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Research Article

EFFECT OF TMPTMA VARIATION ON PHYSICO-MECHANICAL PROPERTIES OF PVC-PLASTISOL

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ABSTARCT
This paper presents the results of the study on the effect of crosslinking agent on the physic-mechanical properties of PVC-Plastisol by varying concentration of Trimethylolpropane trimethacrylate (TMPTMA) in the presence of Benzoyl Peroxide which is an initiator. This includes development of PVC plastisol formulation and making of sheets from it, study of physico-mechanical properties of developed compositions. Concentration of TMPTMA, which is a crosslinking agent, was changed. Results show that PVC plastisol with 3 phr of TMPTMA have shown good/improved mechanical properties.

Key Words: *TMPTMA, PVC, Tensile Strength, Tear Strength, Hardness, SEM*

INTRODUCTION
Polyvinyl chloride (PVC) has large and broad uses in commerce. It is second in volume only to polyethylene which can be attributed to several unique properties. PVC has a unique ability to be compounded with a wide variety of additives, making it possible to produce materials in a range from flexible elastomers to rigid compounds.

The degree of polymerization, n, ranges from 500 to 3500. For commercial PVC the molecular weight is characterized by inherent viscosity or K- value. The K- value of 56 is used for injection moulding, pipe fittings whereas the material with a K value of 70 is used in medical tubing and automotive moulding applications The use of poly functional monomers as additives that increase the yield in the radiation grafting of monomers are Poly functional acrylates, methacrylates, triallylcyanurate and Trimethylolpropane trimethacrylate (TMPTMA) are the most widely used monomers for this purpose.

MATERIALS AND METHODS
Poly Vinyl Chloride
Polyvinyl Chloride (PVC) from M/s Chemplast India of Grade 124 has been used. It is of paste grade resin of medium molecular weight best suited for making leather cloth and for PVC plastisols. Specifications of the said material are given in Table 1.

Table 1: Product specifications of PVC

Property	**Value**
Bulk Density gm/cc	0.57
Inherent viscosity cP	1.60
K value	87
Particle size (microns)	130-180
Porosity cc/gm	0.46
Retention % through 40 mesh	45%

TMPTMA
Trimethylolpropane Trimethacrylate (TMPTMA) of M/s Aldrich Chemicals as crosslinking agent in PVC formulations was used in the present study, whose product specifications are listed out in Table 2.
Molecular Formula of TMPTMA - $C_{18}H_{26}O_6$

Benzoyl Peroxide

The peroxide cross linking of PVC is expected to enhance penetration resistance and service temperature of PVC. Benzoyl peroxide is an organic compound in the peroxide family. It consists of two benzoyl groups bridged by a peroxide link. Its structural formula is $[C_6H_5C(O)]_2O_2$. Benzyl peroxide of M/s SD Fine Chemicals Ltd was used as a peroxide initiator in the present study.

Table 2: Specifications of TMPTMA

S.No	Property	Unit	Value
1	Appearance		colourless to light coloured
2	Physical form		clear liquid
3	Density at 25 ^oC	g/cm^3	1.06
4	Boiling point at 1.33 hPa	^oC	155
5	Viscosity at 25^oC	mPa·s	44
6	Flash point	^oC	115
7	Index of refraction at 20 ^oC		1.47
8	Vapour pressure, 30^oC	mbar	8
9	Surface tension	dynes/cm	33.6
10	Functionality	Theoretical	3

Preparation of Plastisol

We had prepared PVC plastisol using DOP as primary plasticiser, Epoxy Soyabean Oil (ESO) as secondary plasticiser, Octyl Tin Mercaptile (OTM) as thermal stabiliser, Irganox 1010 as antioxidant, Stearic acid and butyl strearate as lubricants. In this, the concentration of TMPTMA was varied using benzoyl peroxide as an initiator. The required components of each batch are properly weighed and are mixed properly in a planetary mixer for about one hour. Planetary Mixer was used for mixing. The speed of the mixer is kept at 600 RPM.

The properly mixed plastisol solution is filtered to remove the undissolved components. Viscosity of the prepared plastisols is measured at different intervals using Brookfield Viscometer.

Viscosity Measurement

The Brookfield Dial Viscometer measures fluid viscosity at given shear rates. Viscosity is a measure of a fluid's resistance to flow. All units of measurement are calculated in units of centipoise (cP). Viscosity was measured to check the stability of the plastisol.

Casting of PVC Sheet

Thin sheets of size 20x20 cms are cast on a glass plate of thickness 2mm and are kept in an oven at 180 ^oC for 45 minutes to facilitate proper curing of the material. The prepared sheet of the each composition has been evaluated for the physico-mechanical properties.

Tensile Strength and Elongation % (ASTM D-638)

The tensile strength and elongation % of the different samples was determined as per ASTM D-638 using an INSTRON UNIVERSAL testing machine.

Hardness (ASTM 2240)

Shore hardness is a measure of the resistance of a material to the penetration of a needle under a defined spring force. Thermoplastic elastomers are measured in Shore A and Shore D according to ASTM. For hard materials Shore-D is used, for soft/flexible material Shore-A is used. The hardness of different samples was determined using Shore-D hardness as per ASTM- 2240.

Tear Strength (ISD 624-91)

Tear strength is the ratio of maximum force required to rupture the specimen and the thickness of the test piece.

Thermal Stability (IS 5831)
The thermal stability is an accelerated method to determine the rate of degradation of the PVC compounds with time under the influence of temperature. Compounds with high thermal stability can with stand continuous processing temperatures. This test method is also known as Congo red method.

Scanning Electron Microscopy
SEM analysis of PVC sheets was carried out using a HITACHI (S-3700N) scanning electron microscope. The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signal at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample.

RESULTS AND DISCUSSION

Effect on Viscosity
Viscosity of PVC plastisol samples at various time intervals of 1, 7, 14 and 21 days are measured. Plastisol samples were prepared with varying DOP concentrations, with varying concentration of TMPTMA for the purpose of measuring viscosity. Viscosity levels measured at different intervals are presented in Table 3, apart from depicting the same in graphical form in Figure 2. Perusal of the results obtained, shows that the viscosity increases with increase in time.

Table 3: Variation in viscosity with time and different compositions of PVC plastisols

Composition	**Viscosity in centiPoise**			
	1 day	7 days	14 days	21 days
1 phr TMPTMA	1069	1110	1130	1364
3 phr TMPTMA	990	1028	1090	1200
5 phr TMPTMA	1023	1047	1060	1180
10 phr TMPTMA	1065	1093	1040	1160

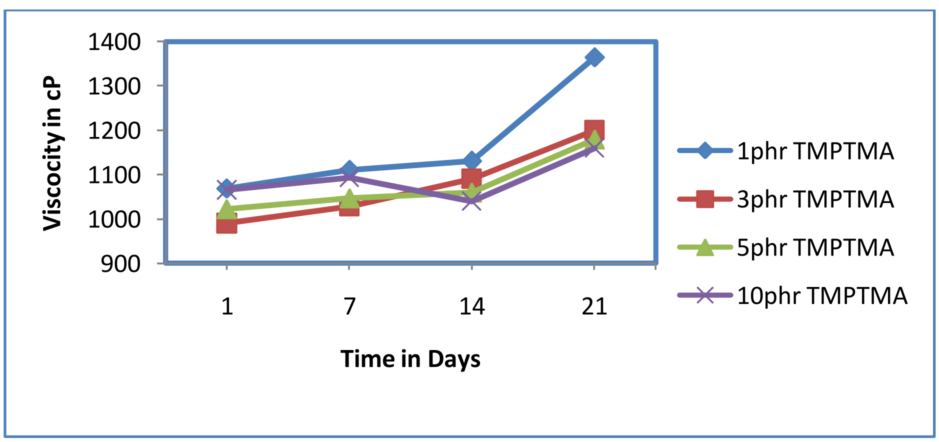

Figure 2: Variation in viscosity with time and different compositions of PVC plastisols

Effect of Crosslinking Agent on PVC Compositions
To study the effect of crosslinking agent in PVC plastisol compositions the DOP concentration was taken as 70 phr. This concentration was considered for the present experimentation/study as our viscosity at this concentration was 1613 cP. Charles E. Wilkes et al (2005) had also stated that DOP is recognised as the benchmark plasticiser for PVC. They had classified that a DOP of 25 phr is semi rigid PVC, between 35 and 85 phr DOP, PVC is considered as flexible and above 85 phr it is called highly flexible. Apart from

this, at 70 phr the formulations which have been developed, in the present study, have retained optimum physico-mechanical properties. As we increased the concentration of the plasticizer we observed a sharp decrease in physico-mechanical properties. Keeping DOP at 70 phr, the cross linking agent was changed in concentration to have first hand information on variation in properties. The quantity of TMPTMA was varied as 1, 3, 5 and 10 parts per hundred resins (phr) and various mechanical properties were evaluated and discussed below.

Effect on Tensile Strength

Results of tensile strength obtained are presented in Table 4 and Figure 3. It can be inferred from the table that with increase in cross linking agent concentration before radiation, the tensile strength has increased significantly, but at higher phr of crosslinking agent it has shown a reduced tensile strength. Thai Hoang and Neil Varshney (2003) studied crosslinking of rigid poly (vinyl chloride) (PVC) by 1, 1-di-(t-amylperoxy) cyclohexane (DAPC) in the presence of trimethylolpropane trimethacrylate (TMPTMA). Ultimate tensile strength (UTS) of the PVC samples rised with increasing concentration of TMPTMA. Maximum UTS of the PVC samples is achieved with 0.4 phr peroxide DAPC for every investigated concentration of TMPTMA.

Table 4: Variation in Tensile strength (MPa) with variation in TMPTMA concentration

TMPTMA	Tensile Strength
0 phr	10.645
1 phr	12.068
3 phr	12.208
5 phr	11.927
10 phr	11.342

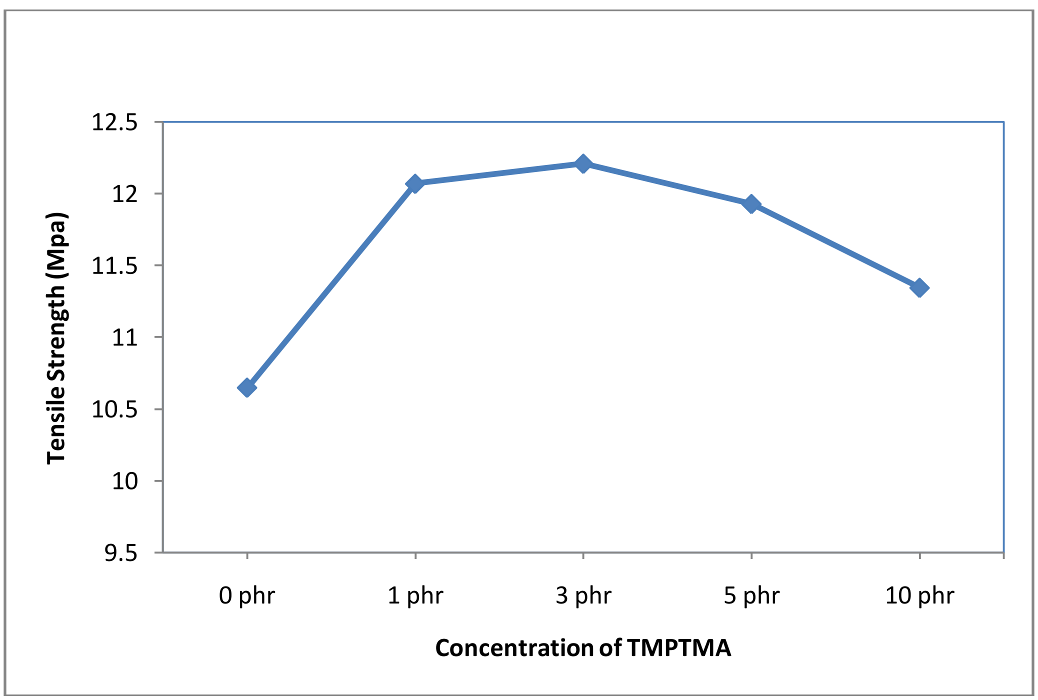

Figure 3: Variation in Tensile strength (MPa) with variation in TMPTMA concentration

Effect on Elongation at Break

The effect on elongation at break of plasticiser with variation in concentrations of TMPTMA was studied. Results obtained are presented in Table 5. It can be seen from the graph that, with increase in cross linking agent concentration, the elongation at break has increased significantly, but at higher phr it has shown a reduced elongation at break, which imparts brittleness to the PVC sheet due to excessive crosslinking. This can be attributed to the fact that formulations containing no functional monomers exhibit poorer physical properties and less integrity than those which contain these monomers. The cross linked network provides added strength which allows the polymer to extend further before it fails.

Table 5: Variation in Elongation at break (%) with variation in TMPTMA concentration

TMPTMA	Elongation at Break (%)
0 phr	535.0
1 phr	618.4
3 phr	653.6
5 phr	665.6
10 phr	650.4

Effect on Tear Strength

The variation in tear strength with variation in TMPTMA concentration is presented in Table 6 as well as in Figure 4. It can be seen from the results obtained that with increase in cross linking agent concentration the tear strength has increased. This may be due to the fact that the monomers are just filling the amorphous regions of the polymer. This can be seen in the SEM image depicted in subsequent section.

Table 6: Variation in Tear strength (N/mm) with variation in TMPTMA concentration

TMPTMA	Tear Strength (N/mm)
0 phr	29.45
1 phr	23.71
3 phr	25.64
5 phr	30.86
10 phr	27.43

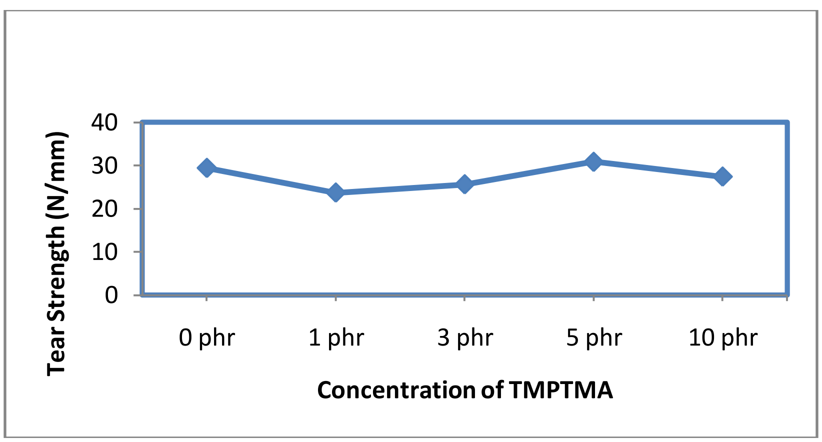

Figure 4: Variation in Tear strength (N/mm) with variation in TMPTMA concentration

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Effect on Hardness

The effect of crosslinking agent on hardness of the PVC compositions were studied by varying the concentrations of TMPTMA from 1 to 10 per hundred (phr) of 70 phr PVC plastisol. Results obtained are presented in Table 7 and Figure 5. Higher functionality monomers like TMPTMA have the highest crosslink density, and hence there is an increase in hardness.

Table 7: Variation in Hardness with variation in TMPTMA concentration

TMPTMA	Hardness
0 phr	72
1 phr	73
3 phr	74
5 phr	75
10 phr	76

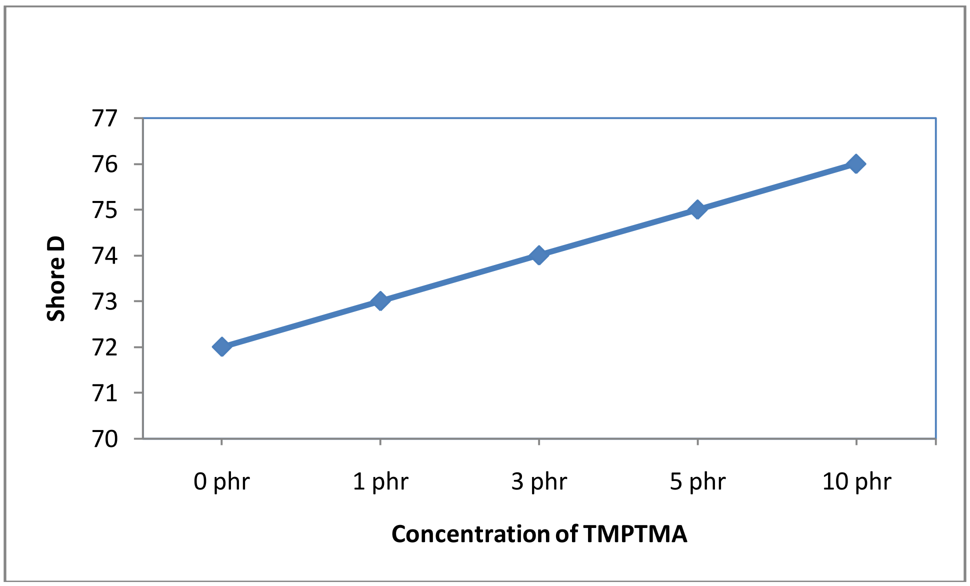


Figure 5: Variation in Hardness with variation in TMPTMA concentration

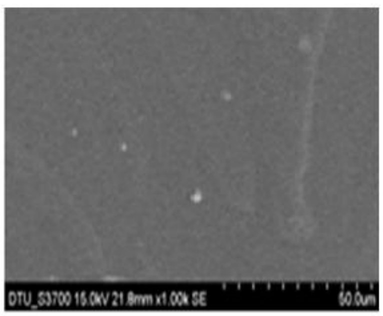
Effect on Thermal Stability

Thermal stability test is used to study the effect of heat on the polymer samples at 200^{o}C and is measured by change in colour of pH paper with time. The time taken by the various samples to change the colour of pH paper is shown in the Table.8. The results show that most of the samples are stable upto a time period of 90 minutes. Thai Hoang and Neil Varshney (2004) studied some thermomechanical characteristics of crosslinked poly (vinyl chloride) (PVC) samples such as glass transition temperature (Tg), softening point (Ts), and linear thermal expansion coefficient (α). Tg, Ts and α of the crosslinked PVC samples were found to be higher than those of the uncrosslinked samples. The highest Tg was observed in the PVC sample containing 0.4 phr of 1, 1-di-(t-amylperoxy) cyclohexane (DAPC) and 10 phr of trimethylolpropane trimethacrylate (TMPTMA). Among the crosslinked PVC samples, the sample with 0.2 phr of DAPC and 15 phr of TMPTMA has the least Ts. The highest α appeared in the PVC sample containing 0.4 phr of DAPC and 5 phr of TMPTMA.

Pedro Miguel Romero Tendero *et al* (2006) employed soft PVC for the manufacturing of a wide range of products with different properties and a relatively low cost. In their work, the crosslinking reaction of plasticized poly(vinyl chloride) (PVC) through difunctional amines was studied. The effect of the addition of crosslinking agents on the thermal stability of the polymer was studied by thermogravimetric analysis (TGA), which revealed that crosslinking reactions promote thermal degradation phenomena in the polymer matrix. This was attributed to the formation of HCl and other species promoting polymer degradation during crosslinking, thus leading to higher weight loss during thermal treatment with respect to unmodified PVC plastisols.

Table 8: Time taken for change of colour

S. No	Sample	Time taken (mins)
1	1 phr TMPTMA	96
2	3 phr TMPTMA	94
3	5 phr TMPTMA	91
4	10phr TMPTMA	91



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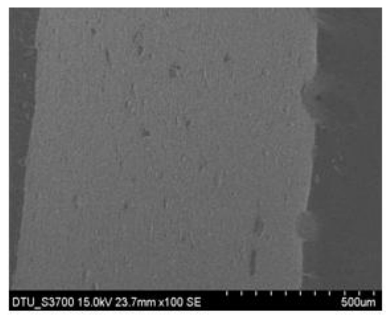

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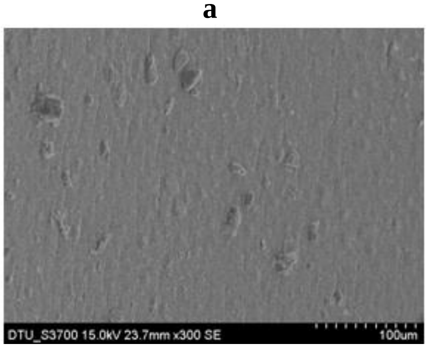

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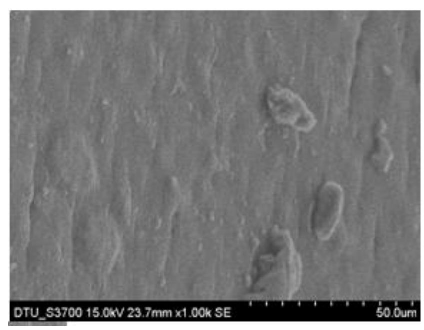

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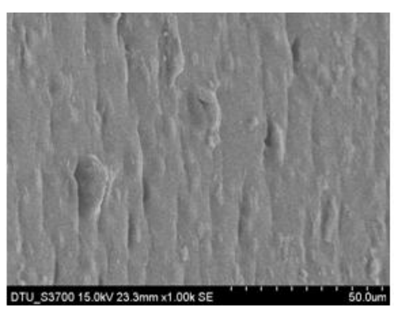

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Figure 6: SEM image of compositions having various TMPTMA concentrations (a) 0 phr (b) 1 phr, (c) 3 phr (d) 5 phr (e) 10 phr

Study of Morphology using Scanning Electron Microscopy (SEM)

Images were also taken using Scanning Electron Microscope (SEM) for various samples. Figure.6. depicts SEM images for the samples containing 70 phr of DOP and with varying concentrations of TMPTMA from 0 to 10 phr. By analysing the images, the following is deduced

- Image a: It is observed that the plasticiser is dispersed uniformly in the plastisol as no spot is seen.
- Image b: Crosslinking has started.
- Image c: There is no phase separation due to uniform crosslinking.
- Image d: Due to excessive crosslinking, phase separation can slightly be seen.
- Image e: Phase separation is very significant and surface cracks can be visualised.

Conclusion

- Mechanical properties of PVC formulations were enhanced with the addition of a crosslinking agent.
- Maximum percentage increase in Tensile and Tear strength is achieved at 3 phr of TMPTMA.
- Thermal stability of all developed compositions is good.

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