Highly-interpenetrated and phase-separated UV-cured interpenetrating methacrylate–epoxide polymer networks: Influence of the composition on properties and microstructure

C. Rocco [a], F. Karasu [a], C. Croutxé-Barghorn [a,*], X. Allonas [a], M. Lecompère [a], G. Riess [a], Y. Zhang [b], A.C.C. Esteves [b], L.G.J. van der Ven [b,c], R.A.T.M. van Benthem [b,d], G. de With [b]

[a] Laboratory of Macromolecular Photochemistry and Engineering, University of Haute Alsace, 3b Rue Alfred Werner, 68093 Mulhouse Cedex, France
[b] Laboratory of Materials and Interface Chemistry, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Den Dolech 2, 5612AZ Eindhoven, The Netherlands
[c] AkzoNobel, Automotive & Aerospace Coatings, 2171AJ Sassenheim, The Netherlands
[d] DSM Ahead BV Netherlands, P. O. Box 18, 6160MD Geleen, The Netherlands

ARTICLE INFO

ABSTRACT

Interpenetrating Polymer Networks (IPNs) based on a polybutadiene dimethacrylate and a dicyclohexyle-poxide mixed at different ratios have been synthesized by photopolymerization. To obtain a complete overview of the formation and phase separation of these IPNs, and to predict the final morphology, miscibility before and after polymerization has been studied. By varying the methacrylate/epoxide ratio, it was possible to move from a miscible and highly-interpenetrated system to a totally immiscible and phase-separated one. Miscibility effects on the polymerization kinetics of both polymer networks, final properties and surface morphology were investigated by RT-FTIR, DMA, AFM and AFAM. This overall characterization gives a better understanding of the formation and phase separation process in this system, depending on the mixture composition.

1. Introduction

Acrylates and methacrylates are widely used as monomers in UV-curing technology because of their high reactivity, commercial availability and moderate costs [1–3]. However, a drawback is a significant shrinkage up to 15% that may appear [4]. Furthermore, early vitrification of the network due to the high monomer reactivity can limit its conversion; combined with the density increase, this can lead to stress and cracks [5]. Furthermore, the free radical photopolymerization is known to be sensitive to oxygen inhibition leading to tacky surfaces [6–8]. Due to the ring opening polymerization, epoxides exhibit less shrinkage [4,9] and reactive species are able to polymerize in dark environment, leading to a full conversion [10,11]. However, the low polymerization rate of epoxides as well as their relative sensitivity to humidity and high brittleness turn out to be shortcomings for industrial applications [10,12,13].

In order to overcome the intrinsic limitations of both acrylate and epoxide polymerizations, Interpenetrating Polymer Networks
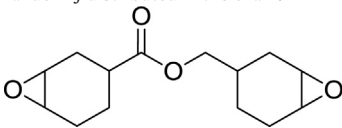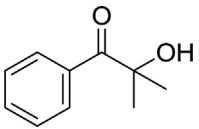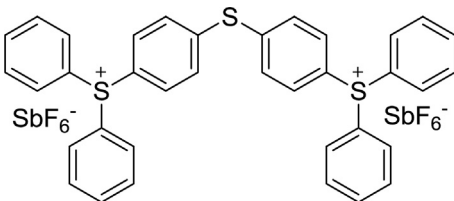
(IPNs) structure based on acrylate and epoxide can be synthesized. In this context, IPNs are defined as a blend of at least two crosslinked polymers which are permanently entangled [14–19]. The monomers polymerize according to different mechanisms [4,18,20] independently from each other [18,21], and the resulting IPNs combine properties of both acrylates and epoxides, which make them suitable for various applications [4,17,18]. They can be achieved in a one-or two-step process [18,21]. In the first case, the polymerization of the two networks occurs simultaneously according to independent and non-interfering reactions [11,12,14,15,18]. In a two-step approach, one polymer is firstly formed; then, it is swollen by a second monomer, which is further polymerized [14,15,18,22].

The formation of IPNs is generally governed by two processes which compete to give a large variety of final morphologies and degrees of mixing: the crosslinking reaction and the phase separation [14,18]. The first one may prevent the formation of domains depending on the reaction kinetics [23,24] whereas the second one is mainly governed by thermodynamics [23,25]. Thus, the final morphology results from the monomers or polymers miscibility and compatibility [20,23], polymerization method and sequence order of reactions [23], crosslinking density [18] and curing kinet-

Table 1
Chemical structures and properties of the compounds used in this work.

Name	Structure	Viscosity (mPa s^{-1})	Refractive index at 19.3 °C	M_w/M_n
CN 301	Mixture of polybutadiene dimethacrylate[a] (80 wt.%) and 1,6 hexanediol diacrylate[b] (20 wt.%). Polybutadiene units are composed of 1,4-*cis*; 1,4-*trans* and 1,2 conformations randomly distributed in the chain.	1000 at 60 °C	1.5013	2.33[a] 1.02[b]
UVR 6110		220–250 at 25 °C	1.4993	1.02
D 1173				
TAS				

M_w/M_n was determined by Size Exclusion Chromatography, using a Shimadzu LC-20AD liquid chromatograph equipped with two Varian PL gel 5 μm MIXED-C columns and a refractive index detector (Shimadzu RID-10A). THF was used as an eluent at a flow rate of 1.0 mL min^{-1}.

ics [20,21,23]. In consequence, the morphology governs the final properties of the resulting IPN [15,26–28].

Homogeneous and highly-interpenetrated IPNs can be identified by a single intermediary glass transition temperature (T_g) and no discernible phase domains [29–31]. On the contrary, the presence of 2 T_gs is an indication of poor or absent miscibility. Increased interpenetration between the two networks results in T_gs that are moving toward each other [14]. The miscibility of the network components can be enhanced by matching the rates of the crosslinking reaction half-lives for formation of both networks (τ_i), and by minimizing the difference in solubility parameter ($|\Delta\delta|$) and T_gs of the linear chain components. The thermodynamic binary interaction parameter (χ) and the Gibbs free energy (ΔG) [30,31] may be decreased for enhanced miscibility.

UV-cured IPNs have been widely reported in the literature [4,19–21,32–36]. The kinetics of network formation, mechanical properties and surface morphology are usually the parameters that are investigated. The miscibility prediction of the final polymer was only described for conventional, thermally cured systems [14,15,18]. To the best of our knowledge, an overview combining a miscibility study, the relative kinetics of formation of both UV-cured networks and the corresponding effects on the final properties and morphology (and in particular the extent of phase separation) has still not been reported. Therefore, the purpose of the present paper is to synthesize UV-cured methacrylate–epoxide IPNs of different chemical compositions in order to get a better understanding of their formation and phase separation. A difunctional methacrylate and a cycloaliphatic diepoxide have been chosen for this study for different reasons: their structure and reactivity in the photocuring process can trigger a phase separation depending on their respective ratio. In addition, the two homopolymers present two different T_gs (low T_g for the methacrylate and high T_g for the epoxide) to afford mechanical resistance and hardness together with flexibility to the resulting UV-cured polymer. To get a complete overview of the formation and phase separation of these IPNs, the miscibility of the network components before and after the polymerization has been investigated. Real time (RT)-FTIR was used to follow the reaction kinetics. The mechanical properties and morphology of these UV-cured films have been characterized

by Dynamic Mechanical Analysis (DMA), Atomic Force Microscopy (AFM) and Atomic Force Acoustic Microscopy (AFAM).

2. Experimental

2.1. Materials

Monomers selected for this study are dimethacrylate from Sartomer (CN 301) composed of a mixture of polybutadiene dimethacrylate and 1,6 hexanediol diacrylate at a ratio of 80–20 wt.% respectively, chosen for its flexibility and low T_g, and (3,4-epoxycyclohexane)methyl3,4-epoxycyclohexylcarboxylate from Dow Chemical (UVR 6110) exhibiting high T_g and reactivity, as well as good mechanical properties. For improved readability, the names methacrylate or epoxide will refer to these difunctional monomers in the following sections. The radical photoinitiator 2-hydroxy-2-methyl-1-phenyl-propan-1-one (Darocur 1173) was obtained from BASF and the cationic photoinitiator, a triarylsulfonium hexafluoroantimonate salt (TAS), was purchased from Sigma–Aldrich. The latter is diluted in propylene carbonate (50 wt.%). All these compounds were used without any further purification. Their chemical structures and properties are shown in Table 1.

Photocurable formulations (Table 2) were prepared by mixing the epoxide and the acrylic resins at different weight ratios. Radical and cationic photoinitiators were added to the formulation at 1 and 2 wt.%, respectively. Since, TAS is diluted in polypropylene carbonate at 50 wt.%, the amount of active photoinitiator remains at 1 wt.% regarding the formulation. In the following, mixtures will be described as xAyE, A standing for the radical system (polybutadiene dimethacrylate + hexanediol diacrylate + D 1173) introduced at x wt.%, and E corresponding to the cationic polymer (diepoxide + TAS) introduced at y wt.%.

2.2. Methods

2.2.1. Miscibility study

For the monomers characterizations, the specific density was taken from the technical data sheet of the producers and M_n was