Studies on Engineering Properties of PVC–PMMA Semi-interpenetrating Polymer Networks

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ABSTRACT: Semi1 and semi2 interpenetrating polymer networks (IPNs) of PVC and in situ formed PMMA have been synthesized using diallyl phthalate and ethylene glycol dimethacrylate as the crosslinkers of PVC and PMMA, respectively. These two types of IPNs have been compared w.r.t their physical, mechanical, and thermal properties and an endeavor has been made to find a correlation of these properties with the morphology generated in these systems. The semi1 IPNs displayed a decrease in their mechanical parameters and the physical properties as well, while in contrast, the semi2 IPNs exhibited a marginal increase in the corresponding values after an initial drop upto about 15% of crosslinked PMMA incorporation when compared to the crosslinked PVC in the case of semi1 IPN and linear PVC in the case of semi2 IPN. The various samples of semi1 and semi2 IPNs showed a two-stage degradation typical of PVC, while confirming the increased stability with the samples having higher percentages of PMMA. The influence of crosslinking of the major matrix in semi1 IPN was almost counterbalanced by the influence of crosslinking in the dispersed PMMA phase in the case of semi2 IPN. The softening characteristics as detected by the extent of penetration of the probe, as has been detected by thermomechanical analysis, are in conformity with their mechanicals. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1725–1735, 2005

Key words: semi-interpenetrating network; TGA; morphology; diallyl phthalate; EGDM

INTRODUCTION

Interpenetrating polymer networks (IPN) typically comprise two crosslinked polymer networks that are physically interpenetrated, one of which is crosslinked in the immediate presence of the other; a semi-IPN consists of linear polymer chains threaded through a crosslinked polymer network. IPNs are characterized by their bicontinuous structure; two polymers are brought into intimate contact, although there is no chemical linkage between them.[1]

When the major component is crosslinked, a semi1 IPN results and when the minor component is crosslinked, a semi2 IPN results. When both polymers are crosslinked, a full IPN results.

When both networks are crosslinked, the morphology is fixed and well defined and the associated properties do not vary much. The properties are dependent on the two-phase morphology that develops during polymerization/crosslinking processes of either phase. The degree of network interlocking between the components has a measurable effect on various mechanical properties such as modulus, hardness, and ultimate tensile strength (UTS), which in turn depends on whether either component of the network is crosslinked (semi IPN) or whether both of them are crosslinked. Increased network interlocking is expected to improve compatibility.[2–6]

The present study focuses on improving the properties of PVC by incorporating PMMA as the polymeric modifier in the form of IPN. The inherent problems of poor impact strength and difficult processing of rigid PVC are quite well known and are usually overcome by incorporation of suitable plasticizers and certain rubbery acrylate modifiers. In such cases, there is every possibility of compromising on the mechanical properties of rigid PVC. In our case, we have tried to modify both linear and crosslinked PVC with PMMA (having very high chain stiffness and rigidity) so that the mechanicals of the blends can be kept at par with original PVC or even better.[7–11] Also, PMMA having a solubility parameter (δ = 9.27 cal/c.c$^{1/2}$) very close to that of PVC (δ = 9.47cal/c.c$^{1/2}$) might be expected to have a very good compatibility with PVC.[12–14]

EXPERIMENTAL

Materials

PVC (Reon) grade K 67 was procured from M/s Reliance Industries Ltd. (India) and was used as the matrix resin. Dioctyl phthalate (DOP) from M/s Burgoyne (India) and tribasic lead sulfate (TBLS) from M/s Kalpana Industries Ltd. (Daman, India) were

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used as suitable plasticizers and stabilizers respectively. Diallyl phthalate(DAP) from M/s Burgoyne was used as a crosslinker for PVC.

MMA from M/s Burgoyne was purified first by washing with 2% aqueous sodium hydroxide solution and then by thorough and repeated washing with distilled water (to make it alkali free as tested by litmus paper) and dried over fused calcium chloride ($CaCl_2$). It was finally vacuum distilled. Benzoyl peroxide from Loba Chemie (India) was purified by repeated crystallization from chloroform and was used as initiator for acrylic polymerization. Ethylene glycol dimethacrylate (EGDM) from Aldrich Chemical Company Inc. was used as the crosslinker for PMMA.

Synthesis of semi 1 and semi 2 IPNs

A weighed amount of purified MMA was taken in a test tube and thoroughly mixed with 2% by weight (based on MMA) of recrystallized Bz_2O_2.PVC resin was weighed such that a predetermined ratio with respect to the monomer as weighed earlier was just made. The resin was taken in an air-tight dry blender and mixed with 30 parts of DOP and 2 parts of TBLS with respect to the amount of PVC resin taken. Five parts by weight of DAP w.r.t PVC was then added in the case of synthesis of semi1 IPN. The monomer containing initiator was then added to the premix of PVC. EGDM in the ratio of 2% by weight of MMA taken was initially added to the monomer mix in case of semi2 IPN. Dry mixing was further continued unless a thoroughly mixed powder was obtained. The mix was then compression molded into sheets by subjecting a three-piece mold under pressure and heat in two stages.

Conditions of molding

Initially, the mold was compressed under a pressure of 15 ton/cm^2 at a temperature of 80°C to initiate and propagate acrylic polymerization. This was allowed to continue for 30 min. Subsequently, the temperature was raised to 160°C while the pressure was maintained at the same level. This condition was maintained for 5 min to ensure complete sintering of PVC and acrylic polymerization. The whole combination was kept in an oven at 100°C for a further 20 min to ensure complete polymerization and crosslinking of residual MMA or PVC or both, as the case may be. The mold was then allowed to cool down at room temperature and the molded sheet was ejected.

Measurements

Tensile properties

An Instron Universal Testing Machine (Model 4204) was used for measuring the tensile properties like UTS, percent elongation at break (% EB), modulus, and tough-

ness. ASTM D 638 method was followed. A crosshead speed of 3 mm/min was maintained. All testings were carried out at room temperature. Toughness of the samples was determined from the area under the load versus elongation plot. The samples were visually inspected before measurements and were found to be free from pores or nicks. The data reported were averages of at least six measurements and the typical scattering range of the results was ±5%.

Physical properties

The two physical parameters, namely specific gravity and hardness, of the various IPNs were determined by following the Archemedis' principle and Shore D scale, respectively.

Thermal properties

Thermogravimetric analysis of the samples were obtained on a Perkin-Elmer Delta Series TGA-7 thermogravimetric analyzer under nitrogen atmosphere at a heating rate of 20°C per min. Samples ranging between 6 and 10 mg in weight were used for the TGA analysis.

The thermomechanical analysis of the various samples was carried out in a TMA apparatus from Shimadzu (Model TMA 50) in the presence of oxygen. The thermo-oxidative characteristics were studied under a constant load of 8 gm throughout the experiment using a compressive mode of probe up to a temperature limit of 180°C following a temperature program in which a heating rate of 10°C/min was maintained right from the ambient temperature.

Morphology

Morphology studies were undertaken in a scanning electron microscope (Model Hitachi S 415A) after suitable gold coating on the samples.

The surface morphology was, however, done in a trinocular Optical microscope from Kruss (optromic), Germany, with a magnification of 20×. The samples were about 0.5 mm thick.

RESULTS AND DISCUSSION

Mechanical properties

The modulus and ultimate tensile strength of semi1 IPN (PVC crosslinked) as depicted in Figures 1 and 2 show a gradual decreasing trend with increasing proportion of PMMA although there is an initial sharp reduction in modulus in going from crosslinked PVC to PVC-PMMA (10%).

The semi2 IPN (PMMA crosslinked), however, differs from semi1 IPN w.r.t their trends in changes of modulus with variation in composition (% PMMA
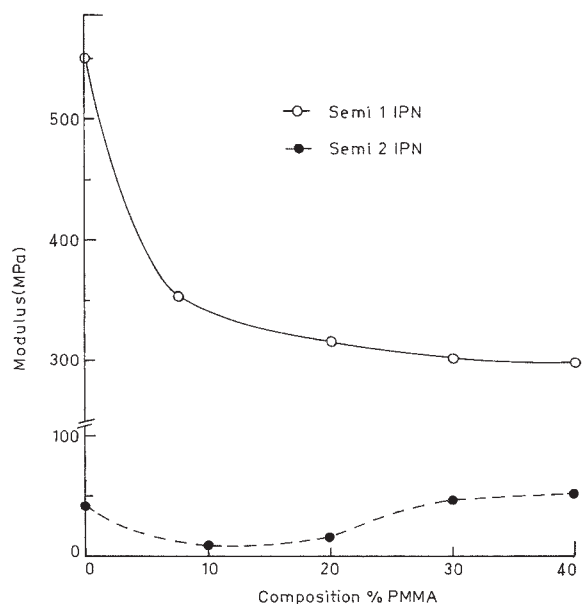
Figure 1 Variation of modulus with IPN composition. —○—, Semi1 IPN; —●—, semi2 IPN.

incorporation). After an initial reduction in modulus up to a level of 10%, there is a slow and steady increase in moduli values with increasing proportion of PMMA. It may, however, be noted that the sharp initial drop in modulus as encountered with semi1 IPN is absent with semi2 IPN.

In case of semi1 IPN, the arrested distribution of the first formed PMMA phase in a crosslinked PVC matrix as governed by the sequence of polymerization controls the morphology and the consequent properties. The initial sharp drop with semi1 IPN can possibly be attributed to the presence of linear PMMA domains, which not only disrupts the regularity of the PVC chain structure but also does not allow the complete crosslinking of
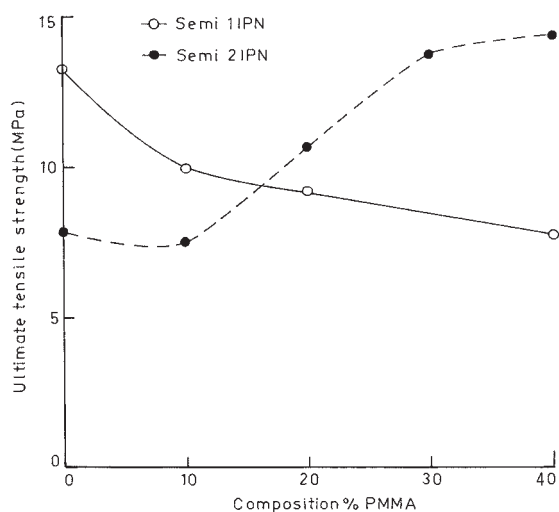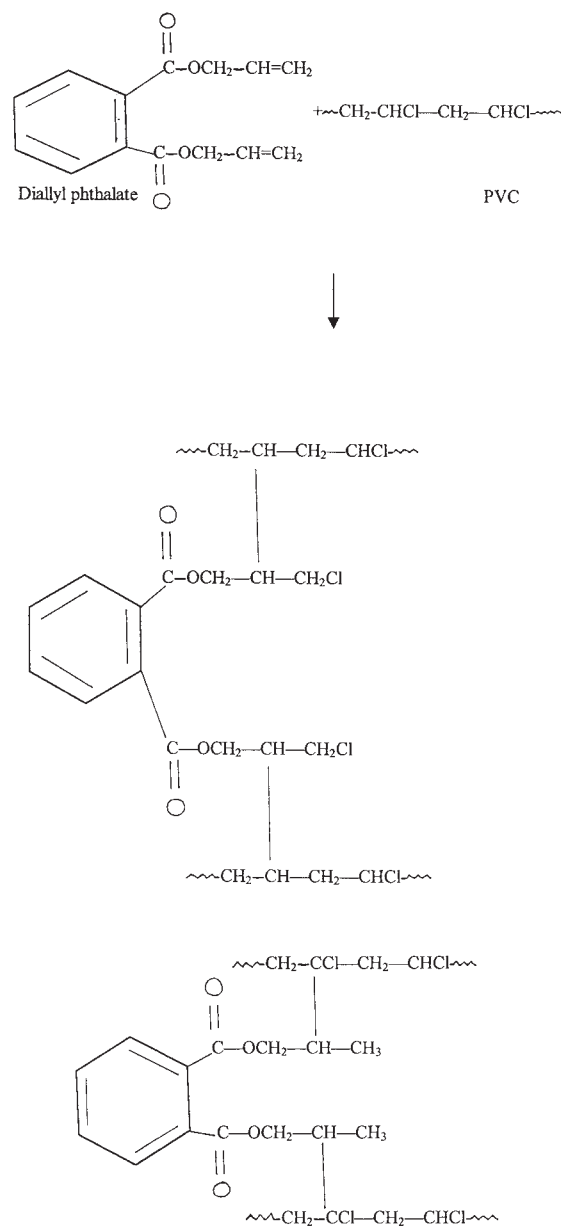

Figure 2 Variation of ultimate tensile strength with IPN composition. —○—, Semi1 IPN; —●—, semi2 IPN.

Scheme 1

the matrix, as they occupy already the interisticial spaces between the matrix chains and increases intermolecular distances. With further increasing proportion of PMMA (beyond 10%), the sluggish drop in modulus can possibly be explained by the inability of the linear PMMA domains to confer chain flexibility possibly due to their entrapment within the long crosslinked chains of PVC. Whatever small flexibility is being observed in the higher ranges of PMMA incorporation may possibly be explained by the flexibility imparted by the long-chain crosslinks, the structure of which is being postulated as in Scheme 1.

Diallyl phthalate pvc

With semi2 IPNs where the major PVC matrix is linear, the initial small reduction in moduli and UTS is
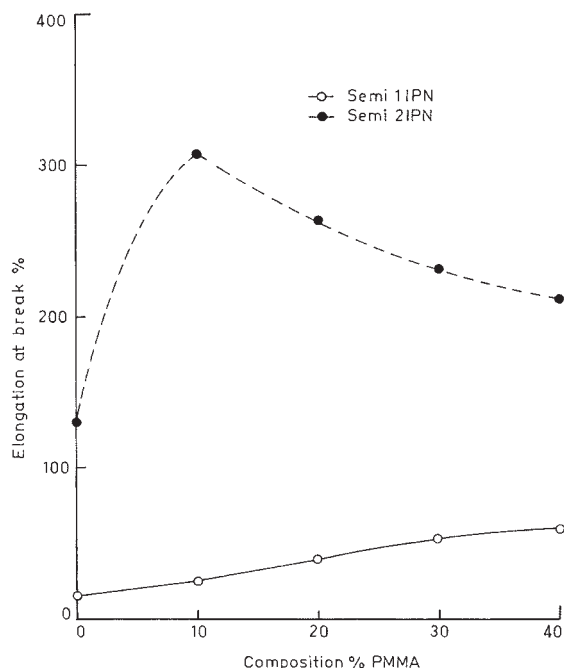
Figure 3 Variation of percent elongation at break with IPN composition. —○—, Semi1 IPN; —●—, semi2 IPN.

possibly due to absolute disruption in the interchain attraction of PVC (dipole–dipole interaction or dipole induced dipole interaction). The subsequent increase in moduli and UTS might be expected as a result of the chain stiffness and rigidity imparted by the dispersed crosslinked PMMA domains over the entire range of PVC matrix (as can be envisaged from the optical light micrographs given in Figure 10). Here the stiff and rigid characteristics of crosslinked PMMA appear to outweigh even the interchain attraction of PVC.

The percentage elongation at break and toughness of the different semi1 and semi2 IPNs of the PVC–PMMA system as shown in Figures 3 and 4 conform to the observation as expected.

In the semi1 IPN system, as the continuous PVC matrix itself is crosslinked, the flexibility imparted by the disruption of the polar PVC chains due to incorporation of PMMA is somewhat restricted. However, the dispersed PMMA domains inhibit the complete crosslinking of PVC and furthermore allow chain slippage across the interphases of their respective domains. The observed restricted increase in percentage elongation at break of this system may possibly be attributed to the cumulative effects of the following factors.

(1) Disruption of the regular chain structure of PVC;

(2) Statistical distribution of somewhat rigid and hard domains of PMMA, which themselves offer very little contribution to the elongation characteristic of the system but can act as sites of chain slippage of PVC;

(3) The somewhat longer chains of crosslinks (which may be considered as consisting of two flexible chain

moieties pivoted around a rigid aromatic ring) confer some flexibility and hence an increase in EB%.

The variation of toughness with composition further reinforces our earlier observation on the changes in EB% with composition. There is a slow and steady improvement in toughness over the entire range of PMMA concentration under study. However, it is interesting to note that beyond a 12–13% linear PMMA incorporation, the increase in toughness is not commensurable with respect to the change in EB%. This can possibly be explained by coalescence of the rigid hard domains of PMMA within the crosslinks of PVC thus contributing some brittle characteristic to the system.

In contrast to the observation with the semi1 IPN system, the semi2 IPNs exhibit an initial sharp increase in EB% followed by a gradual and steady decrease. The effect of crosslinking in the major matrix of PVC being absent in this case, the influence of the crosslinked PMMA domains in increasing the flexibility by occupation of the interspaces of the PVC chains appears to be pronounced. However, in the later stages of PMMA incorporation, the effect of flexibilization appears to be reduced, possibly due to the agglomeration of rigid hard domains of PMMA. The toughness of semi2 IPNs appears to corroborate the observation in the case of variation of EB% with composition.[15]

Physical properties

Specific gravity

The specific gravities of both the semi1 and the semi2 IPN systems as depicted in Figure 5 display positive deviation w.r.t. theoretically calculated specific gravities on the basis of the additivity principle.[11] This is definitely a positive pointer toward interpenetration
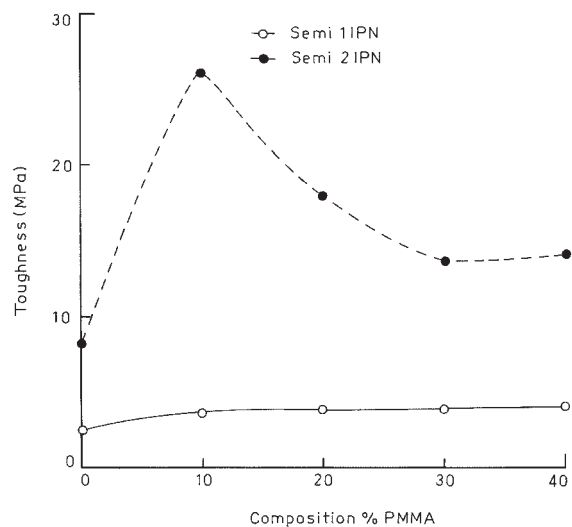

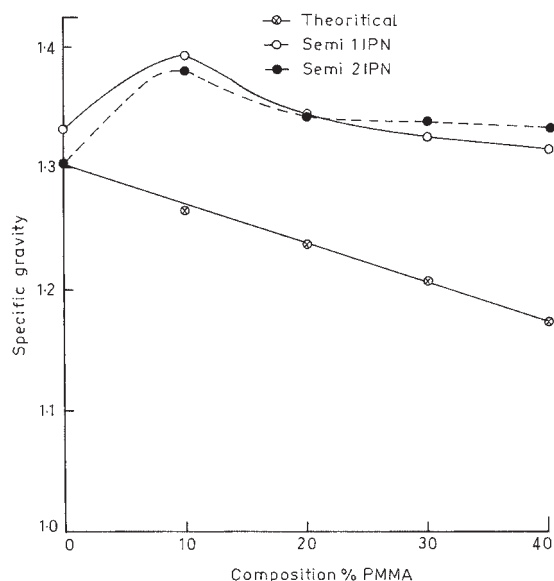**Figure 4** Variation of toughness with IPN composition. —○—, Semi1 IPN; —●—, semi2 IPN.

Figure 5 Variation of specific gravity with IPN composition. —⊗—, Theoretical; —○—, semi1 IPN; —●—, semi2 IPN.

Figure 6 Variation of hardness with IPN composition. —○—, Semi1 IPN; —●—, semi2 IPN.

of the dispersed PMMA phase into the PVC matrix.[16,17] It is quite interesting to note that the positive deviation is not uniform in both cases over the entire ranges of concentration of PMMA under study.[18,19] The initial sharp deviation appears to be somewhat minimized at the later stages. The effect appears to be more pronounced in case of semi1 IPN. In such a case, the crosslinked PVC matrix by virtue of its long-chain crosslinks appears to provide more intermolecular spaces where the dispersed linear PMMA can agglomerate and provide more mass in a definite volume. At the later stages, due to the diminishing volume of crosslinked PVC, the linear PMMA phase gets very little opportunity to be enclosed in such counters.

The fractional free volume of the in situ generated PMMA moieties increase with increasing proportion of PMMA. However, this increase in fractional free volume may possibly not compensate for the holes (empty spaces) generated by the crosslinked PVC itself.

Hardness

In conformity with our earlier observation on the two basic mechanical parameters, namely modulus and UTS, we can find a slow, gradual, and steady decrease of hardness of semi IPN systems with increasing proportion of PMMA (Figure 6). At the higher ranges of PMMA concentration under study, the hardness values almost level off, i.e., the surface hardness becomes almost invariant with composition. The crosslinked PVC matrix appears to be relatively harder and rigid than linear PMMA. This hardness coupled with the chain rigidity due to the dipole–dipole interaction offers hardness far superior to PMMA. With the in-
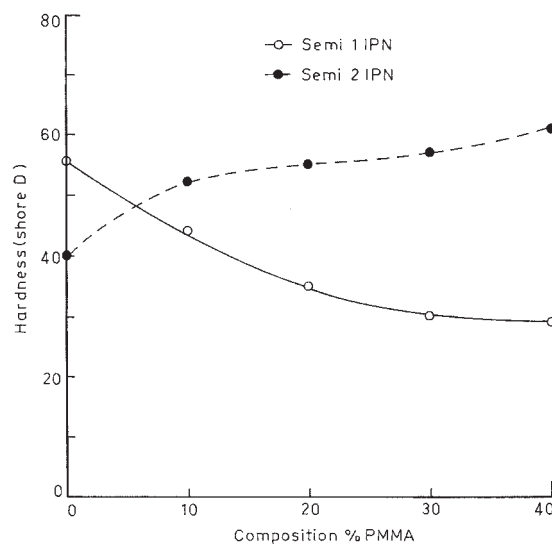
corporation of an apparently hard PMMA phase, we can find a gradual and steady decrease of hardness.

In the case of semi2 IPN (linear PVC, crosslinked PMMA) the hardness of stiff and rigid PMMA being further enhanced by the presence of crosslinks predominates over the intrinsic hardness of linear PVC. The onward increase of hardness with increasing proportion of crosslinked PMMA is exemplified in Figure 6. The modifying influence of the crosslinked PMMA is, however, sluggish at the higher ranges of PMMA incorporation.

Thermal properties

Thermogravimetric analysis. The thermograms of both the semi1 and the semi2 IPNs are shown in Figure 7
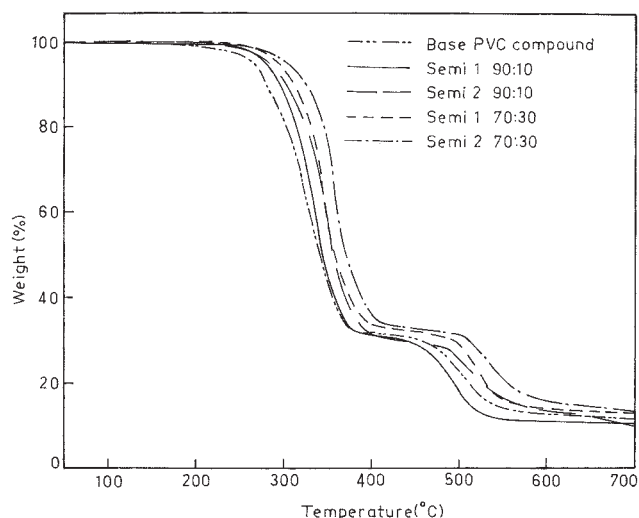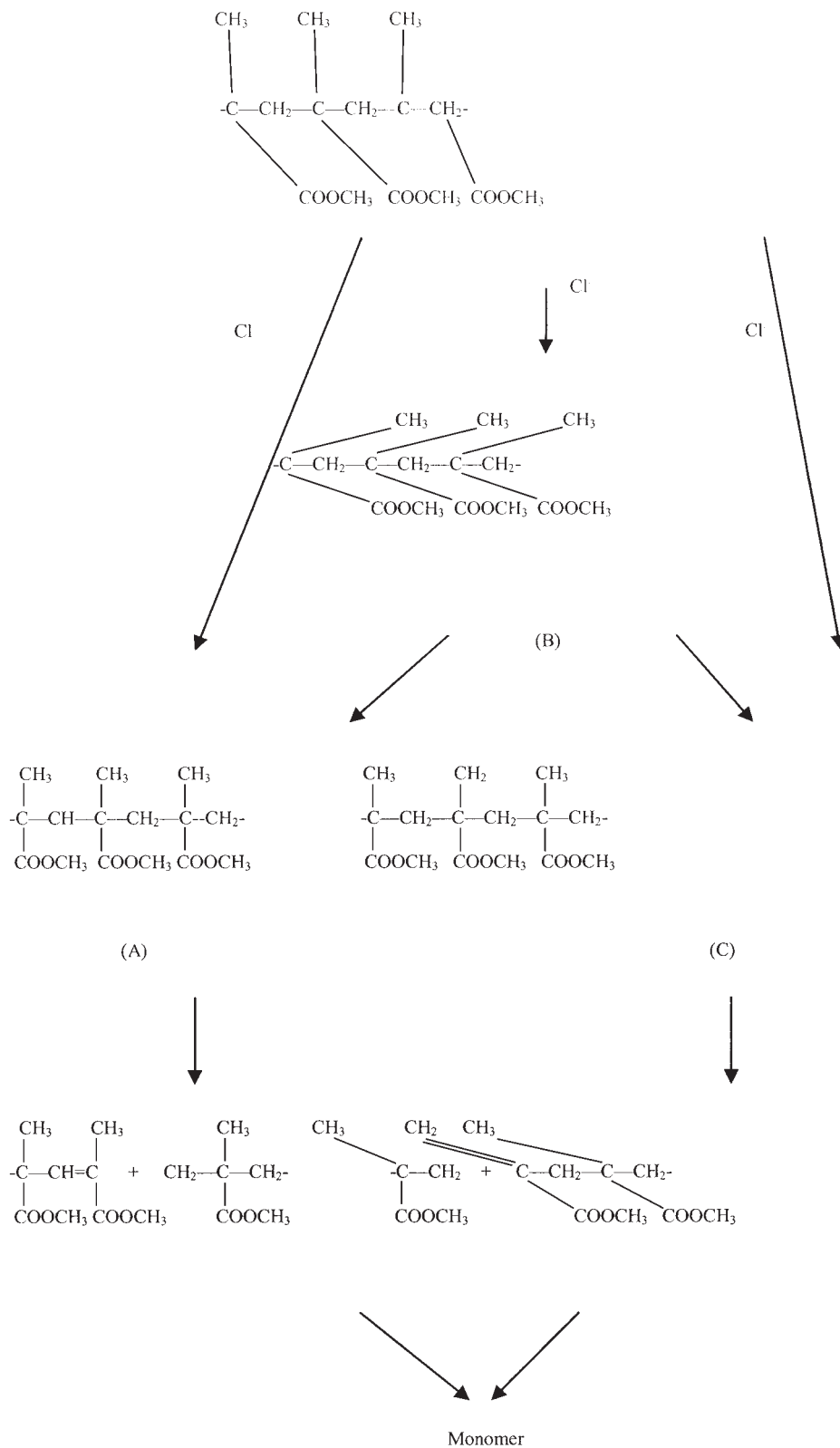

Figure 7 TGA plots for the base PVC compound and the IPN systems. – —, Base PVC compound; —, semi1 PVC: PMMA90:10; —, semi1 PVC:PMMA70:30; — —, semi2 PVC: PMMA90:10; —· —, semi2 PVC:PMMA70:30.

Scheme 2

along with that of pure plasticised PVC. It is quite distinctly evident that the incorporation of PMMA, whether in linear form (as in semi1 IPN) or in a crosslinked state (as in semi2 IPN), results in an over-

all increase in thermal stability of the various IPNs. Furthermore, it can be seen that the semi2 IPNs posses higher thermal stability over the corresponding IPNs of the semi1 type.
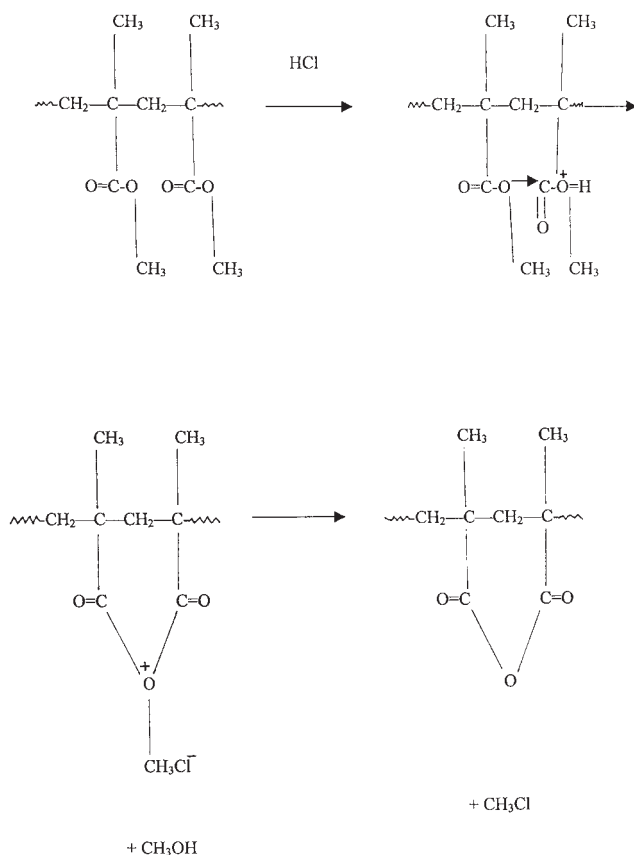
Scheme 3

The two stages of thermal degradation typical of pure PVC, namely the dehydrochlorination with consequent polyene formation followed by the polyene degradation, are greatly influenced by the in situ generated linear and crosslinked PMMA in semi1 and semi2 IPNs, respectively.[20]

The gradual increase in the onset temperature of degradation with increasing percentages of PMMA in both types of IPNs may possibly be attributed first to more and more inaccessibility of the chloride radicals to the α-hydrogen to form HCl due to the agglomeration of the bulky polymethacrylates within the interstitial spaces between the chains and second to the interaction of the chloride radical formed through allylic shift with PMMA as in Scheme 2.[21]

Secondly, even if some HCl is produced, it is possibly consumed in hydrolyzing the ester groups present in PMMA which appears to be a more kinetically favored reaction instead of autocatalysis of the further degradation reactions as is encountered during the degradation of PVC in Scheme 3.

In case of both semi1 and semi2 IPNs, the increasing stabilities at higher percentages of polymethacrylates might be expected, due to more statistical availability of methacrylates to interact with the chloride radicals produced at the initial stages of PVC degradation.

It is interesting to note that the presence of crosslinks in the dispersed PMMA phase appears to influence PVC degradation very little. There are marginal differences between the onset temperatures of degradation at the various stages of degradation and in the rates of degradation of the two different types of IPNs.

Thermomechanical analysis. The thermomechanical data of various IPN systems are shown in Figure 8 In all cases, the probe is slightly pushed up by the expansion of the samples up to a temperature around 50°C displaying marginal expansion. The onset of softening is followed by the penetration of the probe into the samples at a rate inversely related to their moduli in the case of semi2 IPNs only, whereas in the case of semi 1 IPN, it appears that the plasticizing influence of the linear PMMA phase remains unabated until an optimum concentration (20–25% of PMMA) is reached, beyond which possibly the phase-separated dispersed rigid and hard PMMA domains attain much mobility at elevated temperatures to cohere together and offer greater resistance to the penetration by the probe, which results in reduced deformation with semi1 IPN containing higher percentages of PMMA within the range of our study.

In the case of semi2 IPN, the stiff and rigid crosslinked PMMA molecules play a significant role in controlling penetration of the probe, which gradually decreases along with composition within the ranges of PMMA incorporation studied. The influence of crosslinked PMMA (linear PMMA having higher free volume appears to be less influenced on being crosslinked with EGDM) appears to predominate and nullify the influence of the softness imposed by the disruptive forces responsible for the softness of rigid PVC, and thus the degree of penetration follows the pattern as observed.

Morphology

Scanning electron microscopy. The scanning electron micrographs as given in Figure 9 indicate some miscibility between the participating constituents of the IPNs. PVC and PMMA, by virtue of having almost identical solubility parameter values, might be expected to be miscible. The semi2 IPNs where the dispersed PMMA phase is crosslinked appear to be more prominent in this respect as the interphases between the two phases are diffusing in nature. This miscibility with semi2 IPNs probably synergizes the mechanical properties of the IPN system as has been encountered in their corresponding moduli and UTS values. The interpenetrated PMMA fibrils appear to phase out after an optimum level at the higher level of PMMA incorporation under study. The leveling of the mechanical properties beyond an optimum concentration of about 20% PMMA is quite discernable in the corresponding micrographs.

In contrast, the semi1 IPN system exhibits an inherent tendency to throw the PMMA domains out of
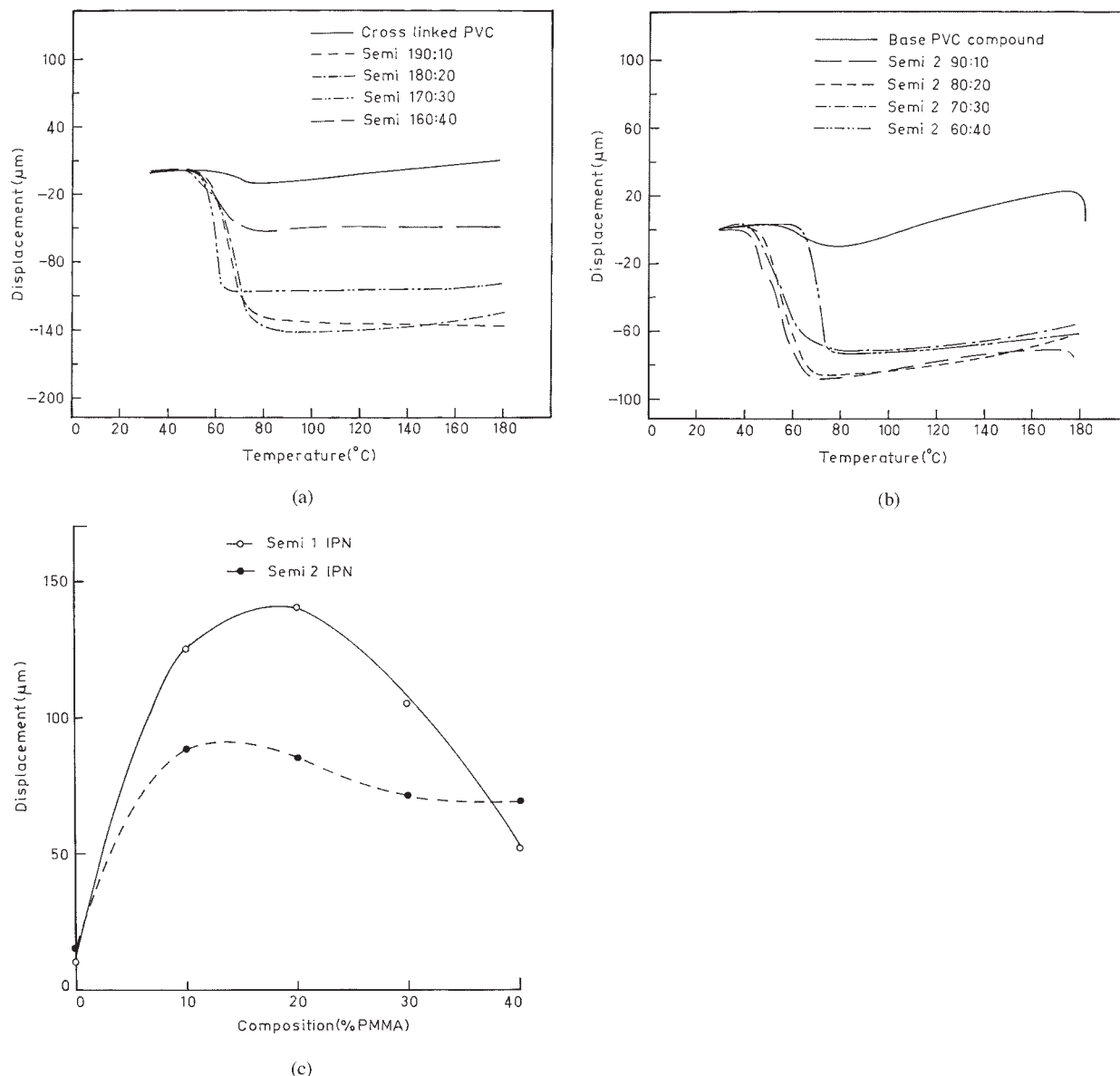
Figure 8 Thermomechanical analyzer (TMA) plots for the base PVC compound, crosslinked PVC and IPN systems. —, Crosslinked PVC; —, semi1 PVC:PMMA90:10; —· —, semi1 PVC:PMMA80:20. (a) —— —, semi1 PVC:PMMA70:30; ——, semi1 PVC:PMMA60:40; —, base PVC compound; ——, semi2 PVC:PMMA90:10. (b) —, semi2 PVC:PMMA80:20;—— —, semi2 PVC:PMMA70:30; —— —, semi2 PVC:PMMA60:40. (c)Variation of displacement with composition. —○—, semi1 IPN; —●—, semi2 IPN.

phase instead of the identical solubility parameters of the constituent polymers. This can possibly be explained by the refusal of the linear PMMA phase by the crosslinked PVC network. This effect increases with increasing proportion of PMMA and decreased content of crosslinked network.

Optical microscopy. The morphology as envisaged by optical microscopy (Figure 10) reveals that the dispersed PMMA phase being entrapped in the crosslinked network of PVC in semi1 IPN gets very little chance of being compatibilized with the matrix in contrast to the semi2 IPNs where the original PVC matrix is linear and the dispersed PMMA phase is crosslinked. It is also interesting to note that in the case

of semi1 IPN, as the proportion of the crosslinked network of PVC decreases (with increasing proportion of PMMA) the extent of phase mixing appears to be improved over what was experienced in the lower ranges of PMMA incorporation under study.[22,23] Upon close scrutiny it can further be inferred that the phase domains of PMMA in the case of semi2 IPN are somewhat more regular in nature (showing a tendency to spherical to elliptical shapes). This can possibly be attributed to the crosslinking of PMMA, which makes it much tighter and enables it to assume a much more defined shape. Here also the extent of phase mixing appears to develop with increasing proportion of crosslinked PMMA (as might be expected
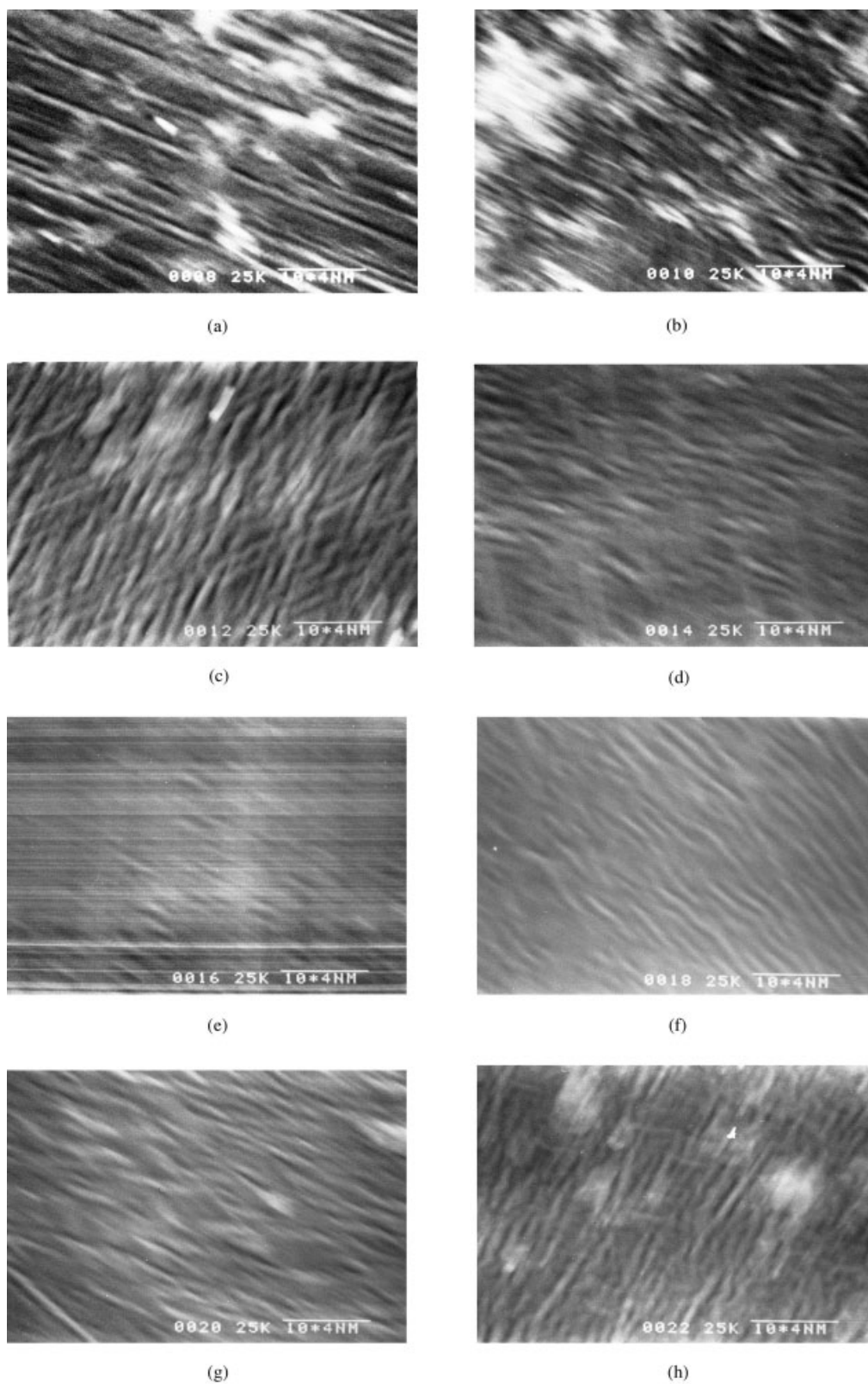
Figure 9 Scanning electron micrographs for IPN systems. (a) semi1 PVC:PMMA90:10; (b) semi1 PVC:PMMA80:20; (c) semi1 PVC:PMMA70:30; (d) semi1 PVC:PMMA60:40;(e) semi2 PVC:PMMA90:10; (f) semi2 PVC:PMMA80:20; (g) semi2 PVC: PMMA70:30; (h) semi2 PVC:PMMA60:40.

Figure 10 Optical micrographs for the IPN systems. (a) semi1 PVC:PMMA90:10; (b) semi1 PVC:PMMA80:20; (c) semi1 PVC:PMMA70:30; (d) semi1 PVC:PMMA60:40; (e) semi2 PVC:PMMA90:10; (f) semi2 PVC:PMMA80:20; (g) semi2 PVC:PMMA70:30; (h) semi2 PVC:PMMA60:40.
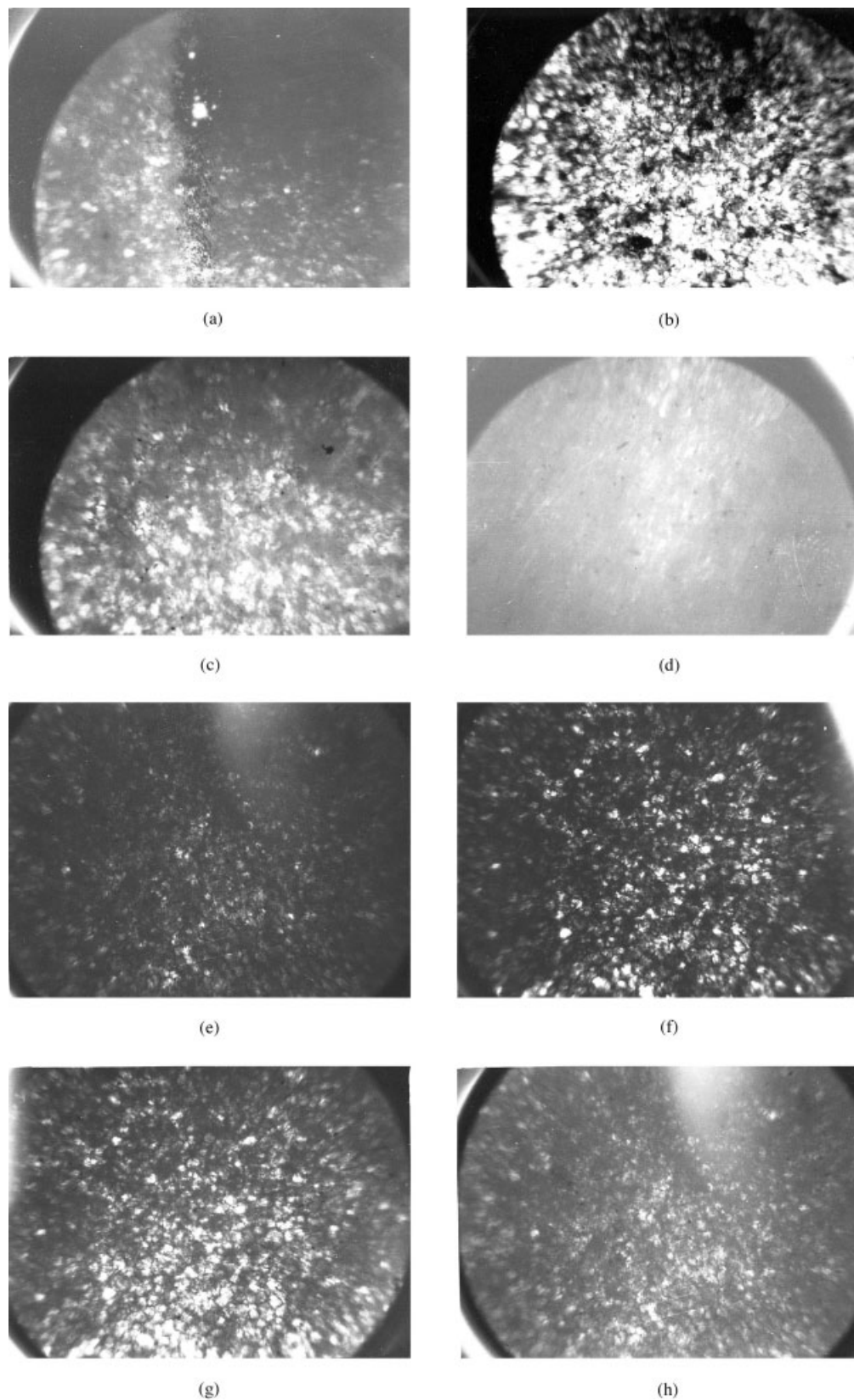
from the identical δ values of the matrices under consideration).[24]

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