ACRYLIC AND CPE MODIFIED PVC-U COMPOSITES – EFFECT OF RICE HUSK ASH ON IMPACT PROPERTIES

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ABSTRACK

PVC-U is an important material nowdays because of its widely used in construction and manufacturing as an alternative materials beside to wood and metal. The impact properties of PVC-U will become brittle once it is exposed to low temperature, subjected to high strain rate and occurrence of notching. The effects of using acrylic and chlorinated polyethylene impact modifiers, white rice husk ash (WRHA) and LICA 38 in PVC-U composites were presented in this research. Mixing was carried out by using a blender. PVC-U composites of different impact modifier and filler loading were compounded using two-roll mill and the specimens for impact strength testing was prepared using hot-press. Impact strength was measured according to Izod mode. The dimension for the specimens was according to ASTM D 256A on an Izod mode. Different composition of acrylic, CPE and WHRA were used in this study. As the impact modifier content was increased from 0 to 8 phr, impact strength increased steadily for both impact modifiers. As the filler content was increased from 10 to 30 phr, impact strength decreased steadily. It is interesting to observe that titanate-coupling agent (LICA 38) is successful in increasing PVC composites with 20 phr WRHA by 58.3% for acrylic modified PVC-U and by 21% by CPE modified PVC-U. This shows that LICA 38 is effective in enhancing the interfacial adhesion between WRHA and PVC-U matrix.

Keywords: Impact strength, impact modifier, coupling agent, rice husk ash, PVC-U composites

ABSTRAK

Sifat kekuatan hentaman bagi PVC-U adalah penting kerana penggunaannya semakin melaus bagi meggantikan pengunaan bahan seperti kayu dan logam. Kajian yang terperinci harus dilakukan memandangkan PVC-U mudah menjadi rapuh sekiranya terdedah kepada suhu yang rendah, mengalami daya terikan yang tinggi dan menpunyai lekuk Tujuan utama kajian ini dijalankan adalah untuk mengkaji kesan kandungan akrilik dan CPE (pengubahsuai hentaman) dan kandungan abu sekam padi putih (pengisi) terhadap sifat kekuatan hentaman bagi PVC-U. Agen pengkupelan juga ditambah ke dalam formulasi untuk meningkatkan sifat mekanikal PVC-U. Proses pencampuran dibuat dengan meggunakan pengisar campur manakala proses pengadunan menggunakan penggiling berkembar dua. Penekan panas digunakan bagi menghasilkan spesimen mengikut piawai yang telah ditetapkan dalam bentuk kepingan. Dimensi spesimen yang dijasilkan adalah berdasarkan ASTM D256-A. Mesin Izod ATS FAAR: Impats 15, model Resilience digunakan untuk meguji kekutan hentaman sample. Akrilik, CPE dan WRHA pada komposisi berlainan telah ditambahkan ke dalam PVC-U untuk melihat kesannya terhadap kekuatan hentaman. Penambahan akrilik dan CPE dari 0 hingga 8 phr telah membawa kepada peningkatan kekuatan hentaman PVC-U. Keadaan sebaliknya berlaku, apabila penambahan pengisi (WRHA) dari 10 ke 30 phr telah meyebabkan kekuatan hentaman menurun. Kekutan hentaman dapat dinaikkan sebanyak 58.3% setelah agen pengkupelan Titanate (LICA 38) ditambah pada komposisi PVC-U terubahsuai dengan akrilik yang turut terisi dengan 20 phr WRHA manakala peninkatan sebanyak 21% bagi PVC-U terubahsuai CPE. Keadaan ini dengan jelas menunjukkan bahwa LICA 38 adalah efektif dalam meningkatkan daya rekatan antara matriks PVC-U dan WRHA sekaligus meningkatkan kekuatan hentaman PVC-U.

INTRODUCTION

Incorporation of various types of fillers into a polymer matrix can be used to developed polymer composites with different properties. Different types of fillers have extensively been used in rubber and plastic industry either to adjust the properties or reduce the material cost. Recently, investigation of utilization of filler derived from agricultural products or waste as an alternative to inorganic fillers in thermoplastics has received much attention (Nawang et *al.*, 2000). Apart from low cost, which is the prime impetus to such growing interest, these materials offer many environmental and technical benefits (Joseph et *al.*, 1996). Sharma et al. reported that Sago starch filled linear low-density polyethylene showed improved degradability of the composites. Incorporation of rubber-wood powder into high density polyethylene improves the tensile modulus and flexural modulus at the expenses of tensile strength, elongation at break and impact strength. In a similar study by Fuad et *al.*, incorporated two types of fillers namely white rice husk ash (WHRA) and black rice husk ash (BRHA) into PP matrix using twin screw compounder. Of the two fillers, WRHA is rich from silica with approximately 96% (w/w) silica while BRHA contains only about 56% (w/w). Both types of fillers exhibited their capability to strengthen the PP matrix (enhance the tensile modulus) at the expense of some other mechanical properties. One of the most important aspects in the materials development of engineering thermoplastics is to achieve a good combination of properties and processability at a moderate cost. As far as mechanical properties are concerned, the main target is to strike a balance of stiffness, strength and toughness. There are at least two approaches that have been identified as potential routes to achieve this goal. This involves the incorporation of short-fiber reinforcements such as rice husk ash and impact modifiers into thermoplastics matrices to from short-fiber reinforced thermoplastics and rubber-toughened thermoplastics respectively. The presence of stiff reinforcement such as rice husk ash inside thermoplastics is associated with an enhancement in stiffness and strength. However, the improvement in toughness is rather limited especially when the materials are subjected to sub-ambient temperatures and high deformation rates. On the contrary, under the same extreme testing conditions, the incorporation of impact modifiers will, in general, result in a significant improvement in toughness but at the expense of stiffness and strength.

Coupling agent has been commonly applied for the improvement of properties in fiber or particulate-filled composites. The most common type of coupling agent presently used are organofunctionalsilanes and organotitanates. The other coupling agent that is less readily available due to a higher production cost is the organozirconate group. (Monte, 1958). All the coupling agents above may be simplified to the general form $R\text{-}M\text{-}X_3$ where R is the organofunctional group, M is the tetravalent base metal (Ti for titanium, Zr for zirconium and Si for silicon) and X is a hydrolyzable group (e.g ethoxy for the silane-based coupling agent). Each coupling agent has its own virtues and limitations. For instance when coupling to silica, the Si-O-Si bond from the silane-based coupling agent being stronger than the Ti-O-Ti bond is likely to impart better mechanical properties to the resultant composites than the titanate-based system. Titanium tends to scavenge free radicals and thus affects cure efficiency while Zr^{+4}, being a peroxide activator, accelerates curing process. (Monte, 1985).

This paper reports on RHA-filled modified PVC-U treated with titanate coupling (LICA38). Effect of acrylic impact modifier and CPE impact modifier in enhancing impact strength discussed in this paper.

EXPERIMENTAL

1. Material

The PVC used in this study is a suspension type homopolymer PVC with solution viscosity k-value 66, MH-66, supplied by Industrial Resin Malaysia (IRM) Berhad. It is a medium molecular weight resins designed for general purpose, rigid applications. The PVC blend formulations are shown in Table 1. Generally, the formulations are based upon typical commercial PVC window frames formulations with some modifications. Different content of rice husk ash are used in this research.

Table 1 : Types and suppliers of additives.

Additves	Types	Supplier	Parts per hundred of PVC resin (phr)
Resin PVC	MH-66 (K-66)	IRM Berhad	100.0
Impact Modifier	Core-shell type acrylic modifier & CPE modifier	Elf Atochem	6.0
Filler	Rice Husk Ash	Bernas Nasional	10.0, 20.0, 30.0 & 40.0
Tin Stabilizer	Tin	Elf Atochem	2.0
Internal Lubricant	Calcium Stearate	Sun Ace Kakoh	0.5
External Lubricant	Stearic Acid	-	0.6
Processing Aids	Acrylic Polymer	Kaneka Malaysia	1.5
Pigment	Titanium Dioxide	Tioxide Sdn. Bhd	4.0
Coupling Agent	Titanate- LICA 38	Kenrich Chemicals	-
Dilution Agent	n-Pentane	Kenrich Chemicals	-

2. Application of Coupling Agents

Filler treatment techniques and dosages of the coupling agent were applied as advised by the manufactures of the respective coupling agents. For the titanate-coupling agents, it was the PVC-U resin itself that was treated rather than the filler. This is contrary to that of the silane-coupling agents where the RHA filler itself underwent coupling agent treatment prior to compounding (Fuad et.*al*, 1994).
The dosage for the LICA 38 was 0.2% by weight of PVC-U plus 0.5% by weight of RHA. The coupling agent was diluted in n-pentane to make up a 5% solution, which was sprayed onto the PVC-U as the latter was rotated in a high-speed mixer.

3. Sample Preparation

The rice husk ash samples were obtained by ashing the coarse ground rice husk in porcelain crucibles using a muffle furnace (Isotemp Muffle Furnace model 186A, Fisher Scientific) at 800 °C for 24 hour. The ash samples were allowed to cool down in desiccators and then weighed. The process was repeated until constant weight as obtained. The samples were collected and stored in airtight containers until needed for the usage as fillers in this research. Dried rice husk samples were then coarse ground through a 75 μm mesh sieve on a medium size Wiley Mill (Model X 876249 Brook Crompton Parkinson) Approximately 1.0 kg of material from the sample obtained was ground so that a sufficient quantity of material would be available for the use in the PVC-U blend. It's characteristics are as follows; Mean particle size 5.4μm, surface area 1.4m^2/g and density 2.2g/m^3. The dry blending of PVC and additives was done using high-speed mixer for 14 minutes. Then, the dry blended PVC and additives are sheeted on a two-roll mill before compression molded to from for impact testing.

4. Testing

The impact strength assessment was done using a ATA FAAR PENDULUM tester. Impact specimens were notched (45°C) using Davenport notch cutting apparatus and tested under Izod mode. Test bars was prepared according to BS2782: Part3: Method 359 (1984). All the reported values for the test were the average values of six specimens.

RESULT AND DISCUSSION

Figure 1 shows a sharp increase in impact strength with increasing impact modifier content. Generally impact strength increased for both CPE and acrylic impact modifier with higher content of impact modifier loading. However, acrylic impact modifier gave higher impact strength compared to CPE impact modifier at 6 and 8 phr. These result is in agreement with the findings of (Lutz, 1993) who stated that the impact strength of impact modified PVC-U is improved as the impact modifier concentrations increases from 2 phr to about 20-25 phr. From his studies, it is also revealed that the impact strength begins to drop off a maximum above 20-25 phr. Impact strength is an indication of tolerability for a sudden impact. When a composite is subjected to an impact, rapid crack propagation is initiated through the material. Such crack propagation is initiated through impact modifier particle in the PVC-U and absorb the energy and stop the crack propagation. Lutz (1993) suggested that impact modifier serve two basic functions to increase the toughness pf a PVC-U matrix:

- Crack stopping, whereby the impact modifier stop the propagation cracks initiated by a sudden blow. This function of energy absorption requires the impact modifier to have a degree of adhesion to the PVC continuum, while at the same time maintaining its integrity as a dispersed phase. Proper particle size (ultimate particle size) and efficient distributions of the impact modifier are essential so that the concentration of impact modifier particles is adequate to "be at the right place" when needed.
- Yield promoting, where by the impact modifier lowers the yield point (stress) of the PVC, allowing it to yield or deform rather than fracture when subjected to a sudden blow. This mechanism makes it possible to suppress brittle or catastrophic failures. A contributing mechanism is the generation of heat when the elastomeric-type impact modifier is deformed in a viscoelastic manner. The instantaneous heating of the surrounding PVC matrix results in raising the glass transition point to allow yield rather than brittle fracture.

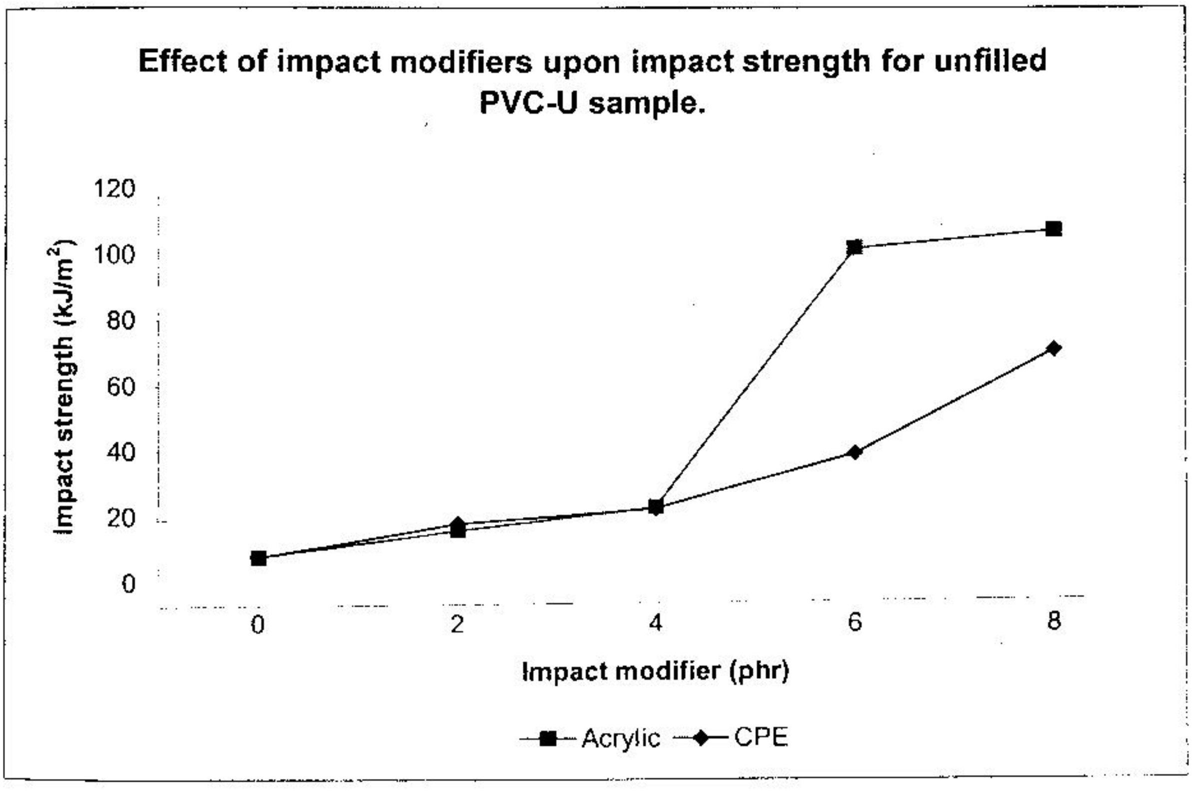


Figure 1: Effect of acrylic modifier and CPE modifier loading upon impact strength.

Incorporation of various types of fillers into a polymer matrix can be used to modify the mechanical properties of polymer composites besides reducing cost. Previous researchers have revealed that stiffness increases with increasing loading of filler content (Fuad *et al.*1994). However the increase in stiffness occurs with a sacrifice in impact strength. The result in Figure 2 shows that the impact strength drops sharply as fillers is incorporated into the composites. The increase in brittleness in the filled composites can be attributed to the weak interfacial adhesion between the RHA fillers and the PVC matrix.

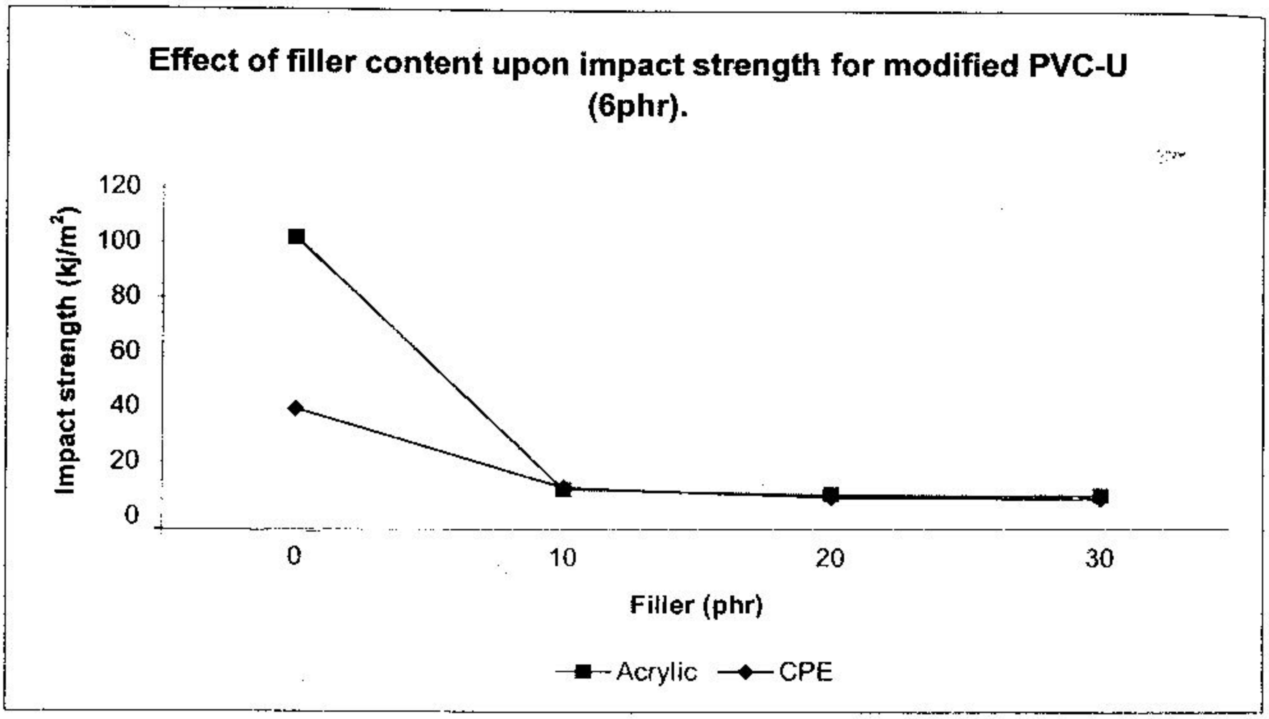


Figure 2 : Effect of filler loading and impact modifiers on the impact strength of modified PVC-U/RHA composites.

The next step is to increase the interfacial adhesion between the fillers and PVC matrix through the use of suitable coupling agent. Generally, it can be seen that coupled RHA exhibit significantly high impact strength than uncoupled rice husk ash in modified PVC-U as shown in figure 3. These results were in agreement with the results reported on impact strength of PP/RHA (Fuad et.*al*, 1994). At filler loading of 20 phr treated with LICA 38 modified PVC-U improved the impact strength of the composites. The impact strength increased by 58.3% at 20 phr of filler loading for the acrylic modified PVC-U compared to untreated sample while impact strength increased by 21% at 20 phr filler laoding for the CPE modified PVC-U. It is interesting to observe that usage of acrylic impact modifier gives the better impact strength compared to CPE modifier. This is probably due to the increasing the chlorine content that brings the adjacent chlorine atoms so close together that they produce intramolecular steric hindrance and electronic repulsion, stiffening the CPE molecule and thus reducing its impact modifying and plasticizing effects. (Rudolph *et.al*, 1996) Thus there is an optimum chlorine content for each desired modifying effect in PVC-I It appears that improved filler-matrix adhesion favored the impact property of filled PVC-U composites. When such crack propagation is initiated through filler particle in the filled composite, filler can absorb the energy and stop the crack propagation if filler-matrix interaction is strong enough.

On the other hand if the interfacial adhesion is poor, at the interfacial region, it cannot resist crack propagation as effectively as the polymer and consequently, propagate a catastrophic crack lowering the impact strength. As both rice husk ash and PVC-U is polar, it is expected that interfacial region is good enough and from this research it is revealed that the usage of LICA 38 gives good enhancement in terms of impact strength. All the values are reported is shown in table 2.

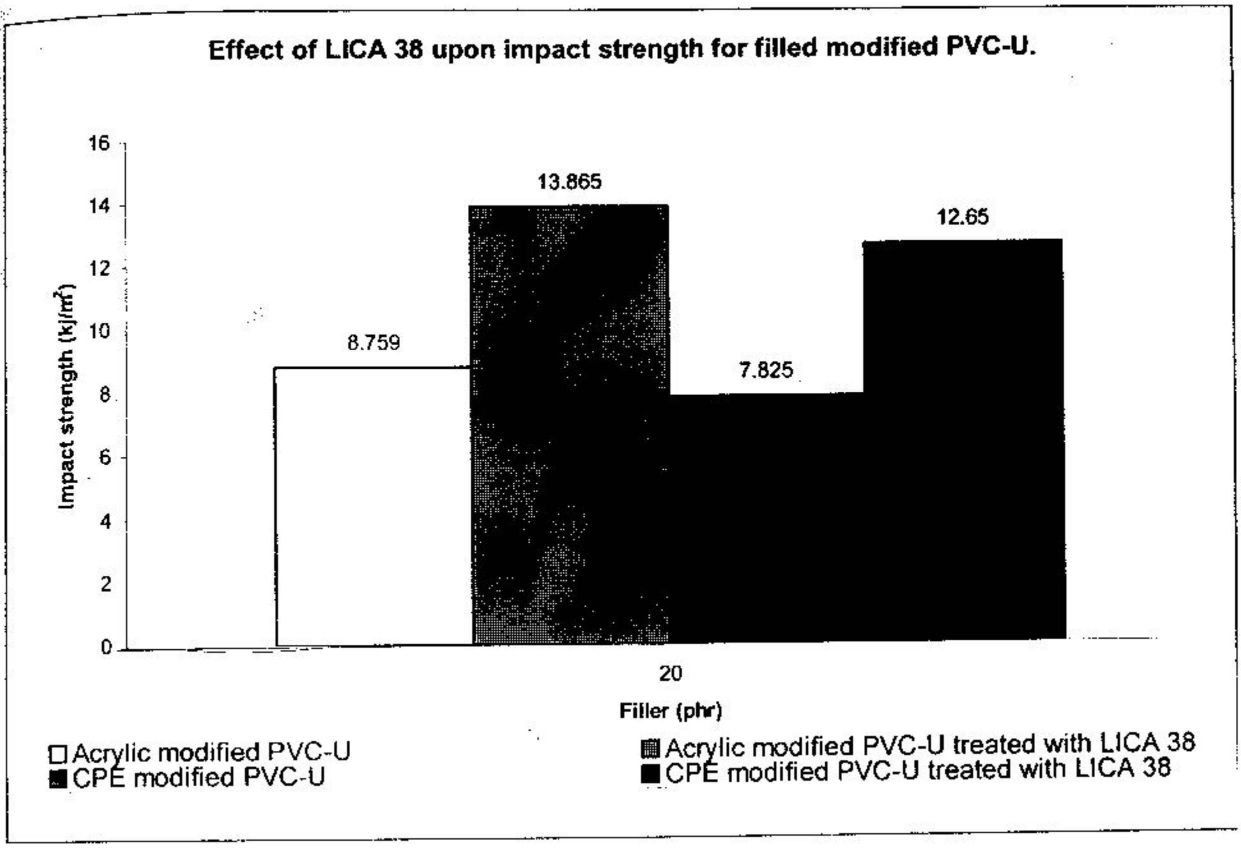


Figure 3: Effect of LICA 38 upon impact strength for filled modified PVC-U at 20 phr of filler loading.

Table 2: Results of Mechanical Tests on RHA Composites.

Property	Impact modifier (phr)	Filler (phr)	Acrylic modified	CPE modified	Acrylic modified treated with LICA 38	CPE modified treated with LICA 38
Izod Impact Strength (kJ/m^2)	0	0	8.1	8.1	0	0
	2	0	16.5	18.6	0	0
	4	0	23.5	23.2	0	0
	6	0	102.1	39.7	0	0
	8	0	107.5	71.0	0	0
	6	10	11.2	10.5	0	0
	6	20	7.8	8.8	13.9	12.7
	6	30	7.5	8.5	0	0

Mechanism of Coupling Agent

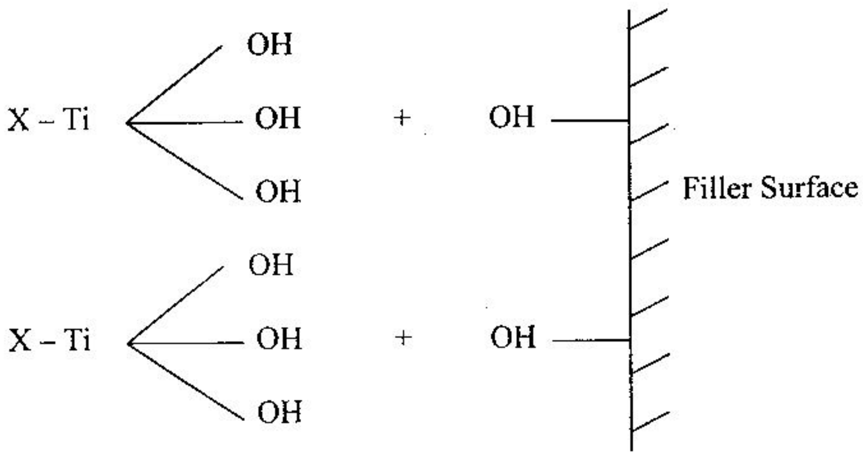
The reaction mechanism of the tetrafunctional oragno-metallic compounds based on silicone and titanium is believed to occur in three steps as shown by the simplified illustration in figure 5. (Fuad et.*al*,1994). First the alkoxy group in the coupling agent undergoes hydrolysis process. Water for the hydrolysis may come form the surface or in the PVC-U resin in the case of the LICA 38 treatment. Next the group reacts with the hydroxyl of the filler surface by hydrogen bond formation. Then Ti-O cross-link are formed between the filler surface and the adjacent functional groups in condensation reaction with the elimination of water.

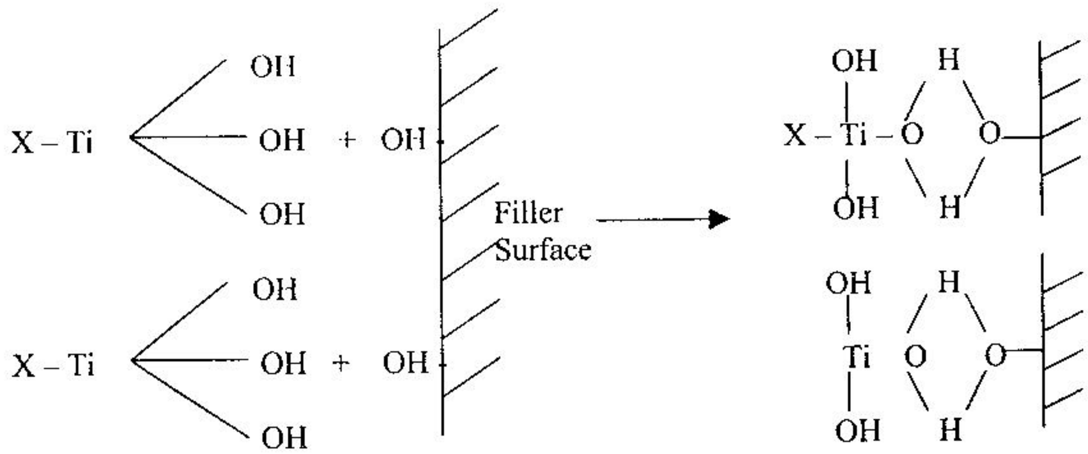
TITANATE TO FILLER'S SURFACE BONDING

Step 1 : Hydrolysis (during mixing)

$$X - Ti(OR)_3 \longrightarrow X - Ti(OH)_3$$

Step 2 : Reaction with filler surface





Step 3 : Condensation

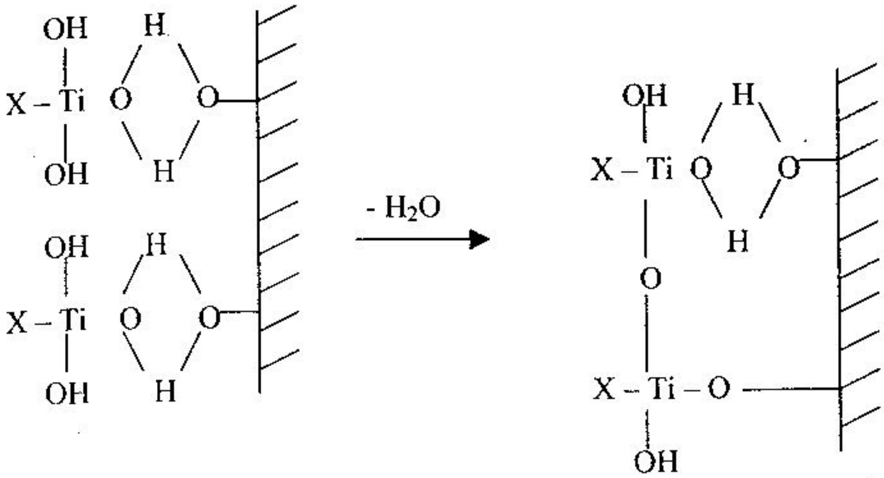


Figure 4: Bonding mechanism of LICA 38 coupling agent to RHA filler's surface.

CONCLUSION

The impact strength of impact-modified PVC increases with increasing content of impact modifier. Acrylic modifier gave higher impact strength compared to CPE at higher content of impact modifier. Addition of RHA caused a reduction in the impact strength of the impact modified PVC-U composites. Coupling agent (LICA 38) was successful in enhancing the impact strength of the RHA filled impact modified PVC-U samples. Overall the application of LICA38 and acrylic modifier provides the optimum balance of mechanical properties for the modified PVC-U/RHA composites.

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