

Surface modification on PMMA : PVDF polyblend: hardening under chemical environment

R BAJPAI*, V MISHRA, PRAGYESH AGRAWAL[†] and S C DATT

Department of Postgraduate Studies and Research in Physics, Rani Durgavati University, Jabalpur 482 001, India

[†]Department of Physics, St. Aloysius College, Jabalpur 482 001, India

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Abstract. The influence of chemical environment on polymers include the surface alteration as well as other deep modifications in surface layers. The surface hardening, as an effect of organic liquids on poly(methyl methacrylate): poly(vinylidene fluoride) (PMMA: PVDF), which is one of the few known miscible blends, has been detected using microhardness testing. Organic liquids like acetone, toluene, xylene and benzene were introduced on the surface of blend specimens for different durations. Vickers microhardness (H_v) was measured for treated and untreated specimens. The study reveals both hardening and plasticization of specimens at different exposure times. The degree of surface hardening is maximum under acetone treatment. All the specimens exhibit surface hardening at an exposure time of 1 h with all the four liquids. This feature is prominent with longer exposures for specimens with increasing content of PVDF. However, the degree of hardening decreases with the time of exposure in the respective environments. In general, acetone and toluene impart surface hardening, whereas, xylene and benzene soften the specimen. PMMA: PVDF (83 : 17) blend exhibits surface hardening under all the four treatments when compared with the respective untreated specimens.

Keywords. Polyblend; surface modification; microhardness; hardening; plasticization; segmental mobility.

1. Introduction

Polymeric materials have a specific feature of stability towards various aggressive chemical environments, which depends on a multiplicity of factors like structure and nature of the polymers and chemical media as well as on the time and temperature of exposure. The influence of chemical environment on polymers include the surface alteration as well as other deep modifications in surface layer (Lashkov *et al* 1986; Krupenya *et al* 1988, 1989). The studies on environmentally affected mechanical behaviour of polymers are reported by several workers (Kojima and Satake 1984; Omar *et al* 1986; Wu and Brown 1986; Pandey *et al* 1990; Maccone *et al* 2000). The controlling of process parameters and use of different solvents allowed the preparation of combined materials having specified levels of resistance. Fluoropolymers have also been regarded as outstanding polymers for applications where a chemical environment and high temperature are dominating factors. Among fluoropolymers, poly(vinylidene fluoride) (PVDF) exhibits the highest mechanical strength coupled with fairly good chemical resistance (Ajroldi 1997). Poly(methyl methacrylate) (PMMA) is a well known polymer which is hard

and transparent with good outdoor weathering. The miscibility of PMMA: PVDF has been reported (Nishi and Wang 1975; Paul and Altamirano 1975). The present paper reports the study on the surface modification of PMMA: PVDF blend system under chemical environment of some organic liquids. The tool used for detection is Vickers microhardness technique. This technique is now being utilized widely for morphological stabilization and plasticization studies of polymers (Gonzalez *et al* 1986; Pandey *et al* 1990; Bajpai *et al* 1992; Mishra *et al* 1994).

2. Experimental

2.1 Preparation of blends

The powders of PMMA (BDH, UK) and PVDF (Aldrich, USA) were supplied by M/s Chemical Agencies, Mumbai, India. The quoted values of molecular weights are 5,00,000 and 3,50,000; glass transition temperatures, 105 and 13°C; melting temperatures, 225 and 171°C and specific gravities, 1.19 and 1.8, respectively. The solution cast technique was utilized for preparing the blends. PMMA and PVDF were taken in suitable and definite compositional ratios and were dissolved in an appropriate amount of dimethylformamide. The solution was then heated in a thermostatically controlled electric oven at a temperature of 110°C for 3 h. The oven was then switched off and the

*Author for correspondence

glass mould along with the solution was given sufficient time to cool down (nearly 24 h). Samples of 1 sq cm size and 0.05 cm thickness were cut from the pellets for the chemical treatment.

2.2 Chemical treatment

Organic liquids viz. benzene, toluene, xylene and acetone, were introduced onto the indentation area from a clean glass syringe at the beginning of each test and in the cases, where rapid evaporation occurred (e.g. acetone), more liquid was delivered from the syringe during the course of indentation so that the test area was always flooded. These liquids were poured onto the surface for a definite time period, after which the liquid was sucked out with the help of blotting paper.

2.3 Analytical method

The blend specimens were indented at room temperature by Vickers diamond pyramidal indenter attached to Carl-

Zeiss NU-2 microscope. The specimens were indented at the load of 80 g. The diameter of indentations were measured using a micrometer eyepiece. For each test the duration of indentation was 30 s. For each load at least five indentations were made at different points of the specimens and average hardness number was calculated. The Vickers hardness number, H_v , was calculated from the relation:

$$H_v = (1.854 \times L)/d^2 \text{ kg/mm}^2,$$

where L is load and d the length of diagonal of indentation in mm.

3. Results and discussion

Figures 1–4 illustrate the decreasing nature of the level of H_v of PMMA: PVDF blends having different PVDF contents (5, 9, 13 and 17 wt%) with increasing pouring time for different chemical environments. Figure 1 depicts the variation of H_v level of 95 : 5 blend. It is observed that the H_v level is different for blend specimens treated under different chemical environments. The H_v level is found to decrease with increasing pouring time for all chemically treated blend specimens. This agrees with the fact that the small amount of plasticizer always increases the strength (Tager 1978; Mishra *et al* 1994). The level of H_v is highest under acetone environment and lowest in case of benzene environment amongst the organic liquids studied. For acetone environment, the H_v profile is such that there is a sharp decrease in H_v level for the 1–5 min duration of exposure and remarkably less change is observed between the 5 and 45 min exposure, beyond which the level of H_v decreases sharply again. The higher H_v levels at all pouring time under acetone environment than that of untreated ones, suggest the occurrence of surface hardening. The degree of hardening tends to decrease with increasing time of exposure. Toluene environment also hardens the blend specimens up to the pouring time of 45 min. The

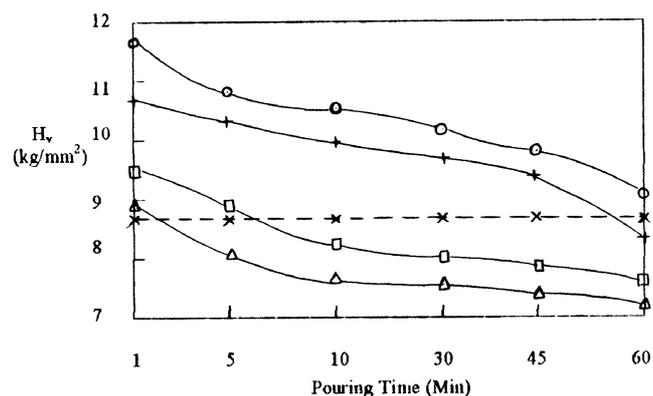


Figure 1. Variation of H_v with pouring time for blend specimens with 95 : 5 wt% ratio: ×, untreated; O, acetone; +, toluene; □, xylene and Δ, benzene.

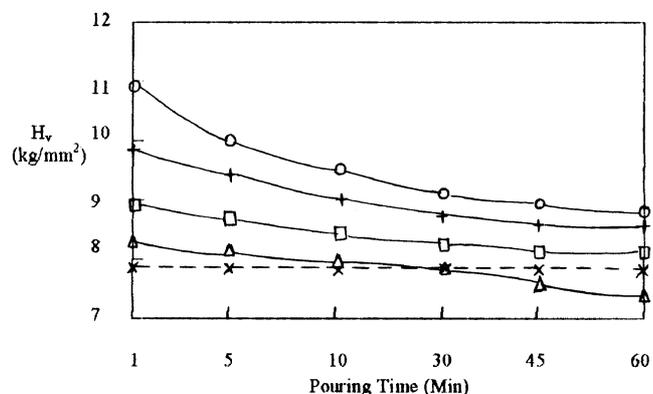


Figure 2. Variation of H_v with pouring time for blend specimens with 91 : 9 wt% ratio: ×, untreated; O, acetone; +, toluene; □, xylene and Δ, benzene.

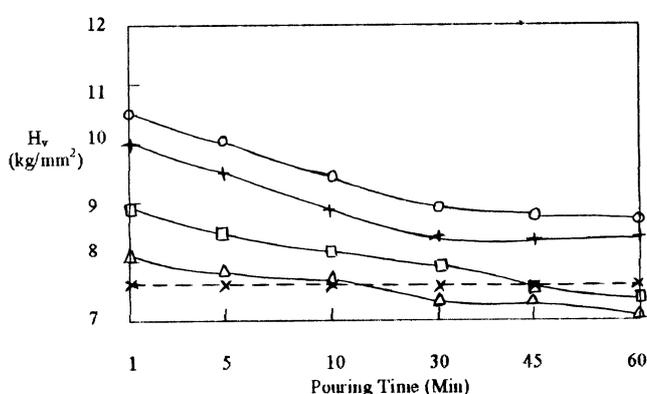


Figure 3. Variation of H_v with pouring time for blend specimens with 87 : 13 wt% ratio: ×, untreated; O, acetone; +, toluene; □, xylene and Δ, benzene.

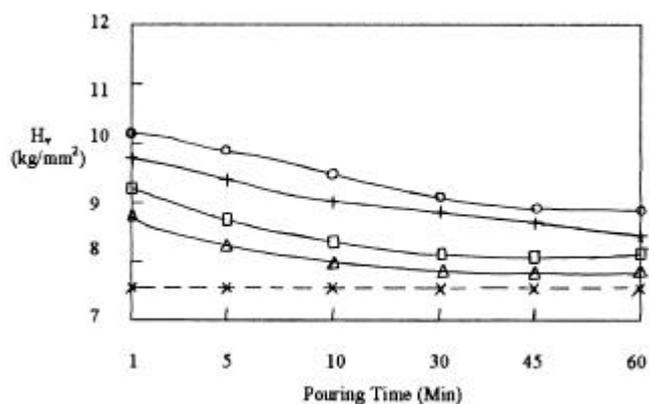


Figure 4. Variation of H_v with pouring time for blend specimens with 83 : 17 wt% ratio: ×, untreated; o, acetone; +, toluene; □, xylene and Δ, benzene.

treatment under benzene environment produces greater plasticization effect after the pouring time of 1 min. The H_v values of blend specimens treated under xylene environment for more than 5 min are found to be lower than the untreated specimen.

Figure 2 depicts that the treatments of 91 : 9 blend with acetone, toluene and benzene induce the surface hardening even up to the exposure time of 1 h. In case of xylene environment the blend specimens are hardened up to the exposure time of 30 min, thereafter the plasticization is observed.

Figure 3 illustrates the surface hardening of 87 : 13 blend at all pouring times in case of acetone and toluene environments while for xylene and benzene environments the hardening is limited up to the exposure time of 10 min. Beyond 30 min, exposure under xylene and benzene gives rise to plasticization which increases with increasing exposure time.

Figure 4 also depicts the surface hardening in case of all organic liquids studied at all pouring times and no plasticization is seen in the 83 : 17 blend, however, the degree of hardening is different for different environments. Moreover, the degree of hardening is becoming less as the exposure time is increased. This blend having the highest PVDF content, in the present investigation and where the highest softening is observed in absence of any treatment reported elsewhere (Bajpai *et al* 1992) shows a tendency of surface hardening under organic media.

The decrease in the level of H_v on increasing plasticizer content or pouring time is due to increasing chain segmental mobility (Elias 1984). Since PVDF is miscible with PMMA, hence on adding, it increases the segmental

mobility of chains which results in the fall in the level of H_v . The anomalies, which are observed with lower plasticizer content or pouring time, are often due to antiplasticization, which is caused by eradication of defects in the polymers (Tager 1978; Elias 1984). The ability of a liquid to plasticize a polymer depends on the difference in their respective values of the solubility parameter; the smaller the difference the greater the degree of plasticization (Pandey *et al* 1990).

4. Conclusions

It can be concluded that the environment of acetone causes overall surface hardening for all blend specimens. Environments of toluene, xylene and benzene harden the blend specimens at smaller exposure times and plasticize the specimens for longer exposures. Moreover, with increase in PVDF content in PMMA matrix, this influence weakens and for blend specimens with maximum wt% (17 wt%) no plasticization takes place even for 1 h pouring time.

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