Mechanical Characteristics of Poly (Vinyl Chloride) PVC and Poly (Methyl Methacrylate) PMMA and Their Blends Investigated by Microhardness and DSC Studies

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Abstract - Specimen of PVC poly (vinyl chloride):PMMA poly (methyl methacrylate) and their poly blends with different weight % ratio has been found to act as plasticizer. The effect of load on the micro hardness of the blend specimens was studied by a Vicker Microhardness tester attached to a Carl Zeiss NU-2 Universal microscope. The curves obtained the effect of load on the microhardness level of the blend and variation on hardness with varying concentration of PMMA in pure PVC. The microhardness of the poly blends is found to decrease with increasing weight % of PMMA in PVC matrix. This is primarily due to plasticization effect which increases the chain flexibility and the elastic characteristics of the blend. This is also confirmed with the DSC (Differential Scanning Calorimeter) studies. The PVC and PMMA are miscible with single phase system.

Key Words: Polyvinyl chloride, poly methyl methacrylate, microhardness, miscible, compatible, DSC

INTRODUCTION
The hardness of polymer is a complex elastic and plastic parameter1-2 and involves reversible and irreversible contribution to deformation. The deformation in crystalline solids occur by defined mechanism-such as slip or twinning whereas for polymers it involves the relative movement of molecules, since the molecules can be very large and occur in long chains, this would be a highly complex process. If true viscous flow occurs then movement of whole molecule must take place and variation in molecular weight should have defined effect on hardness. Alternatively, if the deformation is highly elastic type depending on the rotation of linkage between the molecules, increasing the molecular weight should not greatly increase the hardness.

The hardness of polymer blends depend upon the factor composition, choice of polymers compatibility of polymers, phase morphology and the method of blend preparation. If the polymers are so compatible that they are completely miscible, forming a single phase blend, then the hardness blend properties are said to be related to blends composition in simple linear manner.

In recent year, the micro hardness test has proved to be a versatile technique for studying various physical properties of polymers. This technique is capable to detecting structural and morphological changes in polymers and can be used to characterize the mechanical behavior of polymers. Bajpai et al4 have studied micro hardness of large number of polymeric materials and their blends by Vicker method.

The compatibility of different polymers on a molecular level is usually determined by taking into account that macromolecular chains are mutually interpenetrating is on phase molecular homogeneous matrix5. The decision about compatibility however depends on the experimental method.
applied. The results of different experiment on the same blend system are frequently contradictory. Some of the more powerful techniques preferentially used are differential scanning calorimeter such as DSC. Poly vinyl chloride and poly methyl methacrylate are chemically similar polymers known to form compatible blends over a wide composition range. The present communication reports the results of effect of load on the micro hardness of polymer blends and variation on hardness with varying concentration of PMMA in pure PVC. It has been studied by the microhardness of PVC: PMMA blends and find decreases with increasing weight % of PMMA in the PVC matrix. This implies that PMMA act as plasticizer. This is also confirmed with the DSC (Differential Scanning Calorimeter) studies. The PVC and PMMA are miscible with single phase system.

**Experimental Techniques**- For preparing pure PVC and PMMA specimens the solution cast technique has been utilized. The definite weight of PVC/PMMA (2.5 g) was dissolved in the solvent DMF (Dimethyl Formamide), at a temperature of 40°C and their blends with different weight % ratio PMMA in PVC at a temperature in 60°C using the magnetic stirrer. After a uniform solution was obtained known quantity of this blend solution was poured in a glass mold and kept for evaporation in the oven to yield the blend samples of the size 2.5 cm² and 0.04 cm thickness. The time required for complete evaporation of solvent was nearly 5 hr. Utmost care was taken to prevent the sample to come in contact with dust and other degrading agents and humidity. The use of plasticized polyvinyl chloride (PPVC) is well known specially, in medical products because of the advantages of PVC over other materials and its versatility and wide range of properties that can be improved depending on nature and the amount of additive. The presence of chloride in the polymer results in greater interchain attraction and accounts for better mechanical strength of PVC. It is a solid material\ in powder form with white colour. Its melting point and glass transition temperature are 210° and 81°C, respectively. PMMA is also well known for its mechanical; properties, it is a hard, rigid and highly transparent polymer and has outstanding clarity, its melting point and glass transition temperature are 210° and 105°C, respectively. The individual properties of PVC and PMMA are fascinating. The specimen were indented at room temperature by a mhp160 microhardness tester with a diamond pyramid indenter having a square base and 136° pyramid angle attached to a Carl Zeiss NU-2 Universal microscope. The diameter were measured by the eyepiece micrometer with magnification of K15 X. Vicker's Hardness number H_v is given by

\[ H_v = \frac{1.854 \times L}{d^2} \] (kg/mm²)

Where L is load in kg and d is diagonal length in mm. In this test the indenter is pressed on to the surface of the given specimens for a time (30s, 40s).

DSC (Differential Scanning Calorimeter) of the samples have been carried out with Metler Instrument at Jawaharlal Nehru Aluminium Research Development and Design Center, Nagpur. The heating rate was kept 10°C/min. The glass transition temperature and thermal behavior has been studied using DSC (Differential Scanning Calorimeter) thermograms.

**Result and Discussion**- The variation of microhardness with different weight percentage ratios of the two polymers in the poly blends and the effect of load on the micro hardness has been discussed in this section.

**Variation of Hv with load**- Fig.1 illustrates the variation of H_v with load of indentation ranging from 10 to 100 g for pure PVC, Pure PMMA and PVC: PMMA blend specimen. It can be observed from the figure that initially the microhardness increases with load for all the specimen. However, on approaching a certain load value, the rate of increase of hardness slow down. Finally, the value of H_v tends to saturate. This feature is found to be similar for all specimens. Pure PVC attains a value of 9.67 kg/mm² beyond the load of 60 g and for pure PMMA this value is 10.82 kg/mm² beyond the load of 80 g. Similarly, the saturation value of H_v for blend specimen with 5, 10, 15 and 20 weight
% PMMA are 9.47, 8.72, 8.47 and 7.95 kg/mm$^2$ respectively beyond the load of 70g. The $H_v$ values of pure PMMA are highest and the values for blend specimens are lower than pure PMMA and PVC. Moreover, the saturation load for blend specimen is intermediate of pure PVC and PMMA. It is interesting to observe that pure PMMA which is relatively harder than pure PVC when blended with PVC in smaller weight proportions further soften than PVC. The different values of saturation load value for pure PVC, PMMA and various PVC: PMMA polyblends indicates the changes in the macromolecular structure and morphology.

The increase in $H_v$ with load can be understood on the basis of strain hardening phenomenon in the polymers. There is a spectrum of micromode of deformation in the polymer chain. Each micromode is activated by its characteristic temperature and stress conditions. When sufficient number of micromodes become active, large-scale plastic deformation begins. On applying load, the blend specimen is subject to greater strain hardening and hence $H_v$ increases. This phenomenon can also be explained with the help of theory given by Amontons$^8$. According to him, the microhardness may be correlated with the frictional force. The coefficient of friction decreases with increasing load and the frictional force is found to increase linearly with increasing load. Thus the variation of $H_v$ with load is curvilinear. Thus microhardness initially increases with increasing load. On applying load the polymer is subjected to some strain hardening. Finally, when $H_v$ value tends to become constant the polymer is completely strain hardened. The rate of strain hardening is greater at low loads and decreases at higher loads. The rate of strain hardening in different specimen is related to weight percentage ratio of two polymers in the blend, which governs then degree of cross-linking in the blend. Hence the different saturation load values are observed for different specimen. Microhardness of the blend specimen decreases with increasing content of PMMA in the polyvinyl chloride. It shows that PMMA acts as a plasticizer or softener for PVC. The addition of PMMA leads to the reduction of steric hindrance between PVC chain molecules, thus resulting in the decrease in the value of $H_v$. In other words the studied range of different weight percentage ratio of PVC: PMMA yields softened blends with increased elastic characteristics.

**Variation of $H_v$ with various percentage ratio** - Fig.2 exhibits the variation of Vicker’s hardness number, $H_v$ with various weight percentage of PMMA and PVC at various loads ranging from 10 to 70g. The $H_v$ value for pure PVC (0 weight % of PMMA) are also plotted at different loads. It is observed from the figure 2 that the microhardness decreases with increasing content of PMMA from 5 to 20 weight % in pure PVC. Moreover, the values of microhardness of the blend of the specimen are less than pure PVC and pure PMMA specimen. Thus PMMA acts as plasticizer for PVC when mixed in the proportion range of 5 to 20 weight %. This feature also indicates that PMMA which is relatively hard polymer can be plasticized or softened with PVC in
Fig. 2 Variation of $H_v$ with different weight % of PMMA in PVC in the studied range of 95 to 80 weight % proportion. The increase in the content of PMMA increases the elastic characteristic of PVC. The miscibility of PVC and PMMA leads to further softening of PVC with loosening of chains due to reduction of steric hindrance between the macromolecules and thereby increasing chain flexibility. The rate of decrease in $H_v$ with increase in the content of PMMA in the range 5 to 20 weight % at various load in also indicative of level of compatibility/miscibility between the two polymers in the blend. The decrease in the value of $H_v$ with increase in the content of PMMA is slow at low load (10g), and the rate increases with increase in load. The linear decreasing trend suggests the miscibility of the two polymers. This is also confirmed from the DSC studies which shows the occurrence of single sharp $T_g$ at 61.4°C and 61.3°C for PVC: PMMA blend with 5 and 20 weight % of PMMA. The existence of single $T_g$ suggests the one phase in the blend system moreover, the $T_g$ values are found to be intermediate and less than that of the pure polymers. For polyblends this is due to plasticization i.e. more chain flexibility. The increased rate of decrease in $H_v$ values at higher loads is due to more prominent effect of stress on the softened poly blends.

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