Influence of the Bulk and Surface Morphology on Adhesion of Polystyrene-inter-poly-cross-2-ethylhexyl-methacrylate Films and Particles

LEONTINE A. DE GRAAF,* PIETER-JAN W. ALBERS, and MARTIN MÖLLER†

Department of Chemical Technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

SYNOPSIS

The adhesion behavior of semi-interpenetrating polymer networks (semi-IPNs) of linear polystyrene (PS) in crosslinked poly-2-ethylhexylmethacrylate (EHMA) was studied by variation of the bulk and surface morphology, i.e., domain size, continuity, and concentration in the domains. Semi-IPNs were prepared by liquid-liquid demixing upon cooling of a homogeneous solution of PS in methacrylate monomer, followed by gelation of the PS-rich phase and UV polymerization of the methacrylate resin. Welding of films allowed the preparation of larger objects provided that (1) the samples were phase separated to a high degree and contained domains with a high PS concentration (>90%) and (2) polystyrene was present at the interface. For semi-IPN films, a linear dependence of the adhesion strength on the (crack healing time)" was obtained. Based on these considerations, a process was developed to obtain melt-processable semi-IPN particles, by quenching droplets of the polymer solution into a cold liquid. These particles obtained a PS-rich skin layer and showed good adhesion after blending with a thermoplastic. © 1996 John Wiley & Sons, Inc.

Keywords: adhesion • interpenetrating polymer networks (semi-) • polystyrene • polymethacrylate

INTRODUCTION

In preceding articles, we described the preparation of microphase separated semi-interpenetrating polymer networks (semi-IPNs) by use of a two-step process, separating phase separation and crosslinking/polymerization. In the first step, liquid-liquid phase separation of a polymer solution is induced by a temperature quench, and arrested by vitrification of the polymer-rich phase. In the second step, the still liquid monomer and crosslinker are (UV) polymerized at a temperature below the gelation temperature. By variation of the viscosity of the polymer solution (polymer concentration, polymer molecular weight) and the quench efficiency (quench temperature, sample geometry) it has been possible to control the formation of a two-phase texture. Utilization of this procedure suffers from (1) the limitation in size of the semi-IPN samples because fast heat transfer during quenching is necessary in order to obtain a uniform morphology, and (2) their duroplastic nature, which does not allow melt processing. Both problems might be avoided if a semi-IPN material is prepared as small spheres which can be melt compressed or blended into a thermoplastic polymer. Small droplets of a polymer/monomer solution can be shock cooled by introducing them into a cold medium, where also the radiation induced curing reaction can be performed rapidly.

Because one of the two polymers in a semi-IPN is a linear polymer, some interdiffusion can be expected if such spheres are embedded in a matrix of the same or another but compatible linear polymer. Such interdiffusion is necessary in order to create
entanglements with the matrix polymer and to cause some adhesion.

The present study was directed toward the question whether semi-IPN materials can be welded together or mixed in a matrix of another (thermoplastic) material. To our knowledge, no research has been done so far on the adhesion behavior of (semi-) IPN materials, while a number of studies have been performed on adhesion (welding and crack healing) of linear polymers and occasionally of networks.

The two main objectives of this research have been:

1. To study the influence of the morphology on the adhesion strength of semi-IPN films of atactic polystyrene (PS) in poly-cross-2-ethylhexylmethacrylate by means of model experiments. Large variations in the semi-IPN morphology have been achieved exploiting the peculiar demixing and gelation behavior of polystyrene solutions in 2-ethylhexylmethacrylate (EHMA) in combination with low-temperature UV polymerization. For the present study it was assumed that diffusion of linear PS chains across the interface would be the main mechanism of adhesion. It was thus expected that samples containing the same amount of PS, but with different morphologies (domain size, connectivity, PS concentration in domains), would show different adhesion behavior.

2. Because preparation of semi-IPNs by thin film quenching does not allow the formation of large objects, the second objective was to develop a process to obtain "thermoplastic" semi-IPN materials which would be suitable for compression molding. For this purpose a route had to be developed to prepare small semi-IPN spheres, which were subsequently welded into larger objects. By welding of small particles, semi-IPNs can be processed as a kind of "semi-thermoplastic."

Based on welding and crack healing experiments with semi-IPN films, that is, adhesion between two different samples and between two surfaces of the same sample, respectively, conclusions will be drawn on the requirements for good adhesion regarding the composition and the (surface) morphology of the semi-IPNs. The article ends with a description of a process to prepare semi-IPN particles with the correct surface morphology, and the results obtained with molding of these particles.

ADHESION OF POLYMERS

Adhesion Mechanisms

Adhesion between two solid materials can be defined as the state when two bodies are held together by intimate interfacial contact such that mechanical force or work can be transferred across the interface. A fracture is called adhesive if a bonded structure breaks exactly along the interface. If the fracture propagates through the bulk of the materials, the fracture is called cohesive.

Four different mechanisms of adhesion have been proposed: (1) mechanical interlocking into irregularities of the substrate; (2) formation of a double layer of electrical charges at the interface; (3) the adsorption theory (physical and chemical), stating that intimate molecular contact between surfaces (< 5 Å) will cause adherence because of acting primary and secondary surface forces; and (4) the diffusion theory proposing that diffusion of polymer molecules across an interface is the major cause of intrinsic adhesion of polymers. Though more than one mechanism can contribute to adhesion, adsorption and polymer diffusion are generally accepted to contribute most significantly to adhesion of polymers.

Adhesion and Welding of Linear Polymers

Above $T_g$, two polymer specimens can be rejoined or welded together by diffusion of polymer chains across the interface. Crack healing and welding of polymers occur in three stages, namely surface approach and wetting, diffusion, and entanglement formation. Only after sufficient entanglement formation (randomization) will the maximum adhesion strength be reached. Wetting is an important factor, because incomplete wetting can produce interfacial defects and thus lower the contact area.

Four microscopic models have been suggested to explain the time dependence of mechanical property recovery during healing. The controlling factors are, respectively: the density of molecular contacts or bridges across the interface; the number of polymer bridges across the interface; the center-of-mass Fickian interdiffusion distance, and the average monomer segment interpenetration distance. All models have in common that they result
in similar equations for the time-dependent parameters and that they are based on the reptation model developed by de Gennes for the tube motion of a chain which is entangled with many other chains in an amorphous bulk material. Depending on the diffusion time, small portions of the chains increasing in length, the so-called minor chains, will cross the interface. A diffused chain from one side will entangle with other chains across the interface, and during fracture the chain is strained until it can either disentangle or fracture, depending on rate and temperature of fracture.

With the concept of minor chains, the following relations have been derived for the build up of fracture stress in crack healing and welding of linear chains:

(i) For $t <$ healing time necessary to reach maximum strength:

\[ \sigma \propto t^{1/4} \times M^{-1/4} \]

for surfaces in crack healing

\[ \sigma \propto t^{1/2} \times M^{-1/4} \]

for surfaces in welding

(ii) For $t >$ healing time necessary to reach maximum strength:

\[ \sigma \propto M^{1/2} \]

where $\sigma$ is the fracture stress, $t$ the time and $M$ the polymer molecular weight.

When two surfaces were brought into contact immediately after fracture, rehealing was faster than after an equilibration period, possibly due to excess of chain ends (resulting in faster diffusion) and radicals (chemical bonding) at the initial interfaces. A larger polydispersity of the used polymers resulted in more rapid healing at short times, followed by a slower approach to complete healing.

Interfacial mixing and the development of strength between two chemically incompatible amorphous polymers is controlled by two counteracting forces: enthalpic repulsion of chain segments and the entropy increase by chains crossing the interface. The adhesion strength is limited by the low diffusion depth of polymer chains and the interface does not disappear. Consequently, the strength of these interfaces is low in comparison with compatible interfaces, possibly because the in-compatibility limits the formation of sufficient entanglements. Helfand determined an expression for the interpenetration zone or penetration depth, $d_\alpha$, of a polymer chain with respect to the Flory–Huggins interaction parameter ($\chi$):

\[ d_\alpha \sim 1/(6\chi)^{1/2}. \]

Equation (1) shows that the penetration depth is very small for large values of $\chi$ (incompatible polymers). The experimentally determined interpenetration depths of the two incompatible polymers polystyrene and poly(methyl methacrylate) of $d_\alpha \approx 5$ nm (half the radius of gyration of both polymers) were in good agreement with theory. Because of the small dependence of $\chi$ on temperature, the penetration depth and consequently the adhesion strength was virtually independent of the welding temperature.

**Adhesion of Semi-IPNs**

Crack healing or welding of polymer networks is slower than healing of linear polymers, and the bulk strength can never be reached. The semi-IPNs used in this research consisted of a linear polymer in a crosslinked network. Diffusion of polystyrene from one PS-rich domain to another PS-rich domain was expected to be the dominant process in building up a tensile strength with time. Because the methacrylate network was highly crosslinked, no contribution by diffusion of the network to the tensile strength was expected. However, physical or chemical adsorption could give a possible contribution. Considering the incompatibility of PS and poly-cross-2-ethylhexylmethacrylate, the possible penetration depth of PS into domains of the methacrylate resin was expected to be in the order of a few nanometers, not allowing good adhesion.

Semi-IPN samples which contain the same amount of linear polystyrene, but show different morphologies, might be expected to show different adhesion strengths. Variations in the domain sizes and domain connectivity, and of the PS concentration within the domains will cause differences in the formation of entanglements across the interface and the penetration depth.

**EXPERIMENTAL**

**Materials**

Atactic polystyrene PS89K was obtained from Polysciences. Monomer 2-ethylhexylmethacrylate
(EHMA, Fluka) was crosslinked with up to 8 mol % (8 wt %) ethyleneglycol-dimethacrylate (EGDMA, Röhm).

The molecular weights of polystyrene and linear poly-2-ethylhexylmethacrylate were measured by GPC equipped with a low angle light scattering detector LALLS (Waters and Chromatix KMX-6): PS89K, $M_n = 89,300$ g/mol, $M_w/M_n = 1.06$; PS168K was obtained from DOW Chemical with $M_n = 168,100$ g/mol and $M_w/M_n = 1.88$. Linear poly-EHMA after UV polymerization $M_n = 217,000$ g/mol, $M_w/M_n = 2.2$; linear poly-EHMA after 20 h $120^\circ$C $M_n = 151,800$ g/mol and $M_w/M_n = 2.0$. The radius of gyration of PS89K ($R_g = 9.2$ nm) was measured in toluene at $25^\circ$C, using a laser-modified Sophica 42000 apparatus.

**Phase Diagrams**

Cloud point curves were visually determined by turbidity measurements at a cooling rate of 0.2°C/min. The temperature at which opalescence was observed was assumed to be the demixing temperature $T_d$ ($\pm 1^\circ$C). Gelation temperatures ($T_{gel}$) of low concentrated solutions were determined by slowly cooling the solutions in test tubes, until elastic behaviour was observed qualitatively, as the solution could be removed in one piece. Glass transition temperatures of highly concentrated solutions were measured by differential scanning calorimetry (Perkin Elmer DSC7) and extrapolated to 1°C/min heating rate.

**Semi-IPN Preparation**

**Films**

Homogeneous solutions of 25 wt % polystyrene in EHMA/EGDMA and benzoin methylether (UV-initiator, Lowi), were rapidly quenched to a temperature below the gelation temperature using molds for thin films and molds for cylindrical tablets (diameter 9 mm, thickness 1 and 2 mm for welding and crack healing, respectively). Samples were covered with polyethylene foil to avoid evaporation of the methacrylate monomer. The alumina cooling block (cooled by liquid nitrogen) was covered with a cooled alumina lid to allow double-sided cooling. Cooling rates of 60–140°C/s could be obtained by quenching to $-60^\circ$C and $-100^\circ$C, respectively.$^2$ UV polymerization was initiated below $T_{gel}$ with two 4-W UV lamps (366 nm) and the samples were irradiated at low temperature for 10 h to ensure a high conversion of the methacrylate monomer. Postcuring was performed by UV irradiation at room temperature (15 W), and by a heat treatment of 20 min at 100°C without noticeable changes in the morphology.$^2$

**Particles**

A homogeneous solution of PS/EHMA/EGDMA and benzoinmethylether was injected through a syringe into a mixture of methanol/dry ice ($-76^\circ$C) under UV irradiation (366 nm). After 3 h, the gelled and partially polymerized particles (diameter 2 mm) were transferred to the aluminum cooling block for further polymerization below $T_{gel}$.

**Morphology**

For investigation of the surface morphology, samples were embedded in an epoxy resin and cured at 60°C during 20 h before microtoming (EMBED-812 kit, Electron Microscopy Sciences). Thin sections of 80–100 nm thickness for transmission electron microscopy (TEM) were cut on a LKB 2188 Ultratome Nova. Sections were transferred to copper grids and stained with RuO$_4$ vapor to enhance contrast. A JEOL 200 CX TEM (200 kV) was used to study the morphology. In the TEM micrographs, polystyrene is visible as the dark phase.

**Mechanical Behaviour**

A Myrenne torsional pendulum was used at a frequency of approximately 1 Hz. Samples of 12 mm length, 8 mm width, and 1 mm thickness were monitored at a heating rate of 1.5°C/min. The glass transition temperature ($T_g$) was identified as the temperature where the loss modulus, $G''$, had a maximum.

**X-Ray Photon Scattering (XPS)**

XPS measurements were performed with a Kratos XSAM-800 apparatus using a MgK$_\alpha$ source (15 kV, 10 mA, Manchester, United Kingdom). The analyzer was placed perpendicular to the sample surface. The spectra were recorded in the low resolution mode (pass energy 40 eV, FWHM Ag$^{3d}_{3/2}$: 1.2 eV). Detail scans (20 eV windows of the binding energy) were used to determine the elements present at the surface quantitatively (approximately outer 10 nm).
ADHESION OF SEMI-IPNs OF POLYSTYRENE IN POLY-cross-EHMA

Welding and Crack Healing

Welding

Samples for welding experiments were prepared using the cooling block described above. A cured, circular semi-IPN film (a) (1 mm thickness, diameter 9 mm) was pressed on a gelled polymer solution (b) to obtain good wetting. After UV irradiation through the upper half of the sample, a heat treatment of 20 min at 115°C was applied. Subsequently, the samples were subjected to a pressure of 5 bar in a nitrogen-flushed oven at 120°C (welding). The welded object (a + b) was glued between two square aluminum tensile holders (glue: Bisonite, adhesion strength 8200 kN/m²). The adhesion strength was determined by measuring the force necessary to separate the two surfaces using an Instron tensile test machine with a crosshead speed of 0.5 mm/min. An average of five measurements was taken. See Figure 7 for the procedure.

Crack Healing

A circular semi-IPN film (thickness 2 mm) was glued between two tensile holders and fractured by a tensile test machine with a cross head speed of 0.5 mm/min. Within 15 to 60 min after fracture, the sample was reconnected at a pressure of 2.5 bar and placed under nitrogen into an oven at 115°C. The adhesion strength of the crack-healed sample was measured at room temperature. An average of five measurements was taken. See Figure 8 for the procedure.

Compression Molding

Semi-IPN particles of 50 μm diameter (pulverized with a Fritsch pulverisette with a 0.12 mm rasp) were mixed with polystyrene in a Brabender W50 EH at 200°C. Semi-IPN particles or milled particles were mixed with EHMA monomer or pulverized PS and pressed into bars (dimensions: 60 × 10 × 1 mm³) in a Lauffer OPS 40 press (at 160–190°C for 5 min at 10 bar).

RESULTS

Phase Behavior

The phase diagram of solutions of polystyrene (PS89K) in 2-ethylhexylmethacrylate with 8 wt % ethyleneglycoldimethacrylate (EHMA/8 wt % EGDMA) is shown in Figure 1. The solutions showed a critical temperature of −35°C at 16 wt % polystyrene and a T_gel of −42°C. At 25 wt % PS89K the demixing temperature was −37°C. The PS concentration at the intersection point of the demixing curve and the T_crit-concentration line, the gelation concentration, was approximately 50 wt %.

Solutions of 25 wt % PS168K showed a slightly higher demixing temperature of −28°C at 25 wt % polystyrene and a T_gel of −33°C.

Demixing and gelation temperatures of solutions of PS in EHMA decreased upon addition of the crosslinker, EGDMA. Figure 2 shows a linear dependence of both T_dex and T_gel on the weight percentage EGDMA. In order to obtain the same quench depth (T_dex - T_quench) for samples containing different concentrations of EGDMA, different

![Figure 1](image1.png)

Figure 1. Phase diagram of PS89K in EHMA with 8 wt % EGDMA. (○) Demixing temperatures, (■) gelation temperatures.

![Figure 2](image2.png)

Figure 2. Demixing and gelation temperatures of solutions of 10 wt % PS89K in EHMA as a function of EGDMA content. (○) Demixing temperatures, (■) gelation temperatures.
quench temperatures were applied during semi-IPN formation (see Fig. 4).

**Bulk Morphology**

Solutions of 25 wt % PS89K in EHMA/8% EGDMA were quenched to different temperatures, thereby inducing different rates of cooling and gelation. This way it was possible to arrest different stages of demixing.

Samples quenched to -80°C and -60°C [Fig. 3(a,b)] showed a percolating PS-rich phase. The black domains represent areas with the highest PS concentration. As it had been shown before, these areas can be assigned to the peaks in polystyrene concentration fluctuations which vitrified upon passing the gelation temperature.

Slower cooling upon quenching to the gelation temperature (-42°C) or to the demixing temperature (-37°C) yielded structures which were more coarsened and which had developed towards a cellular PS phase with spherical poly-cross-EHMA inclusions of approximately 0.2-0.5 μm [Fig. 3(c,d)]. Upon quenching to -42°C, both small and large cellular domains of poly-EHMA can be observed (<0.15 and 0.5 μm, respectively). This is due to breaking up of the PS cell walls and coalescence of small domains into larger domains.

When a sample was prepared by methacrylate polymerization at room temperature, a cellular structure was obtained with a cell size of 0.5-2 μm diameter [Fig. 3(e)]. Bulk morphologies of PS168K samples which were quenched to -80 and -60°C and polymerized at room temperature were indistinguishable from the corresponding PS89K samples.

Mechanical measurements indicated that a short heat treatment immediately after UV curing resulted in an increase of the \( T_{g_{\text{ps}}} \) from 80 to 95°C (see Fig. 4). Obviously, after UV curing some methacrylate solvent and polymer were still trapped in the PS-rich phase. The monomer was sufficiently mobile to diffuse out of this phase or to be further polymerized. Chemical reorganization of the poly-cross-EHMA network (e.g., depolymerization/repolymerization) is also indicated by the decrease of the molecular weight of linear poly-EHMA due to heat treatment at 120°C. Probably, repolymerization will have occurred also in the case of poly-cross-EHMA.

Samples quenched to -37 and -42°C and polymerized at room temperature showed a \( T_{g_{\text{ps}}} \) at 100-105°C after annealing, indicating a pure PS phase. In order to cure the methacrylate networks as completely as possible, all samples were subjected to a heat treatment of 20 min at 120°C, which did not lead to detectable changes in the morphology.

In order to investigate the morphology changes as a result of annealing and to obtain an indication of the mobility of the polystyrene chains, samples with different methacrylate crosslink densities were exposed to 115°C for several hours. Figure 5(a,b) shows a sample which was prepared from a solution of 25 wt % PS89K in EHMA/8% EGDMA. First the solution was quenched to -60°C and cured, then it was annealed for 22 h at 115°C. The PS-rich domains became spherical with a diameter of 20 nm, indicating mobility of the PS chains.

A sample containing 3 wt % EGDMA which had been quenched to -53°C [same quench depth (\( T_{\text{demix}} - T_{\text{quench}} \)) as the EHMA/8% EGDMA sample] showed major coarsening after only 3 h at 120°C [Fig. 5(c,d)]. After heat treatment, the PS domains grew distinctly larger to about 40 nm in diameter.

A blend of PS89K and linear poly-EHMA, which had been prepared by quenching a solution of PS89K in EHMA to -47°C, showed initially the same morphology as Figure 5(c). After 1 h at 120°C, the sample had lost its coherence and embrittled spontaneously. TEM showed large spherical PS domains comparable to Figure 5(d).

**Semi-IPN Films**

**Surface Morphology**

Because adhesion is a surface phenomenon, both the surface morphology and the surface composition play an important role. A surface layer of several micrometer thickness was observed in all quenched samples. This had a denser morphology and smaller domain size than was found in the bulk. On top of this layer, a nonstained skin layer was observed which increased in thickness when the time between quenching and start of UV irradiation, i.e. the gel time, was increased (Fig. 6, from 0.05 μm after 30 s gel time up to 0.15 μm after 30 min gel time). The skin layer also became thicker when the sample thickness was increased. Samples polymerized at room temperature did not show such a colorless skin layer.

X-ray photon scattering (XPS) indicated a higher oxygen content in the colorless surface layer than in the bulk [C/O ratio surface 3.64, bulk: 4.50, expected ratios for PS/poly-cross-EHMA (25/75 w/w) were 4.0 and 5.5, respectively]. Considering also the
Figure 3. TEM pictures of samples containing 25 wt % PS89K in EHMA/8% EGDMA, quenched to different temperatures. (a) Quenched to −80°C; (b) quenched to −60°C; (c) quenched to 42°C; (d) quenched to −37°C; (e) polymerized at room temperature.
Welding

In order to ensure intimate welding, a polymerized circular semi-IPN film was pressed onto a gelled polymer solution, which was subsequently polymerized by UV irradiation at low temperature. The samples were welded in a nitrogen-flushed oven at 120°C.

A typical example of the welding procedure and a TEM picture of the interface is shown in Figure 7. The measured adhesion strengths and bulk strengths of the materials used are summarized in Tables I and II. The neat strength of the UV-polymerized samples before welding at 115°C could rise to 900 kPa and showed adhesive fracture. This indicates the contribution of interfacial energy and possibly also chemical bonding to adhesion. After welding the samples at 115°C, a nonstained interface layer was observed between the samples. Probably, this interface layer is the skin layer which was present already on the polymerized semi-IPN tablet (Fig. 6). Though mainly cohesive fracture occurred, the adhesion strength was only 2650 kPa. This value is...
Figure 6. TEM pictures of samples containing 25 wt % PS89K in EHMA/8% EGDMA, quenched to −60°C. (a) 30 s gel time; (b) 30 min gel time.

of the same order as the fracture strength which was measured when two poly-cross-EHMA samples without PS were welded together at the same conditions. In this case, welding experiments resulted in cohesive fracture at a strength of 2300 kPa.

Crack Healing

For crack healing experiments a 2-mm-thick sample was fractured, after which the two fracture surfaces were reconnected within 15–60 min and placed in an oven at 115°C at a pressure of 2.5 bar. Figure 8 shows a scheme of the crack healing procedure and a TEM image of the sample interface. The semi-IPN sample had been prepared by quenching and curing the solution at −60°C, and was fractured at ambient temperature before the crack was finally healed for 15 h at 115°C. To the eye, the initially formed interface had disappeared. The TEM picture shows that the two fracture surfaces were connected by the bulk morphology, yielding a thin (black) PS-rich layer in between. Thus, polystyrene at the interface could contribute to adhesion.

Crack healing experiments which were performed at different temperatures showed that after 20 h of crack healing at 70°C no adhesion was found, while at 85°C an adhesion strength of approximately 2000 kPa was obtained (equal to the welding experiments). In contrast, at 115°C the maximum strength was 4400 kPa. The strength of the virgin poly-cross-EHMA and semi-IPN samples did not decrease significantly due to heat treatment.

The time dependence of the maximum adhesion strength after crack healing at 115°C, of samples which had been prepared by quenching to −60°C, is shown in Figure 9. The linear dependence of adhesion strength as a function of (crack healing time)$^{1/4}$ would be expected when crack healing was (among others) the result of PS diffusion across the interface. In comparison to welding experiments, the obtained values for the adhesion strength were higher, up to 4400 kPa, though the bulk strength of the semi-IPN sample of 7400 kPa was never reached. In most cases, new fracture surfaces were formed.

Samples which were prepared by UV polymerization at room temperature [Fig. 3(e)] appeared to reach a high adhesion strength after shorter crack healing time than quenched samples.

DISCUSSION

When samples were quenched to the gelation temperature, −42°C [Fig. 3(c)], more time was available before phase separation was arrested by vitrification than in the case of quenching to −80°C and −60°C. Consequently, a more coarsened structure was obtained. When the polymer/monomer solution was quenched to the demixing temperature, −37°C [Fig. 3(d)], phase separation, but no gelation, occurred. The PS-rich phase vitrified only when the demixing curve shifted upward during the subsequent polymerization of the EHMA, and the intersection temperature of demixing curve and $T_g$-concentration line reached −37°C. Moreover, due to the slow upward shift of the demixing curve, the sample was not quenched rapidly through the binodal into the spinodal region, but, instead, slowly entered the binodal region. Thus, extensive phase separation could occur before vitrification and arrest of demixing, which explains the droplet texture in Figure 3(d) with PS-rich cell walls. Mechanical measurements indicated that samples quenched above −42°C or cured at room temperature consisted of rather pure PS and methacrylate phases.
The fraction of black areas in the TEM pictures decreased from more than 50% in a sample quenched to \(-80^\circ\text{C}\) [Fig. 3(a)] down to 25% for a sample polymerized at room temperature [Fig. 3(e)]. This gives an indication of the volume fractions and the degree of phase separation. Quenched samples contain a PS-rich phase while nonquenched samples contain rather pure PS and pure poly-cross-EHMA phases.

All quenched samples had a smaller domain texture in the surface layer than in the bulk. This surface layer was covered by a nonstained skin layer, which most probably consists of poly-cross-EHMA. Possible explanations for these surface layers are (1) faster cooling at the surface resulting in a denser morphology, and (2) gel contraction (syneresis) and subsequent expulsion of monomeric EHMA solvent, both before and during curing of the resin. It is unlikely that skin layers of 50–150 nm thickness result from surface energy effects due to the presence of the polyethylene covering foil. In that case the surface layer should not exceed a thickness of 10 monolayers of methacrylate, i.e. maximum 10 nm.

During sample preparation, the initially homogeneous polymer solutions were quenched from room temperature to below the phase separation temperature, inducing chain contraction.\textsuperscript{34,35} In this fast process, chain shrinkage might be faster than chain disentanglement, so chain contraction was restricted by entanglements.\textsuperscript{36–38} As a result, gel shrinkage was accompanied by expulsion of the methacrylate solvent. When more time was allowed for gel shrinkage before the domain structure was chemically fixed by UV irradiation, both the "solvent" skin layer and the layer with denser morphology increased in thickness (Fig. 6). With respect to the total sample thickness, shrinkage was approximately 0.01–0.1%.

In none of the quenched samples used in welding experiments could polystyrene be observed at the sample surfaces (Fig. 6) or at the interface (Fig. 7). Taking into account that welding of two poly-cross-EHMA samples resulted in an appreciable adhesion

<table>
<thead>
<tr>
<th>Sample</th>
<th>Adhesion Strength (kPa)</th>
</tr>
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<tbody>
<tr>
<td>Welding: semi-IPN/semi-IPN (quenched (-60^\circ\text{C}))</td>
<td>2650</td>
</tr>
<tr>
<td>Welding: poly-cross-EHMA/poly-cross-EHMA</td>
<td>2300</td>
</tr>
<tr>
<td>Crack healing: semi-IPN/semi-IPN (quenched (-60^\circ\text{C}))</td>
<td>4400</td>
</tr>
<tr>
<td>Crack healing: semi-IPN/semi-IPN (RT)</td>
<td>4780</td>
</tr>
</tbody>
</table>
Table II. Bulk Strength of Materials

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bulk Strength no Heat Treatment (kPa)</th>
<th>Bulk Strength 20 h 120°C (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>24,000</td>
<td>24,000</td>
</tr>
<tr>
<td>Poly-cross-EHMA</td>
<td>4600</td>
<td>4450</td>
</tr>
<tr>
<td>Semi-IPN</td>
<td>7400</td>
<td>7150</td>
</tr>
</tbody>
</table>

strength, the absence of PS at the surface indicated that adhesion during welding might be the result of chemical reorganization of the poly-EHMA network, either into linear or crosslinked poly-EHMA. The assumption of (re-)polymerization is supported by the fact that both the molecular weight of linear poly-EHMA and the polydispersity decreased due to heat treatment.

In crack healing experiments, two fracture surfaces were connected with a thin PS-rich interlayer. The data are more consistent with a linear dependence of the adhesion strength to (crack healing time)$^{1/4}$ than to (crack healing time)$^{1/2}$. When crack healing experiments were performed at 70°C, no adhesion was found. At 85°C an adhesion strength of approximately 2000 kPa was obtained (equal to the welding experiments), while at 115°C the maximum strength was 4400 kPa. This indicated that at 70°C both methacrylate reorganization and PS diffusion are impossible, probably due to the fact that this temperature is below the $T_g$ of the poly-

styrene phase. At 115°C both repolymerization and diffusion can contribute to adhesive bonding. In this case, PS diffusion yielded adhesion strengths which were twofold higher than those obtained in welding experiments. The bulk strengths before heat treatment, as listed in Table II, were never reached. Samples which were prepared at room temperature seemed to reach a rather higher adhesion strength after shorter crack healing time than quenched samples. It appears to be better for good adhesion to have a limited number of domains with a high PS concentration (>90%), than many domains which are only rich in polystyrene (<90%). For the quenched compositions, polystyrene diffusion might

Figure 8. Crack healing procedure and TEM picture of sample containing 25 wt % PS89K in EHMA/8% EGDMA, quenched to −60°C after 15 h crack healing at 115°C.

Figure 9. Adhesion strength as a function of (crack healing time)$^{1/4}$ of samples containing 25 wt % PS89K in EHMA/8% EGDMA at 115°C. (■) Quenched to −60°C, (□) polymerized at room temperature.
be limited because of enthalpic repulsion between PS and the methacrylate matrix.

Based on the model experiments on adhesion of semi-IPN films, the following conclusions can be drawn: (1) polymethacrylates contribute to adhesion; (2) the presence of polystyrene at the interface significantly enhances adhesion, and therefore a methacrylate skin layer has to be avoided; (3) the PS domains have to be rather pure. Thus, semi-IPNs with a high degree of phase separation and with a PS-rich skin layer are preferred for good adhesion. The next paragraph describes a process to obtain particles which fulfill these requirements.

WELDING OF SEMI-IPN PARTICLES

The factors which favor adhesion are also essential requirements for obtaining semi-IPN particles which can be processed thermoplastically. A high degree of phase separation is favorable compared to partial demixing, and the particles should have a skin layer which is rich in polystyrene. A small particle diameter can be helpful to ensure a large surface-to-volume ratio and consequently a high volume fraction of the skin layer with the material active in welding. Such particles can be obtained by suspending a solution of PS and EHMA monomer at low temperatures in a mixture of methanol and dry ice (−76°C). A UV lamp allowed curing the methacrylate resin in situ.

The solubility of the EHMA/EGDMA monomers and the UV initiator in cold methanol is limited but not negligible (under the employed conditions, we observed a maximal extraction of 10% of the total volume of the dispersed droplets). Three processes occurred simultaneously: (1) quenching and gelation of the polymer solution; (2) partial dissolution of EHMA and EGDMA in methanol; (3) UV curing of the methacrylate. Because of almost instantaneous gelation due to vitrification of the PS-rich phase, dissolution of the methacrylates is diffusion controlled and restricted to the skin layer of the particles. Eventually it will be stopped as the UV initiated polymerization proceeds.

Figure 10 depicts the morphology of PS/poly-cross-EHMA particles prepared this way. The bulk morphology of the particles was very similar to that of a PS89K sample quenched to −80°C. Due to dissolution of the monomer in methanol, the surface layer is porous or fringed and consists mainly of PS, in contrast to the poly-cross-EHMA skin layer found for the films.

Welding of the nonpulverized semi-IPN particles with 5 wt.% EHMA monomer yielded an interface...
layer which contained no or little PS, as it was also found upon welding film samples [compare Figs. 11(a) and 6(a)]. EHMA polymerization, and possibly depolymerization/polymerization of the network to linear and/or crosslinked poly-EHMA, appeared to be the main mechanism of adhesion, yielding bars with an adhesion strength of 2100 kPa and mostly adhesive fracture. The relatively thick interface layer can be explained by the too small volume fraction of the PS-rich skin layer.

In a preliminary experiment to improve compression, the spheres were milled to yield an average diameter of about 50 μm. Although this procedure gave sufficiently small particles to allow good compression, it did not allow the advantage of a polystyrene-rich skin layer to improve welding. Mixing the pulverized semi-IPN particles with 10 wt % polystyrene PS168K resulted in better contact between the materials [Fig. 11(b)]. Bars were obtained which showed a distinctly higher adhesion strength of 3100 kPa and cohesive fracture. Bars of 10 wt % pulverized semi-IPN particles (diameter 50 μm) in a matrix of PS168K showed an adhesion strength of 21,000 kPa (compared to 24,000 kPa for pure PS), but no increased fracture toughness compared to pure PS.

CONCLUSIONS

Adhesion of semi-IPNs depends significantly on the degree of phase separation between the linear and the crosslinked components which constitute the semi-IPN. Adhesion was least upon welding films, which had a surface layer of poly-cross-EHMA, although in this case tensile strengths were achieved which approached that of the pure methacrylate resin. This is explained by some chemical reorganization of the methacrylate resin during heat treatment, i.e., depolymerization/repolymerization. Adhesion was best when the phase separation of polystyrene and poly-cross-EHMA had developed to yield domains of rather pure PS, and when polystyrene was present at the interface. Twofold higher adhesion strengths were obtained in crack healing experiments than by welding. A linear dependence of the adhesion strength on (crack healing time)\(^{1/4}\) was observed, indicating a contribution of PS diffusion to efficient adhesion.

An approach toward “melt-processable” semi-IPNs was proposed, based on the formation of semi-IPN droplets by suspending a homogeneous PS/methacrylate monomer solution in a cold liquid under UV irradiation. Due to partial dissolution of the methacrylate monomer, the dense surface layer and poly-cross-EHMA skin layer were not present, while the particles had the same bulk morphology as semi-IPN films quenched to the same temperature. The addition of a linear polymer to a resin particle was shown to significantly enhance the adhesion of these particles to other polymers.

So far, it has not been possible to realize efficient welding of these particles. Reduction of the particle size and an increase of the surface-to-volume ratio is expected to improve the adhesion properties. Achieving an optimum size and surface morphology of small semi-IPN particles is a subject of ongoing research. Further research is also needed to explain the origin of the apparent correlation between the domain purity and the adhesion strength of semi-IPNs. By using other vinyl monomers instead of methacrylates (e.g., acrylates), depolymerization at increased temperature might be avoided. In that case the contribution of polystyrene diffusion to adhesion, and its time dependence can be determined more accurately.

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REFERENCES AND NOTES


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