Influence of TiO_2 in Absorbing Electron Beam Radiation on Silicone Rubber

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Abstract

The influence of electron beam radiation on silicone rubber compounded with TiO_2 was studied with variation in doses of the pigment. The rubber was mixed with TiO_2 and a proportionate quantity of silicone rubber cross linker which was then subjected to varying doses of electron beam. The physico-mechanical and the ageing properties of the rubber was investigated with increasing incorporation of the TiO_2 pigment. It was observed that the tensile strength of the polymer rose marginally with a corresponding marginal reduction in the value of elongation at break. The tear strength also displayed a pattern similar to that of the changes in elongation with the highest value lying with the base rubber compound. The heat ageing behaviour indicated a profound positive effect on the retention of tensile properties with increasing content of TiO_2 at different doses of radiation. Considering all the results, the concentration level of TiO_2 and radiation dose has been optimized to achieve a modified silicone elastomer having the best possible physico-mechanical properties.

Keywords – *Electron beam radiation, Silicone rubber, TiO_2, Tensile strength, Elongation at break, Tear strength*

I. INTRODUCTION

Silicone rubbers form a class of elastomers which has diversified applications in spite of their relatively high cost. Silicones are widely used where elastomers come in contact with food and pharmaceuticals and where heat resistance and retention of properties over a wide range of properties are required [1]. It is also known for its weatherability and electrical insulation. It is resistant to oxidation, has low surface energy and resists degradation from ultra violet radiation [2]. These properties contribute enormously to the specified application of silicone elastomers. The distinctive properties of silicone originate from the structure of the polymer which has strong silicone-oxygen bond in the main backbone of the polymer. Organic side groups attached to the silicone atoms contribute to the cross linking and tailored applications [3,4].

Silicone elastomers can be cross linked by a number of curing methods. The peroxide curing methods are normally employed to crosslink silicone by the conventional method [5]. However, ageing tests reveal post curing in case of peroxide cured silicone elastomers if they are subjected to sterilization. This imposes property change with time. Dicumyl peroxide which is often used to cross link silicone elastomers, release organic compounds like acetophenone and cumenalclcohol at the end of the reaction process [6]. Some other studies also involve the cross linking of silicone by thermal process which finds application in pressure sensitive adhesives. In this perspective, a new technique was developed to cross link silicone polymers under the influence of electron beam [7,8].

The electron beam irradiation method of producing cross linked silicone rubbers is often an easier method to employ and control than conventional chemical methods [9]. The technique is extensively used in a wide range of commercial applications like cross linking of heat shrinkable materials, wire and cables, surgical goods and other types [10]. Several investigations have been carried out on the influence of electron beam on several kinds of polymers under different set of reaction conditions. Dworjanyn et.al [11] and Datta et.al [12] reported the effect of electron beam radiation on polymers blended with multifunctional acrylates and methacrylates like TMPTMA (trimethylolpropane trimethacrylate). Studies on ethylene vinyl acetate blended with TMPTMA and TAC (triallyl cyanurate) in presence of electron beam was elaborated by Chaki et.al. [13]. Besides, other experiments with the impact of electron beam were carried out by several authors [14,15]. Polymers mainly like polypropylene (PP), polyvinyl chloride (PVC), ethylene methyl acrylate (EMA) etc. were used in the process [16, 17]. Based on the literature survey, it was revealed that there was enough scope to investigate the effect of electron beam behavior on silicone elastomers and to understand the effect of process variables on cross linking. It was also felt that studies on the incorporation of titanium dioxide (TiO_2) on silicone polymers would account to be an interesting area as titanium dioxide partially absorbs a definite magnitude of radiation. This would possibly minimize the intensity of discolouration produced during the cross linking process by electron beam. So, cross linking of silicone elastomers with electron beam in the presence of titanium dioxide is expected to be significant from the process engineering point of view.

In the present investigation, a thorough and programmed study has been carried out on the curing of silicone elastomer with electron beam in the presence of titanium dioxide. The resulting polymer was characterized by mechanical and ageing properties and the results analysed with respect to variation of electron beam dose and titanium dioxide levels. Since in any polymer industry, the selection of the optimum level of operating variables for manufacturing process is of utmost importance, the present study attempts to optimize the concentration level of TiO_2 and radiation dose to achieve a modified silicone elastomer having the best possible physico-mechanical properties. Silicone rubber NE 9370 LV was used as the base polymer which is the low voltage grade with hardness 70 Shore A. A definite quantity of peroxide in minute amount was added to the elastomer prior to electron beam curing in order to maintain dimensional stability of the samples. The samples were then subjected to electron beam dose and investigated for the nature of electron beam absorption by TiO_2 which is reflected in the characterization reports carried out subsequently.

II. MATERIALS AND METHODS

Silicone elastomer NE 9370 LS was supplied by M/s D J Silicone, China. Titanium dioxide (grade Anatase) was manufactured by Kilburn Chemical Ltd. and supplied by East Corp Chemical Ltd. The peroxide Perkadox 14-40 was obtained from Akzonobel Polymer Chemicals, China.

For preparation of samples one hundred parts by weight of silicone rubber was mixed with 3, 5 and 7 parts by weight of TiO_2 respectively. Each of the individual mixtures was treated with 0.35 parts by weight of the peroxide Perkadox 14-40. The entire mass was well mixed in a Haake Rheocord (Model Haake Rheocord System 40) and subsequently sheeted out from a two roll mill with 2 mm nip gap. The sheets were then compression moulded between aluminium foils under a pressure of $14x10^6$ N/m^2 in an electrically heated press. Aluminium foils were used to reduce the shrink marks on the moulded surface. The mouldings were cooled under compression to maintain the overall dimensional stability of the samples. The thickness of the films obtained was about 1.5 mm. (w/w).

For radiation purpose, the silicone samples in the form of rectangular sheets were irradiated by an electron beam accelerator at Nicco Corporation Ltd., Cable Division, Shyamnagar. The beam energy of the accelerator was 1 – 3 MeV and the beam power was 0.5 to 150 kilo watt. Radiation doses of 20, 40, 60 80 and 100 kGy were used.

Tensile strength, elongation at break and modulus at 100% elongation were measured on dumbbell specimens according to ASTM D412 in a Zwick –1445 Universal Testing Machine at a strain rate of 50 mm/min at 27± 2^0C. The average was taken on four samples and the experimental error was ±5%.

The tear strength was measured on trouser shaped specimen following ASTM D412 in a Universal Testing machine model no. ZMGI-25. Hardness of the prepared samples were measured by Durometer on Shore A scale. Heat ageing of the samples is carried out in a hot air oven at 200°C for 10 days. The tensile strength and elongation at break of the aged samples are measured and their percentage retention values are calculated with respect to the un-aged ones.

III. RESULTS AND DISCUSSIONS

A. *Mechanical Properties*

1) *Tensile Strength*

The influences of variation in TiO_2 content when irradiated with electron beam of different doses for a particular period of time have been investigated through the study of different mechanical parameters developed in the samples due to such irradiation. The modifying influences in terms of tensile strength have been shown in Fig. 1.

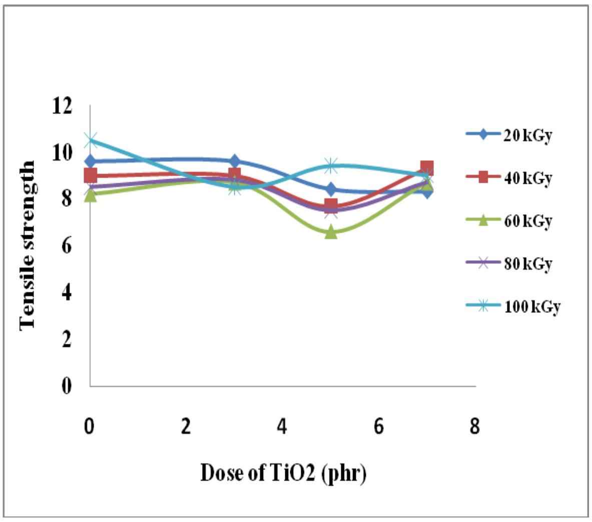

Fig. 1 Variation of Tensile Strength with TiO_2 dose

It is interesting to note that silicone rubber compound containing no TiO_2 cured with PF-40 (same dose for all the formulation) and irradiated with electron beam of different doses within the range of 20 kGy – 100 kGy exhibit quite mentionable changes particularly with respect to silicone rubber which is supposed to be a mechanically weak rubber (as denoted on the ordinate of Fig. 1). It can be observed that the sample treated with doses of 100 kGy possess the highest TS & the samples treated with the other doses of electron beam vary in their values of TS within very narrow range. It is interesting to note that irrespective of the doses of irradiation within the range under study, i.e. (20 – 100) kGy, there is an initial tendency of the T.S. to undergo a slight increase with increasing doses of TiO_2 incorporation with reference to the unloaded, (i.e. without TiO_2) sample for each dose of irradiation, except the one irradiated with 100 kGy which shows a slight downward trend. Once a minimum is reached for each level of irradiation, a minimum fall in tensile strength occurs which then becomes either asymptote or increases further marginally. For any given dose of TiO_2 loading, the tensile strength variation for different doses of irradiation occurs within close range and is somewhat anomalous with respect to changes in doses of irradiation.

Though marginal, the initial change in tensile strength with the immediate incorporation of TiO_2 for a given dose of irradiation (up to 80 kGy) may possibly be ascribed to crosslinked structure formation of silicone rubber. For a given dose of irradiation, it may be assumed that at the lower doses of TiO_2 incorporation, the crosslinking of silicone rubber proceeds unaffected owing to the development of structure and hence rise in tensile strength. Beyond 3 – 3.5 phr of TiO_2, the presence of large number of particles may determine the possibility of interaction between the crosslinking sites of silicone & irradiation. TiO_2 particles may also be assumed to absorb the radiation beyond the critical concentration of TiO_2 & consequently do not allow the formation of structure. This breakdown proceeds till a minimum is reached beyond which possibly the reconstruction / formation of structure takes place further. For every dose of radiation there is a certain threshold concentration / dose of TiO_2 beyond which structure formation & the consequent rise in strength is observed. In the present case, this critical dose of TiO_2 is found to remain almost the same for all other except that of 100 kGy. The minimum dose in case of samples irradiated with 100 kGy appears a little bit earlier. TiO_2 is well known for its characteristic of absorbing electron beam radiation. However for a given dose of electron beam possibly a minimum amount of TiO_2 is required for its absorption & deactivation. However when TiO_2 is present in excess of the minimum dose, the excess amount possibly goes for its reinforcement & the consequent increases in T.S.

*2) **Percent Elongation at Break***

As expected, the % EB of electron beam irradiated samples of silicone without any loading of TiO_2 (as given by the ordinate in Fig. 2) are found to be minimum in case of sample irradiated with 100 kGy while the maximum was obtained with those of 20 kGy irradiated samples. In all the cases, the % EB is found to vary over an extremely narrow range throughout the entire sweep of TiO_2 loading under consideration. The incorporation of TiO_2 in increasing doses is supposed to stiffen the polymer chains by immobilizing the chain segments resulting in reduced flexibility & chain slippage. Hence an onward reduction in % EB should have been the result. On the contrary, the almost constancy of the % EB over the entire range of TiO_2 incorporation for a particular dose of e-beam radiation indicates its ineffectiveness over the doses under study. However in absence of TiO_2, the lower the dose of irradiation the higher is the % EB, possibly because of lower extent of structure formation due to cross linking.

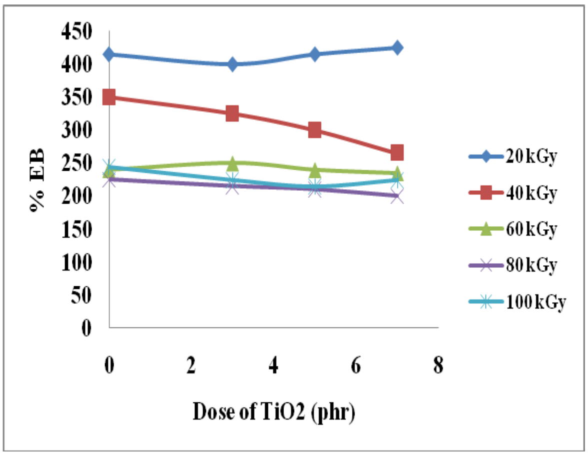

Fig. 2 Variation of Percent Elongation at Break with TiO_2 dose

*3) **Tear Strength***

The course of variation in tear strength of the TiO_2, loaded samples of silicone rubber irradiated with electron beam at different doses of irradiation is shown in Fig. 3. The pattern of changes in the behaviour of tear strength follows the same trend as is obtained in the made of changes in % EB. The unloaded (no TiO_2) samples when irradiated with 20 kGy of e-beam possess the highest tear strength followed by the unloaded samples irradiated with subsequent highest doses of irradiation.

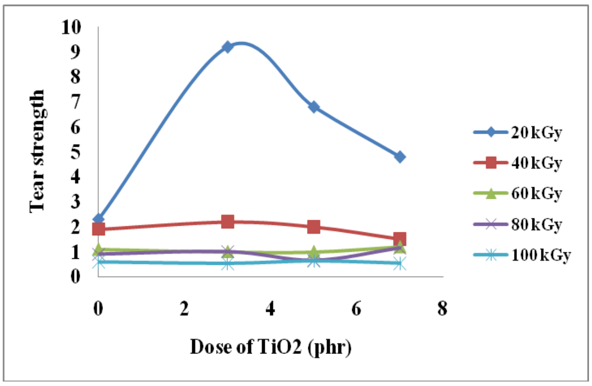

Fig. 3 Variation of Tear Strength with TiO_2 dose

The sample with 100 KGY of treatment has the lowest tear strength. The effect of variation in treatment level on tear strength is only somewhat reflected in case of unloaded (no TiO_2) samples while the loaded samples (in varying doses of TiO_2) maintain a constancy over the entire range of loading value, tear strength remaining almost the same as that of the unloaded one. Thus it appears the interaction between the radiation & silicone rubber at its unloaded stage remains unaffected & unaltered. TiO_2 seems to be inert to the physical irradiation.

B. Ageing Behaviour

1) Retention of Tensile Properties on Air Oven Ageing

Silicone rubber is well known for its resistance to ageing on air oxidation. An accelerated ageing test has been passed out by subjecting the silicone samples loaded will varying proportions of TiO_2 & also irradiated with electron beam radiation & different levels of treatment as shown in Fig. 4. The objective was to investigate the combined effect of irradiation at different level and at different doses of TiO_2 loading. The results have been shown as % retention of tensile strength as a function of TiO_2 loading. It is apparent that, for each level of treatment there is a gradual & steady decrease in % retention of tensile strength with increasing doses of titanium dioxide with reference to the unloaded (without TiO_2) silicone. One interesting feature of importance is to note is that towards the higher level of treatment, beyond a certain TiO_2 dose, the % retention of tensile strength tends to reach an equilibrium value and becomes asymptotic. On the contrary, the % retention curves for the samples being treated with lower level of treatment in the range under study exhibit an uprising tendency beyond its corresponding lower limit of TiO_2 dosing.

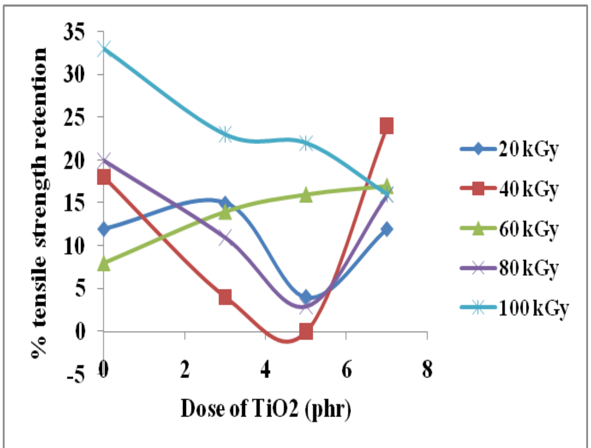

Fig. 4 Variation of Tensile Strength Retention with TiO_2 Dose in Hot Air Oven Ageing

This observation corroborates our earlier findings on the behaviour of changes in tensile strength. It can possibly be argued that up to the critical minimum, a breakdown in structure in the form of chain cleavage might have happened as the concentration of TiO_2 is not sufficient enough to absorb the radiation & make it ineffective. Beyond this minimum the radiation is not only completely absorbed by TiO_2, the excess TiO_2 particles act as reinforcements & hence % retention is improved upon.

2) Retention of Elongation at Break on Air Oven Ageing

The percent retention of elongation has been plotted as a function of TiO_2 loading for the entire range of radiation under study as in Fig. 5. For the treated samples without any loading of TiO_2 the % retention of EB varies marginally over an extremely narrow range. The % EB of samples for a particular level of treatment does not appear to be much affected by increasing doses of treatment.

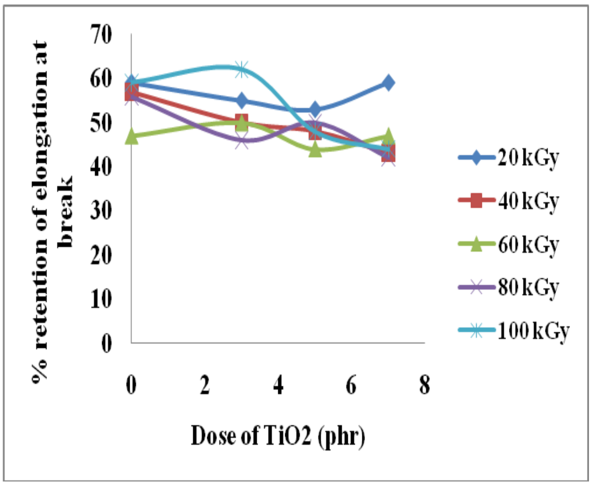

Fig. 5 Variation of Retention of Elongation at Break with TiO_2 Dose in Hot Air Oven Ageing

IV. CONCLUSIONS

The present study deals with the effect of TiO_2 concentration on silicone rubber under the influence of electron beam radiation. This has been applied with different dosages of irradiation. While tensile strength and percent elongation at break are slightly affected by the irradiation of electron beam in the presence of TiO_2, tear strength shows a notable change at 20kGy irradiation at different doses of TiO_2 concentration though other doses of electron beam radiation has no significant changes. Regarding retention of polymeric properties under air oven ageing, tensile strength reaches an equilibrium value and shows asymptotic nature beyond a certain TiO_2 dosing while increasing doses of TiO_2 does not have significant effect on retention of elongation at break. Present findings may be helpful for the future researchers for analyzing further polymeric properties under the influence of electron beam radiation in different dosing of TiO_2 pigments.

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