Thermo-mechanical Properties of Interpenetrating Polymer Networks (IPNs) Filled with Fumed Silica Nanoparticles

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*In this study interpenetrating polymer networks (IPNs) based on bisphenol A diglycidyl dimethacrylate (**BisGMA**) and diglycidyl ether of bisphenol A (**DGEBA**) with or without native fumed silica nanoparticles were prepared by in situ polymerization. The properties of the IPNs and hybrid IPNs were evaluated using different thermal techniques as differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and thermogravimetrical analysis (TGA). The mechanical properties were also determined.*

Keywords: dimethacrylate, epoxy resin, interpenetrating polymer network, fumed silica

Most thermosetting resins are used with reinforcing agents to produce a composite material with better mechanical and thermal properties. Enhanced properties of thermosetting polymers for a specific application were achieved by mixing of thermosets to form "Interpenetrating Polymer Networks" (IPNs) [1].

IPNs are ideal compositions of two (or more) chemically distinct polymer networks held together exclusively by their permanent mutual entanglements [2-5]. The entanglement of multiple crosslinked polymers leads to forced miscibility compared to simple blends and the resulting IPN materials exhibit excellent size stability. These kinds of polymer combinations, in their majority, lead to materials with improved mechanical and thermal properties. The IPN materials have drawn the attention as polymeric matrix for nanocomposites with organo-clay or colloidal silica, and their morphologies and mechanical properties are widely investigated [6-10]. Depending if the polymer components are crosslinked or not two types of IPNs may be formed: full-IPNs (both polymer networks are crosslinked) and semi-IPNs (one of the components is crosslinked and the other is linear) [11].

In this study IPNs based on bisphenol A diglycidyl dimethacrylate (**BisGMA**) and diglycidyl ether of bisphenol A (**DGEBA**) with or without native fumed silica nanoparticles were prepared by in situ polymerization. The presence of the bisphenol A diglycidyl structure in both the vinyl esters and epoxy resins respectively enhances miscibility in the formed IPN.

The properties of the IPNs and hybrid IPNs were evaluated using different thermal techniques like differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and thermogravimetrical analysis (TGA). The mechanical properties were also determined.

Experimental part

Materials and methods

Diglycidyl ether of bisphenol A (**DGEBA**) with an epoxy equivalent weight of 180 was purchased from Dow Chemical. The dimethacrylate monomer, bisphenol A diglycidyl ether dimethacrylate (**BisGMA**), fumed silica and the anionic initiator, 1 methyl imidazole (**1-MeI**) were received from Sigma Aldrich. The azoinitiator, azobis(isobutyronitrile) (**AIBN**) was puchased from Merck. All raw materials were used without further modification.

The structures of the materials used in this study are shown in figure 1.

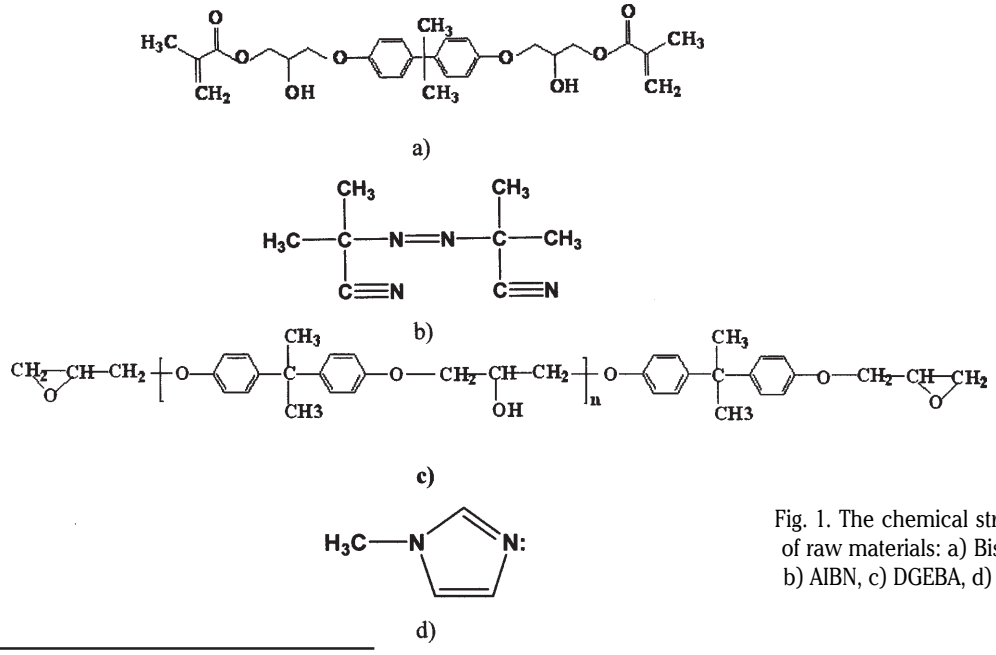

Fig. 1. The chemical structure of raw materials: a) BisGMA, b) AIBN, c) DGEBA, d) 1-MeI

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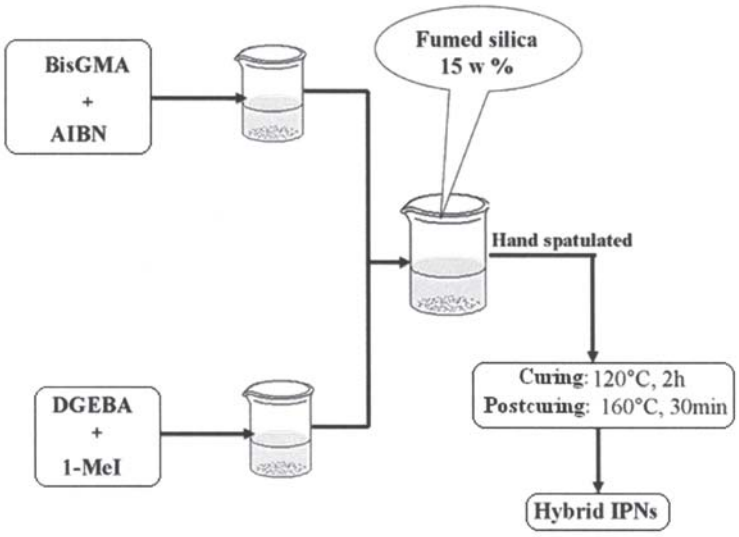


Fig. 2. Preparation of BisGMA/DGEBA IPN with 15 w % fumed silica

Synthesis of IPNs based on BisGMA/DGEBA

In order to obtain IPNs, several weight ratios of BisGMA/DGEBA (100/0, 75/25, 50/50, 25/75 and 0/100) were blended. Azobisisobutyronitrile (AIBN) was used as curing agent for BisGMA in concentration of 1 w %. DGEBA resin was cured by an anionic initiator (1-MeI) at a concentration of 2 w % against the resin.

Both the dimethacrylate and the epoxy monomer were individually mixed with their corresponding initiators before being combined in different ratios. The blends were poured into Teflon moulds, then cured at 120°C for 2 h, and finally postcured at 160°C for 30 min.

For hybrid IPNs, 15 w % fumed silica nanoparticles were added for each BisGMA/DGEBA combinations as well for the simple homopolymer matrices.

In the figure 2 the main steps for synthesis of BisGMA/DGEBA IPN reinforced with 15 w % fumed silica are shown.

Characterization

Differential Scanning Calorimetry (DSC)

The DSC curves were registered on a Netzsch DSC 204 F1 Phoenix equipment, using a heating rate of 5°C/min. The sample was heated from 20 to 200°C under a constant nitrogen flow rate (20 mL/min).

Dynamic Mechanical Analysis (DMA)

The DMA tests were run on a TRITEC 2000 instrument, at three different frequencies (0.316, 1, 3.16 Hz), from 25 to 250°C using a heating rate of 5 °C/min.

Thermogravimetric Analysis (TGA)

The TGA results were obtained on a Q500 TA instrument. A typical sample was heated from 20 to 650°C at a heating rate of 10°C/min under a constant nitrogen flow rate (balance flow 10 mL/min, oven flow 90 mL/min).

Mechanical properties (Compression strength)

The mechanical properties of the samples were measured on an Instron 3382 instrument, equipped with a 2 kN cell at room temperature (25±1°C) and 50±10 % relative humidity. The square –shaped (10 mm × 10 mm) samples of 5-6 mm thickness were placed on the lower plate and compressed by the upper plate at a constant compression rate of 1 mm/ min until fragmentation of the studied sample occurred. Measurements were replicated 4 times for each sample and the average value was calculated and reported.

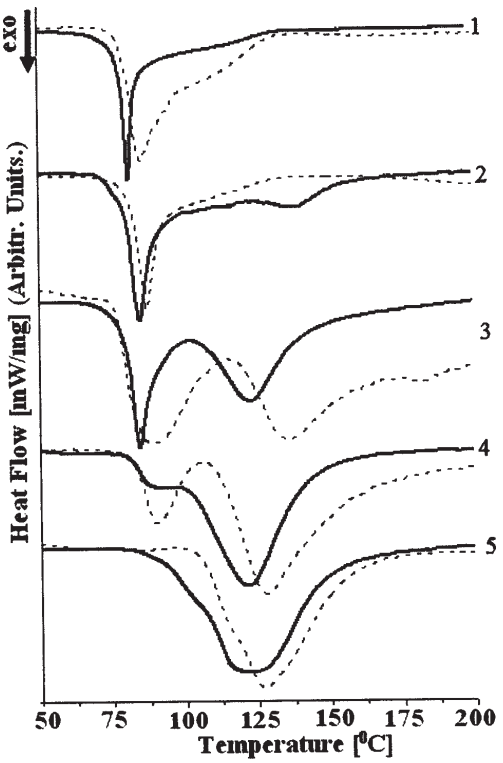


Fig. 3. DSC thermograms of: solid line simple IPN; dash line IPN with 15 % w fumed silica
(1) BisGMA/AIBN; (2) 75:25BisGMA/AIBN:DGEBA/1-MeI; (3) 50:50BisGMA/AIBN:DGEBA/1-MeI; (4) 25:75 BisGMA/AIBN:DGEBA/1-MeI; (5) DGEBA/1-MeI

Results and discussions

DSC analysis

The curing kinetics of IPNs based on BisGMA/DGEBA in various ratios with / without 15% w fumed silica have been studied by DSC. The DSC thermograms presented in figure 3 provide specific information about the curing behaviour of the corresponding IPNs.

The DSC results are summarized in table 1.

From figure 3 and table 1 it may be noticed that both BisGMA and DGEBA homopolymers exhibit separated exothermic peaks at 82 and 120°C respectively. The maximum polymerization enthalpy was assigned at 82°C for methacrylic groups in BisGMA, and at 120°C for epoxy groups in DGEBA. The IPN based 50:50 BisGMA/

Table 1
HEAT OF POLYMERIZATION AND PEAK TEMPERATURES FOR BISGMA/AIBN, DGEBA/1-MEI AND IPNS FORMED FROM THESE RESINS WITH / WITHOUT 15 % w FUMED SILICA

IPNs \ Hybrid IPNs	T_1, [°C]	T_2, [°C]	ΔH_1, [J/g]	ΔH_2, [J/g]
BisGMA/AIBN	82	-	187	-
BisGMA/AIBN+**15%FS**	86		117	
75:25 BisGMA/AIBN:DGEBA/1-MeI	85	139	83	10
75:25 BisGMA/AIBN:DGEBA/1-MeI **+15%FS**	87	203	80	14
50:50 BisGMA/AIBN:DGEBA/1-MeI	84	123	71	105
50:50 BisGMA/AIBN:DGEBA/1-MeI **+15%FS**	89	136	42	29
25:75 BisGMA/AIBN:DGEBA/1-MeI	90	121	10	195
25:75 BisGMA/AIBN:DGEBA/1-MeI **+15%FS**	91	127	19	84
DGEBA/1-MeI	-	120	-	440
DGEBA/1-MeI+**15%FS**		126		319

AIBN:DGEBA/1-MeI shows two exothermic peaks shifted to slightly higher temperatures (84 and 123°C), which is probably caused by the dilution effect of the reactants. The DSC curves of the IPNs based on 25:75 BisGMA/AIBN:DGEBA/1-MeI and 75:25 BisGMA/AIBN:DGEBA/1-MeI exhibit lower and upper intensity exothermic peaks with intensity proportional to the weight fractions of the two monomers. The DSC results are in good correlation with data obtained by [12].

Incorporation of 15% w fumed silica leads to higher curing exothermic temperatures for all the studied specimens (homopolymers and IPNs). Fumed silica nanoparticles exhibit high specific surface area (390 ± 40 m^2/ g) which cause an inportant agglomeration and thus the mobility of the polymeric chains are restricted, being less available for the polymerization process.

When fumed silica nanoparticles were included, the initial enthalpy corresponding to polymerization reaction decreases due to the silica nanoparticles agglomeration.

DMA

DMA is a common and useful technique to study the glass transition temperatures (T_g) of IPNs [13,14].

Figure 4 illustrates the dependencies of tan δ versus temperature corresponding to 25:75 BisGMA/AIBN:DGEBA/1-MeI IPNs with and without 15% w fumed silica.

The corresponding T_g values for all the studied IPNs and homopolymers are listed in table 2.

It can be noticed that DGEBA/1-MeI and BisGMA/AIBN homopolymers exhibit different T_g values. In the case of IPNs a single value of T_g was observed indicating no phase separation probably due to a good compatibility between BisGMA/DGEBA monomers.

The compatibility could be the result from the strong intermolecular hydrogen bonding between the C=O from methacrylate group or free -OH of BisGMA and the epoxy ring of DGEBA monomer [15].

The obtained 50:50 BisGMA/AIBN:DGEBA/1-MeI IPN has the Tg at 169°C, which is the average between the T_g of DGEBA/1-MeI homopolymer (176°C) and the T_g for neat BisGMA/AIBN (163°C). These results indicate that the

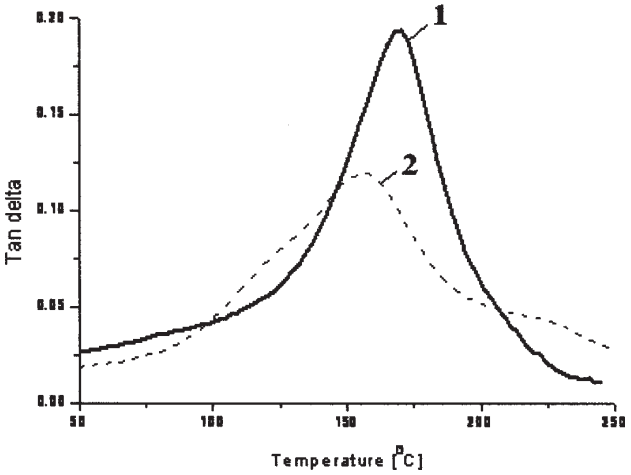


Fig. 4. DMA curves for 25:75 BisGMA/AIBN:DGEBA/1-MeI IPNs (1) solid line - without 15 % w fumed silica; (2) dash line - with 15 % w fumed silica

Table 2
GLASS TRANSITION TEMPERATURES (T_g) OF THE BisGMA/AIBN, DGEBA/1-MEI AND THE IPNs FORMED FROM THESE RESINS WITH / WITHOUT 15% w FUMED SILICA

Sample	T_g, [°C]	T_g, +15%FS, [°C]
BisGMA/AIBN	163	149
75:25 BisGMA/AIBN:DGEBA/1-MeI	165	145
50:50 BisGMA/AIBN:DGEBA/1-MeI	169	148
25:75 BisGMA/AIBN:DGEBA/1-MeI	171	158
DGEBA/1-MeI	176	167

phase structure of IPNs is strongly influenced by the miscibility of the IPNs components and also by the polymerization reactions.

The incorporation of 15% fumed silica leads to significantly decrease of the T_g values for hybrid IPNs. Thus, in this case silica nanoparticles are acting like a filler more than a reinforcing agent in the final structure of the obtained hybrid IPNs.

TGA

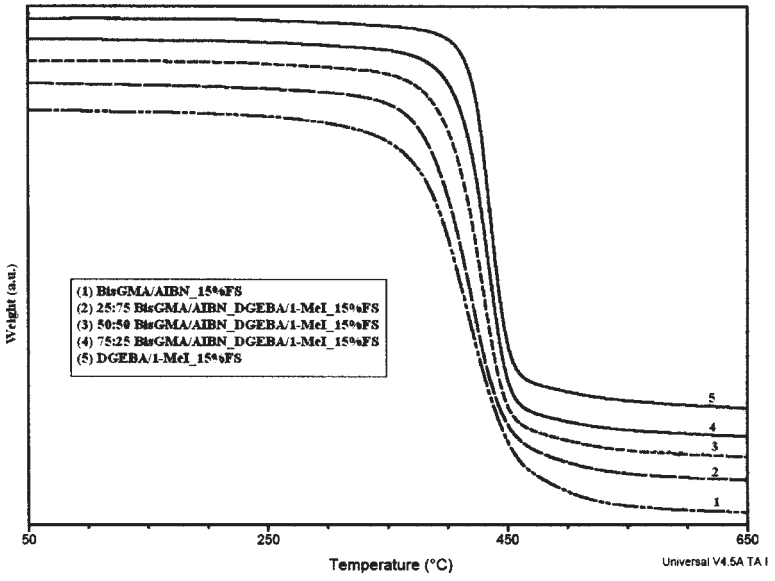
TGA was supplementary used to prove the compatibility and also the thermal stability of the IPNs and hybrid IPNs [16]. The thermal decomposition behaviour provides more specific information regarding the internal structures of the polymeric materials.

The TGA/DTG curves for the hybrid IPNs are shown in figure 5. For a better visualization the curves were vertically displaced.

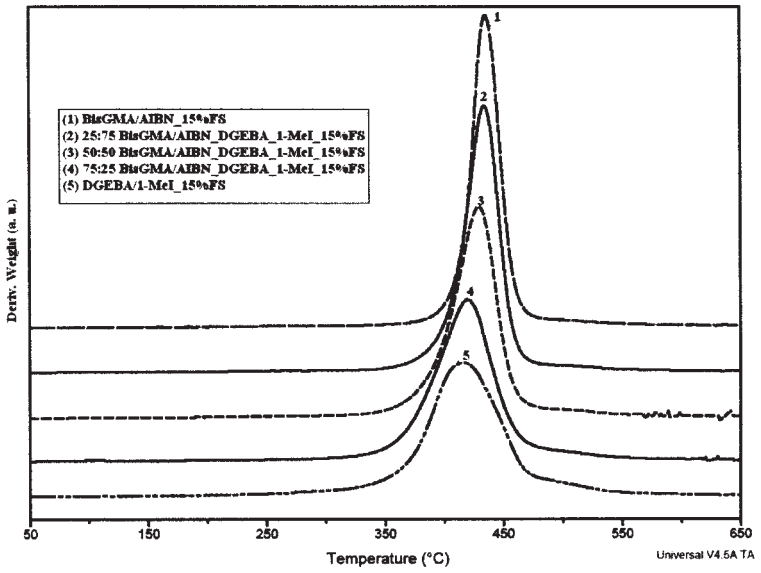
From figure 5 and table 3 it could be noticed that within the experimental temperature range, all the samples displayed similar degradation profiles. The existence of fumed silica did not significantly influence the degradation mechanism of the polymeric matrix. The thermal decomposition of these samples occurs in one major step [16].

The thermostability of the hybrid IPNs increases if inorganic component (fumed silica) was added.

For simple IPN the residual mass is about 12% while for hybrid IPN the residual mass increases at about 26% due to the incorporation of 15% fumed silica in the corresponding IPNs.



a)



b)

Fig. 5. a) TGA; b) DTG curves of IPNs with 15% FS

IPNs / Hybrid IPNs	$T_{onset,3\%}$, [°C[	T_{max}, [°C]	Weight loss, %
BisGMA/AIBN	316	417	88
BisGMA/AIBN+**15%FS**	340	419	77
75:25 BisGMA/AIBN:DGEBA/1-MeI	337	420	89
75:25 BisGMA/AIBN:DGEBA/1-MeI+**15%FS**	341	421	76
50:50 BisGMA/AIBN:DGEBA/1-MeI	357	427	87
50:50 BisGMA/AIBN:DGEBA/1-MeI +**15%FS**	361	429	76
25:75 BisGMA/AIBN:DGEBA/1-MeI	369	434	89
25:75 BisGMA/AIBN:DGEBA/1-MeI+**15%FS**	372	434	76
100%DGEBA	390	437	88
100%DGEBA+**15%FS**	394	435	75

Table 3
THERMOSTABILITY OF THE BisGMA/AIBN, DGEBA/1-MEI AND THE IPNs FORMED FROM THESE RESINS WITH / WITHOUT 15 % w FUMED SILICA

Mechanical properties

In general, the overall mechanical properties of a polymer composite are determined by several factors. These factors include the mechanical properties of the polymer and filler, the degree of polymerization for the monomer, the degree of particle aggregation, and the strength of the particle–matrix interphase [17-18].

The obtained compression strength results for simple IPNs and for hybrid IPNs filled with 15% fumed silica are shown in figure 6.

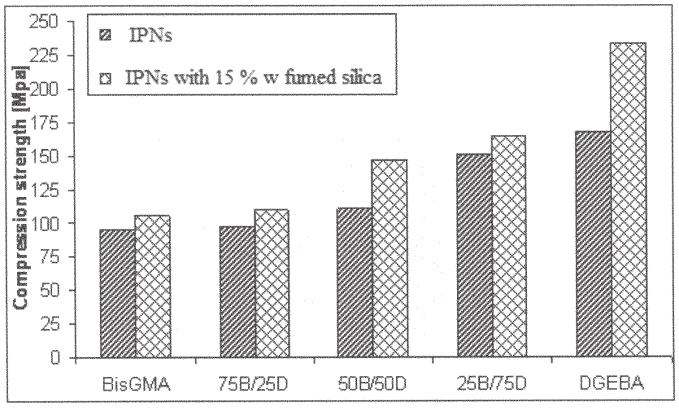


Fig. 6. Compression strength values of BisGMA/AIBN, DGEBA/1-MeI and the IPNs formed from these resins with / without 15 % w fumed silica

Compressive strength results were experimentally determined, used to compare materials which are brittle and generally weak in tension.

As it was expected, it may be observed that the IPNs filled with 15 % w fumed silica exhibit higher compression strength. These results are in good agreement with the TGA data.

Conclusions

Interpenetrating polymer networks (IPNs) based on bisphenol A diglycidyl dimethacrylate (**BisGMA**) and diglycidyl ether of bisphenol A (**DGEBA**) with or without fumed silica nanoparticles were prepared by in situ polymerization.

The curing kinetics of IPNs based on BisGMA/DGEBA in various ratios with / without 15% w fumed silica have been studied by differential scanning calorimetry (DSC). For all the studied specimens (homopolymers and IPNs) it may be observed that the incorporation of 15% w fumed silica leads to higher curing exothermic temperatures and lower initial polymerization enthalpy which is caused by the agglomeration of silica nanoparticles.

The DMA tests of pure components exhibit a single maximum peak as did the IPNs, indicating a single phase morphology.

The introduction of the inorganic component (fumed silica) increases the thermostability and the compression strength of the final hybrid IPNs.

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