on the particle surface and reduce the surface hydration. Surface hydration causes retardation in sulphur cure systems and decreases the physico mechanical properties of vulcanizates. But calcination does not contribute to structural breakdowns of filler particles.(21)

In addition to the calcination, sample CLX-2 was subjected to (8 hours) ball milling to reduce particle size of kaolin. Sample CLX-3, CLX-4 and CLX-5 were also ball milled while mixing with required chemicals and polymers. (see table 5.1) Presumably the process of ball milling provide vacant active sites of kaolin for in situ reactions with (polar) polymers/chemicals which are already added to the medium thereby preliminary reduce the agglomeration or increase the dispersion in rubber compounding. (10)

When comparing the modulus of compound Nos.(1) and (2), (see graph 6.2 ) compound No.(1) shows abrupt rise due to the addition of unmodified clay as a filler in compounding, may be ascribed to the predominance of agglomerates remain relatively un dispersed in rubber and contributes higher modulus.(18)

Wallace plasticity readings of compound No.(3) shows lower value than compound Nos.(1) and (2) (see table 6.2) due to higher dispersion property. In compound No.(3), the filler (sample CLX-3) was modified in such a way that the added oxine makes a dative bond with aluminium ions (of aluminates of kaolin) and reduce the attraction between Silicate and Gibbsite layers or reduce the agglomeration of kaolin. (12) It is important to note that oxination is not affected by the pH value of the medium but always advantages if it is ammonical in rubber compounding with sulphur cure systems. And also the advantage of oxination is that the hindering power of active aluminium sites leads to increase active silicate sites which can be reacted with polar polymers or coupling agents. Therefore oxine can be used as surface modifying agent of kaolin. (1) (14)

Graph (6.1) represents typical results obtained from the TGA (Thermo Gravimetric Analysis) measurements of oxine treated china clay (sample CLX-3) showing weight percentage loss over the temperature range from 30-800°C. The oxinated kaolin showed small weight loss at relatively low temperature and could be due to the loss of organic layers (groups) on the filler surface which are not hydrolysed and the cleavage of siloxane bonds or in other word loss of bound water molecules.(2) Mostly my effort in this thermo gravimetric analysis was to find any effect on kaolin due to oxination in and around the temperature range where the compounds are subjected to vulcanization.

Generally in rubber compounding, kaolin produce relatively greater reinforcement with more polar elastomers such as NBR and CR than non polar Natural rubber, BR. and SBR.(20) The lack of reinforcement properties or incompatibility of unmodified kaolin with non polar polymers (NR) be corrected mainly by using silane coupling agents. In the silanization mechanism, kaolin change their reinforcing characteristics. This effect largely precludes the formation of a silicate network.. The introduction of covalent silica/silicate-rubber bonds, the

strongest conceivable contribution to rubber reinforcement (16). But silanes are very costly in the rubber chemical market. Therefore using silane or silane modified kaolin in the local rubber industry is rare.

Therefore it was decided to improve the compatibility of kaolin with non polar polymers (Natural rubber) in such a way that premodifying the kaolin surface by grafting acetate and/or acrylate polymers to give rise to improved mechanical properties of cured compounds through maximum dispersion and reinforcement.

Treatment of kaolin with functional acetates are widely used in surface modified clay industry. In this experiment, (sample CLX-4) vinyl acetate (non-aqueous) was mixed in the pentane medium because vinyl acetates hydrolyse in water medium and (26) and therefore not effect in attaching or reacting with caolin particals.

Cure characteristics of compound No.(4) was improved only after the addition of DEG.(Diethylene Glycol ) DEG esterify with the bound water on the clay surface and then only increase the cure rate. (3) Therefore it is evident that bound water on kaolin surface was not much effected by the acetate treatment in the non aqueous medium.

In the sample CLX-5 modification, acrylate polymer (emulsion grade) react with silanols of clay surface. The resultant effect is the solubilisation of kaolin particles in the acrylate polymer matrix with consequent enhancement of the modulus of cured compound No.(5). (see table 6.4)

The most important fact in the acrylate polymer treatment is that the cure characteristics of compound No.(5) has improved up to the level of compound No.(8). <sup>(Table 6.1)</sup> Therefore it is evident that modified clay filler (sample CLX-5) shows similar properties to sulphur cured carbon black (N-330) in compounds. This optimum cure properties related to the modified clay, is due to almost all the silanols of kaolin particles have been reacted with acrylate polymers and reduced

almost all the bound water molecules which are contributing to the retardation in sulphur cure systems.(5)

Therefore it is evident that in sample CLX-5, silanols on kaolin surface are fully exhausted by mechanical and chemical means and exhibit improved physical properties of relative vulcanizates. (18) Maximum filler dispersion also contributes to a higher modulus may be due to the ammonia in the sample CLX-5. Ammonia is capable in disrupting the filler-filler bonding.(2)

It is well known that bound rubber value of carbon black compound (compound No.8) is due to interaction between carbon black and (NR) hydrocarbon rubber. (see table 6.7) But theoretical explanation to the bound rubber of silica/silicate compounds are very complicated. In this experiment, acetate and acrylate treated clay filled compounds (compound No.4&5) show high bound rubber values due to gel formation. According to the suggestions of Polmenteer and Lentz (2) apparent gel formation (in compound No.5) is due to ammonia, known to be crosslinking agent for polymers. Untreated, oxinated and sedimented clay filled compounds (compound Nos.1,2,3&6) show relatively no bound rubber values.

Plasticity of the rubber compound has an inverse relationship to the Wallace rapid plasticity number. According to the table (6.2), compound No.(3), (4) & (5) show lower Wallace plasticity numbers due to higher dispersion. Compound No.(6) & (7) show higher Wallace plasticity numbers than compound No.3,4 & 5 as sediment clay shows lower dispersion.

According to micro photographs, compound No.(8) shows highest dispersion of filler particles due to very high surface area and high structure of carbon black. (N-330). Compound No.(3), (4) and (5) show better dispersion than compound No.(6) and (7) because the process of oxination combined with ball milling is more efficient than the process of sedimentation method that was followed. Non polar pentane gives better filler particle dispersion to the compound No.(4). And

compound No.(5) also shows higher filler dispersion due to efficient particle size reduction caused by higher shear rate in water medium ball milling.(10)

From the summarised physical test results (see tables 6.2,6.3,6.4,6.5,6.6) it is evident that compound No.(5) is the most effective in increasing physical properties of vulcanizates such as modulus, tensile strength, abrasion resistance and resilience out of modified clay filled rubber compounds. Here the relative modified clay filler (sample CLX-5) contributes to the maximum reinforcement reaching towards the properties of carbon black (N-330). And also the compound No.(5) shows cure characteristics as same as reinforcing carbon black filled compound without adjusting the accelerator system or extra addition of amine or amino functional derivatives. (see table 6.1) Apart from the above properties, this modified china clay gives toxicological safety to the reactions products.

In this acrylate polymer treatment of kaolin, (sample CLX-5) reinforcing effect may not be due to the coupling effect of polymer-filler bonding such like in silanization. But lengthy or bulky polar polymer molecules which are attached or grafted to the surface of kaolin particles, entangle with non polar polymer (NR) chains in rubber compounding and increase the stiffness or increase the immobilisation of chain segments of cured compounds and influence the physical vulcanizate properties. Due to the mechanical shear also in compounding, NR polymer chains as well as acetate/acrylate polymer chains (already attached to the filler particles) form radicals. These radicals may cause polymer-polymer branching and leads to a polymer-polymer- filler attachments. This is an aspect of reinforcement with china clay (silica/silicate) in particular to which little attention has been paid so far.(3)

The phenomenon of (polar) polymer grafting is very interesting for the technology point of view and need further developments through optimisation and variation of functional groups such as nitriles, carboxilates etc. attached to the (grafting) polymer so as to obtain vulcanizates of desired properties.

## 8. CONCLUSION

The action of reinforcement of surface modified china clay or kaolin in (non polar) rubber compounding was studied. The resulting effect of the modification, arose from the dispersion and the reinforcement due to the nature of grafted polar polymer to the kaolin surface.

It was established and experimentally confirmed that the acrylate polymer treatment of kaolin, improved the physico mechanical properties as well as cure characteristics in sulphur cure systems. And this modified filler showed properties closer to the reinforcing carbon black..(N-330)

Principal aspects of modification and the effect was presumed in four steps as follows:

- \* Ball milling provide higher surface area for in situ reaction with polar polymers or oxine in the medium.

- \* Oxine reduces filler-filler agglomeration by reacting with Aluminium ions of Gibbsite (hydrous alumina) layers of kaolin thereby increasing the availability of active silica sites to be reacted with (grafting)polar polymer.

- \* The polarity of grafting polymer governs the rate of reaction with china clay.(Silica/Silicate)

- \* The compatibility of surface modified (polymer grafted) clay with non polar rubber (NR) in compounding, depends on the characteristics of the grafted polymer.

As a whole it was found that acrylate polymer treatment is far better than acetate treatment in surface modification of china clay. Also the acrylate treatment is more advantages than the calcination, in the process of bound water reduction from the kaolin surface. And the process of oxine treatment/ball milling is more efficient than the process of sedimentation/polymer flocculation.



## **9. SUGGESTIONS FOR FURTHER IMPROVEMENT**

### **9.1 Changing the Amount of Filler**

The filler concentration for this project was only 30 phr. It will be useful to continue this project by changing the acrylate polymer modified filler (sample CLX-5) concentration and compare the variation of properties with same amount of reinforcing carbon black filler loading in rubber compounding.

### **9.2 Surface Modification of China Clay with Nitrile Rubber**

- (a) As in the acrylate polymer modification (Sample CLX-5), china clay surface can be modified with 'nitrile latex' by replacing acrylate polymer. It is important to note that nitrile latex grade should be selected by considering its properties (viscosity, -CN pendant group concentration etc.) and the suitability for this application. It is useful to optimize the nitrile latex concentration for easy processing and maximum reinforcing effect in rubber compounding.
- (b) China clay surface can be modified with nitrile latex in such a way that excess amount of -CN pendants groups are available after the modification. It is known that -CN group can be chemically converted into -COOH group. If china clay is modified with -COOH pendant groups attached to the clay surface, it may act similar to carbon black in rubber compounds.

### **9.3 NMR Analysis**

In the china clay surface modification, the silicate (china clay)/polar polymer intermediates and products, can be subjected to solid state NMR spectroscopic analysis to determine the reaction mechanism between polar polymer and clay particles. It is useful in evaluation peaks and their intensities obtained from spectra. By analysing the spectra, it may be possible to describe in detail the chemical reaction.



#### **9.4 Optimize Tire Compound Formulations with Modified China Clay**

- (a) It is very much useful to optimize the bicycle tire compound formulations with modified china clay. Here filler can be completely replaced by modified clay or maximize the amount with less amount of high structure reinforcing carbon black. However the cost also should be considered.
- (b) For white side wall tire compounds, silica filler can be replaced completely or partially to reduce the cost.



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