Modification of vinyl ester and vinyl ester–urethane resin-based bulk molding compounds (BMC) with acrylated epoxidized soybean and linseed oils

S. Grishchuk · J. Karger-Kocsis

Abstract Acrylated epoxidized soybean and linseed oils of different characteristics were incorporated in the absence and presence of polymeric methylene diphenyl isocyanate (PMDI) in a vinyl ester (VE) resin-based bulk molding compound (BMC) up to 15 wt% (with respect to VE resin). The thermal, thermo-mechanical, static fracture mechanical, dynamic impact (Charpy), and thermal degradation properties of the BMC compounds were determined. With increasing amount of functionalized plant oils the glass transition temperature (T_g) of the matrix, the stiffness (E modulus) and Charpy impact strength of the BMCs decreased. The static fracture toughness was slightly increased and the fracture energy remained unaffected by the modification with increasing amount of oil. Additional crosslinking of VE, induced by PMDI, markedly enhanced the T_g but yielded a large drop in the glassy modulus. This finding was traced to resin dilution and to unfavored PMDI/kaolin interactions triggered by the water content of the latter. The thermal degradation of the BMCs was less affected, however, their degradation started earlier for the modifications either with functionalized plant oil or PMDI. Dilution of VE-based BMCs with acrylated epoxidized plant oils requires reworking of the corresponding recipes to keep the property degradation limited.

S. Grishchuk
Institut für Verbundwerkstoffe GmbH (Institute for Composite Materials), Kaiserslautern University of Technology, PO Box 3049, 67663 Kaiserslautern, Germany

J. Karger-Kocsis (✉)
Department of Polymer Engineering, Faculty of Mechanical Engineering, Budapest University of Technology and Economics, Budapest 1111, Hungary
e-mail: karger@pt.bme.hu

Introduction

Bulk molding compounds (BMCs) are extensively used to produce different high-performance parts in various application fields, especially in the electrical/electronics sectors. BMC formulations are used for mass products demanding low shrinkage and good surface properties. The resin component of BMC is usually unsaturated polyester (UP) or vinyl ester (VE) resin, eventually epoxy resin (EP). BMC is heavily filled (additives, fillers and reinforcements may be as high as 70 wt%). An important additive of BMC recipes is the thickening agent (usually MgO) which insures the easy handling of the related compounds in their uncured stage at ambient temperature. When heated in the mold, the viscosity of the thickened resin drops. This allows a long range flow before the curing of the UP and VE resin starts at elevated temperature.

VE is usually cured by free radical induced copolymerization with styrene. The related products exhibit good to outstanding mechanical, thermal properties, and chemical resistance and thus often compete with EP-based ones. To overcome their brittleness modification with liquid rubbers are recommended in close analogy to EPs [1]. The other toughening option is resin hybridization. This may be achieved by co-reactive compounds, such as diacrylates [2] or adding resins which generate an interpenetrating network structure (IPN). Exceptional good toughness was reported for IPN-structured VE/EP hybrids [3–5], and the related combinations were tried also as matrices in advanced composites [6].

The hybridization strategy proved to be useful tool to enhance the thermal resistance of VE. The secondary hydroxyl groups in the backbone of VE can be reacted with isocyanate groups of suitable polyisocyanates whereby the crosslinked structure becomes tightened (see later) [6, 7].

The glass transition temperature (T_g) of the VE urethane hybrids (VEUH) produced is markedly higher than that of the parent VE. Because VEUH is more brittle than VE, its toughening via different methods has also been addressed in the past [6–8].

VEs are synthesized from petroleum-based feedstock. Therefore, their partial or full replacement by bio-based resins from renewable resources is a very challenging and acute task. Use of materials from renewable resources in polymer synthesis is often termed "greening". Acryl functionalized plant oils seem to be promising candidates for greening VE resins. Among the plant oils soybean and linseed oils are the preferred versions for functionalization due to their relative high unsaturation and availability in abundance.

The use of functionalized plant oils in heavily filled BMC compounds is very straightforward from the following viewpoints. Functionalized plant oils when cured alone [9, 10], or when copolymerized with styrene and/or divinyl benzene [11], or with VE [9], yield thermosets with relatively low stiffness and T_g. However, the effect of a soft matrix on the properties is the less pronounced the higher the related composite is filled/reinforced. Acrylated and epoxidized vegetable oils may also work as reactive diluents in VE formulations, similar to the presently used styrene. Accordingly, their introduction in VE may contribute to reduce the styrene emission at the processing site.

The interest in the academia is focused on the full replacement of "petroresins" in BMCs and sheet molding compounds by renewable ones. Pioneering works in this field should be credited to the group of Wool (e.g., [12, 13]). Major resin suppliers already offer UP resins and related compounds with "renewable content".

In the open literature less information is available on how functionalized plant oils affect the mechanical and thermal properties of BMC compounds. Accordingly, major aim of this study was to "green" traditional BMC formulations by diluting them with acrylated epoxidized soybean oil (AESO) and acrylated epoxidized linseed oil (AELO). To compensate the expected property deterioration the resin

hybridization concept, exploiting the benefits of the urethane chemistry, was followed.

Experimental

Materials

The BMC compound (BMC B10-022 VE) was kindly provided by Polynt GmbH (Miehlen, Germany). Its major components are listed below: novolac based VE resin (styrene content: about 36 wt% with respect to VE): about 26 wt%; fillers including thickening agent (kaolin, chalk, MgO): about 56 wt%; reinforcement (short and milled E-type glass fiber, SGF): about 18 wt%. This BMC compound was modified with two sorts of acrylated epoxidized soybean oil (EASO and AESO, respectively) and with one sort of AELO. The difference between EASO (epoxidized acrylate of soybean oil) and AESO is that the former is a fine chemical, purchased from Sigma-Aldrich Chemie GmbH (Taufkirchen, Germany), whereas the latter was a pilot scale product, similar to AELO, produced by the group of Prof. M. Döring (Forschungszentrum Karlsruhe, Karlsruhe, Germany). Characteristics of these functionalized plant oils with the generic formula given in Fig. 1 were disclosed previously [14].

As network modifier a polymeric methylene diphenyl isocyanate (PMDI; isoPMDI 92150 of BASF Group, Elastogran GmbH, Lemförde, Germany) served in this study. It is noteworthy that the secondary –OH groups of VE may react with the isocyanate (–NCO) groups of polymeric isocyanates whereby additional crosslinks are generated. This is reflected in improved stiffness, strength and T_g, however, at cost of toughness [7]. It has to be added that acryl functionalization of epoxidized vegetable oils results in the appearance of secondary –OH groups (cf. Fig. 1). The created hydroxyls are also capable for reaction with the –NCO groups of the PMDI in hybrid formulations. The possible reactions taking place during crosslinking of the modified matrix resin are summarized schematically in Fig. 2.

Fig. 1 Generic molecular structure of the acrylated epoxidized triglycerides. *Note* it was presumed that the –OH group formed by reaction between the epoxy groups of epoxidized oils and acrylic acid may also enter in reaction with the acrylic acid during the acrylation procedure
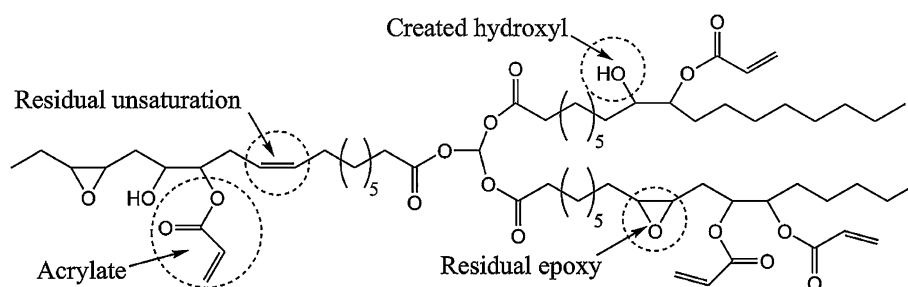
Fig. 2 Possible crosslinking reactions between VE, acrylated epoxidized triglycerides, styrene, and polyisocyanate
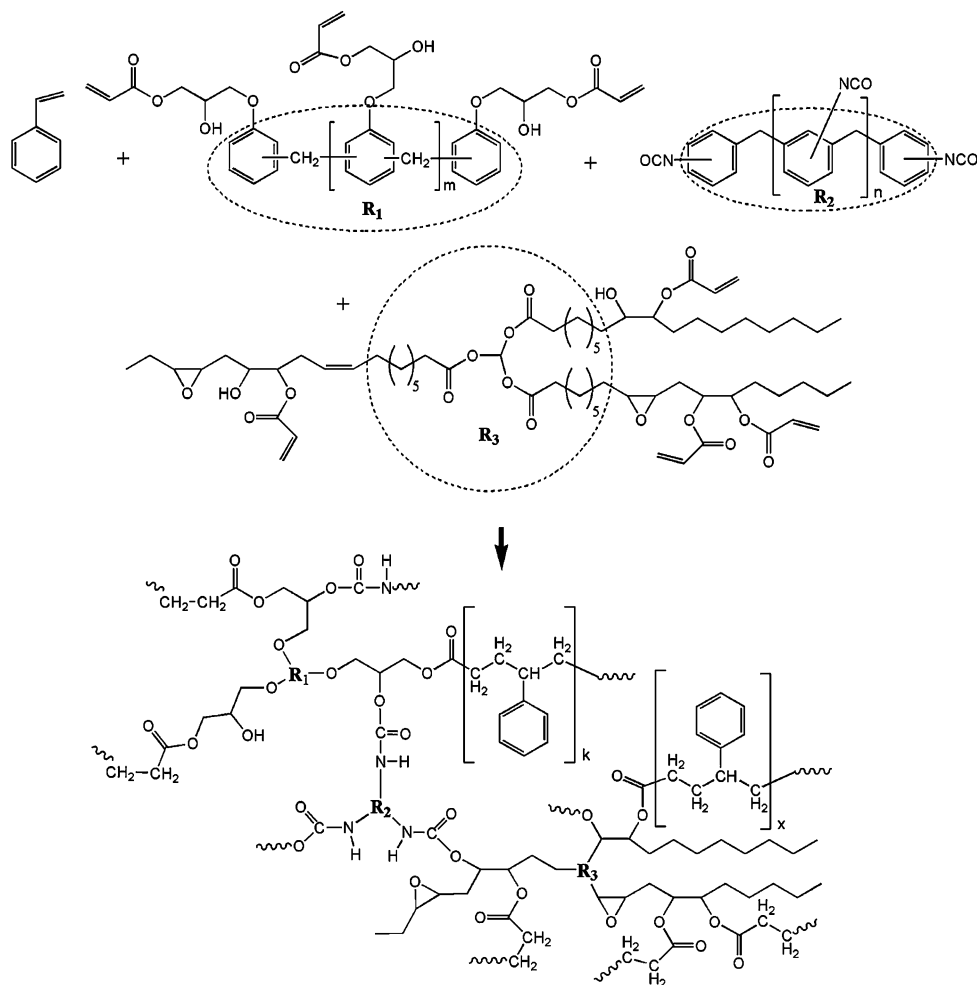
Specimens' preparation

The oils were incorporated in 5, 10, and 15 wt% (with respect to the base resin) in the parent BMC by mixing in a laboratory Brabender Plastograph (Düsseldorf, Germany) kneader equipped with a 50 cm^3 mixing chamber. Kneading occurred at 100 revolutions per minute (rpm) at ambient temperature for 7 min. PMDI was introduced in the BMC compound, diluted by the vegetable oils used, also by kneading in the Brabender chamber. Throughout this article the following coding was used: BMC—resin type (VE)—plant oil type—plant oil amount (in %).

When PMDI was added the urethane hybridization (UH) route was followed using the coding VEUH. Three PMDI/VE weight ratios were selected: 0.6:1 (VEUH1), 0.65:1 (VEUH2), and 0.7:1 (VEUH3). The numbers after VEUH, viz., 1, 2 or 3, reflect the PMDI/VE (without styrene) weight ratios. Plaques (160 × 100 mm^2) of ca. 4 mm thickness were produced by hot pressing at (T) = 170 °C for 5 min using 160 kN load. These conditions were selected based on differential scanning calorimetric tests

performed on the BMC compound. Specimens from the plaques were cut by sawing.

Testing

The thermo-mechanical performance of the BMCs was studied by dynamic-mechanical thermal analysis (DMTA). DMTA traces (storage modulus, E'; and the mechanical loss factor, tanδ vs. temperature) were determined on rectangular specimens (60 × 8 × 4 mm; length × width × thickness) by DMA Q800 of TA Instruments (New Castle, DE, USA) in flexural mode at 10 Hz frequency. Tests were performed under displacement control (15 μm amplitude) using sinusoidal oscillation under dynamic conditions in the temperature range of −100 to +300 °C at a heating rate of 1 °C/min.

The static fracture toughness (K_c) and fracture energy (G_c) were determined on the compact tension (CT) specimens (dimension: 35 × 35 × 3 (thickness) mm). The CT specimens were cut from the plaques, notched by sawing and the notch root sharpened by razor blade tapping before

testing on a Zwick 1445 machine (Zwick, Ulm, Germany) at room temperature with velocity = 1 mm/min crosshead speed. K_c and G_c were computed in accordance with the ISO 13586-1 standard. The fracture surface of the CT specimens was inspected in a scanning electron microscope (SEM; JSM-5400 of Jeol, Tokyo, Japan). Prior to SEM the fracture surfaces were sputtered with a platinum/palladium alloy to create a conductive cover layer.

The dynamic impact properties were characterized by the Charpy impact strength (a_K), measured on unnotched specimens according to ISO 179/1. The specimens (80 × 10 × 4 mm—length × width × thickness, span length 62 mm) were subjected to high-speed (3 m/s) impact bending at room temperature on an instrumented pendulum of Ceast (Pianezza, Italy). The energy of the hammer used was 4 J.

The resins were subjected to thermogravimetric analysis (TGA) in a DTG-60 device of Shimadzu (Columbia, MD, USA). The TGA experiments were conducted under nitrogen atmosphere in the temperature range of 25 to +900 °C with heating rate 10 °C/min.

Results and discussion

DMTA behavior

Figure 3 shows the E' versus T and tanδ versus T traces for the VE-based BMCs containing 5 wt% (with respect to the base resin, i.e., without styrene) functionalized plant oil. One can recognize that incorporation of 5 wt% functionalized plant oil in the co-reactive VE matrix slightly reduced the stiffness (E' modulus) of the BMCs. Oil dilution affected mostly the stiffness in the glassy state. The slightly higher rubbery modulus of BMC VE-AELO 5% compared to those of the AESO and AESO modifications (cf. Fig. 3) may be linked to the fact that AELO has a higher functionality than AESO and EASO, and thus results in higher crosslink density. Incorporation of the plant oils reduced the intensity and slightly broadened the α-relaxation peak. Enhanced broadening suggests that a wider range of segmental units is involved in the α-relaxation process due to the fact that a more irregular network compared to the reference one formed. The shoulder in the temperature range of 60 °C is linked with the homo- and copolymerization reactions (with both styrene and VE) of the related plant oils. The β-relaxation attributed to the motions of the phenyl rings around the methylene links [15], peaked at a temperature of −75 °C, and has not been affected.

Figure 4 displays the E' versus T and tanδ versus T traces for the VE-based BMCs as a function of the EASO content. The glassy modulus is monotonously reduced with increasing amount of EASO and a prominent drop was
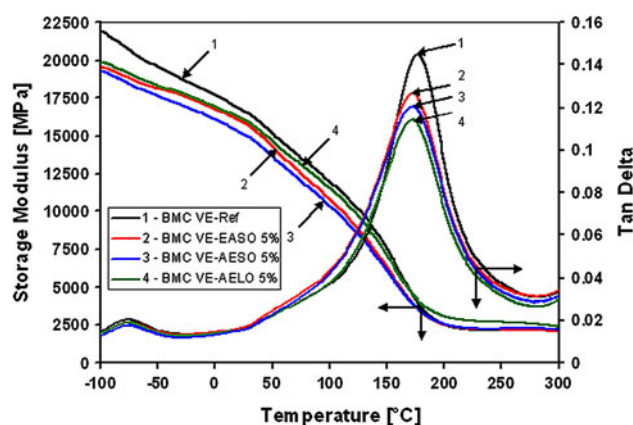
Fig. 3 Storage modulus and mechanical loss factor (tanδ) in function of temperature for BMCs modified in 5 wt% with different functionalized plant oils
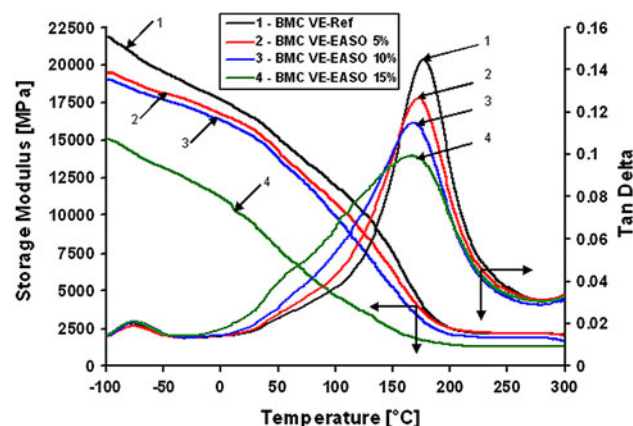
Fig. 4 Storage modulus and mechanical loss factor (tanδ) in function of temperature for BMCs containing various amounts of EASO

observed for the BMC with 15 wt% EASO. The other striking effect is the broadening of the α-relaxation transition (T_g) with increasing amount of EASO. This was associated with a small shift in the T_g peak (read as the temperature at the maximum of this transition) toward lower temperatures. The latter suggests that the oil acted as reactive plasticizer for the VE resin lowering its crosslink density. As mentioned above the broadening of the α transition is traced to the development of a heterogeneous crosslinked network structure. This is due to the various reaction pathways between the components resulting in different segments (length, backbone) between the crosslinks [9]—see also Fig. 2. The T_g values for the systems studied are listed in Table 1.

Some unexpected results were obtained by hybridization of VE with PMDI as demonstrated on the example of BMC VEUH2-Ref and VEUH2-EASO 5%. The T_g values of the hybrids were markedly higher compared to the corresponding reference compounds, i.e., BMC VE-Ref

Table 1 Dynamic mechanical, fracture mechanical, and impact properties of functional plant oil modified VE- and VEUH-based BMC compounds

Designation	E' (GPa)	E' (GPa)	T_g (°C)		K_c (MPa m$^{1/2}$)	G_c (kJ m^2)	a_K (kJ/m^2)
	25 °C	T_g + 50 °C	Shoulder	T_g			
BMC VE-Ref	16.65	2.19	~80	178	3.64 ± 0.48	1.96 ± 0.22	3.76 ± 0.36
BMC VE-AELO 5%	16.00	2.77	~80	175	4.05 ± 0.23	2.39 ± 0.21	4.93 ± 0.89
BMC VE-AESO 5%	15.10	2.30	~77	175	3.78 ± 0.23	1.98 ± 0.22	5.09 ± 0.48
BMC VE-EASO 5%	15.85	2.26	~77	175	3.90 ± 0.14	2.34 ± 0.19	4.00 ± 0.65
BMC VE-EASO 10%	15.40	1.88	~72	172	4.20 ± 0.17	2.11 ± 0.35	3.94 ± 0.43
BMC VE-EASO 15%	9.60	1.30	~65	170	4.22 ± 0.42	2.28 ± 0.32	3.77 ± 0.61
BMC VEUH1-EASO 5%	11.30	1.28	~90	226	4.45 ± 0.69	2.49 ± 0.43	5.12 ± 0.20
BMC VEUH2-EASO 5%	11.40	1.50	~95	231	4.19 ± 0.24	3.13 ± 0.34	4.81 ± 0.42
BMC VEUH3-EASO 5%	11.90	1.99	~110	234	4.38 ± 0.35	3.05 ± 0.34	4.10 ± 0.54
BMC VEUH2-Ref	11.60	1.47	~103	225	3.43 ± 0.55	2.00 ± 0.56	4.71 ± 0.41

and VE-EASO 5%, respectively (cf. Fig. 5). This is in accordance with the expectation because the urethane linkages formed between the –OH groups of the VE and –NCO groups of the PMDI represent additional crosslinking sites. So, the crosslink density of VEUH is higher than that of the VE the macroscopic appearance of which is a shift in the T_g toward higher temperatures [7]. Completely unexpected was, however, the drastic reduction of the stiffness caused by the incorporation of PMDI. This is either due to a strong dilution effect (lowering the filler/reinforcement content), or due to the formation of an interphase on the fillers' surface not supporting the stress transfer from the matrix. Recall that the amount of the added PMDI is comparable with that of the parent VE resin. As far as the weak interphase concerns: it is surmised that the reaction of isocyanate with the water content of kaolin (>10%) may be responsible for that. The kaolin, covered by a soft interphase layer, is likely losing its filler activity. To prove this hypothesis it is necessary to produce

BMC compounds containing no kaolin or other fillers with crystal water.

Dilution with 5 wt% EASO has only a marginal effect on the stiffness of the hybrid BMC, as shown on the example of the VEUH2 based systems (cf. Fig. 5). Modification with EASO was accompanied with a small increase in the T_g along with the reduction of the intensity of the T_g peak. This hints for a better reinforcing effect of the fillers, well reflected also by a higher modulus in the T_g region. This finding is in line with the above proposed mechanism: –NCO reacts with the secondary –OH groups of the EASO instead with the crystal water of kaolin.

When this explanation holds then with increasing amount of PMDI the stiffness of the BMC VEUH-EASO 5% should be enhanced, and in addition, the T_g transition reduced and shifted toward higher temperatures. This is the case, in fact, as one can trace in the corresponding curves in Fig. 6.
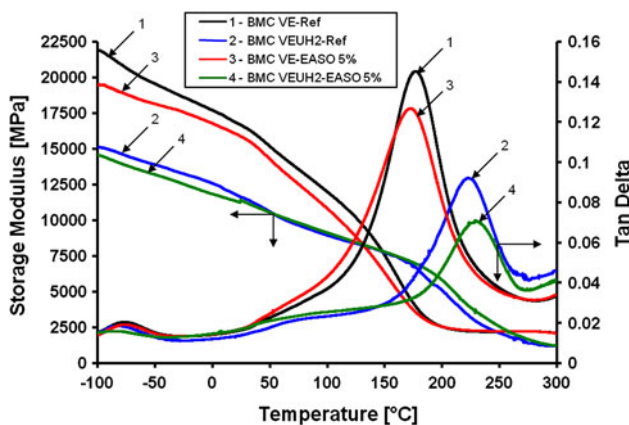
Fig. 5 Influence of hybridization with PMDI on the storage modulus and mechanical loss factor (tanδ) as a function of temperature for BMC VE-Ref and VE-EASO 5%
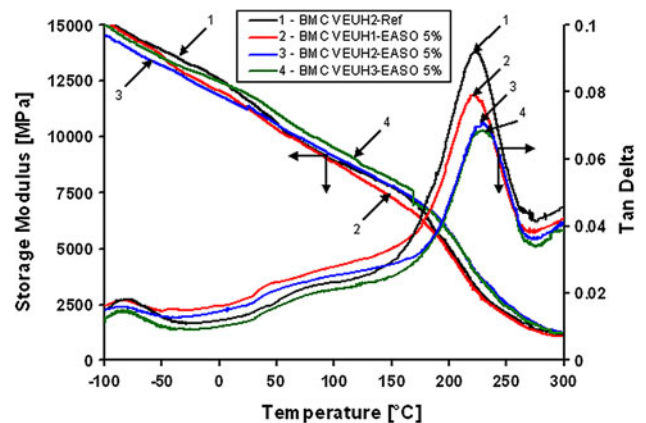
Fig. 6 Storage modulus and mechanical loss factor (tanδ) as a function of temperature for selected BMCs hybridized with different amount of PMDI. *Note* PMDI content increases with increasing number

In order to provide a better survey on the modifications done the glassy and rubbery moduli of the BMCs at room temperature and at $T_g + 50$ °C, respectively, were summarized in Table 1. This table also contains the T_g data, and position of that shoulder in the $\tan\delta$ versus T trace which is prominently affected by the hybridization with the plant oil.

Static fracture mechanics and related failure

The fracture toughness (K_c) and energy data (G_c) are also summarized in Table 1. Based on the related data, and considering their scatter range, the following trends can be deduced:

– at 5 wt% oil modification both K_c and G_c were slightly improved with respect to the BMC VE-Ref;
– K_c slightly increased, whereas G_c practically did not change with increasing EASO content;
– PMDI incorporation (BMC VEUH2-Ref) did not affect the fracture mechanical parameters compared to the unmodified VE (BMC VE-Ref);

– with increasing PMDI amount at 5 wt% EASO content K_c remained practically constant and G_c slightly increased.

As the K_c and G_c data of the BMC samples were only marginally effected by the oil modification (type and amount), no change was expected in respect to their failure modes. This was the case, in fact, as demonstrated in Fig. 7. The SEM pictures, taken from the fracture surface, give explanation for the scatter in the K_c and G_c data (cf. Table 1). Note that the orientation of the discontinuous GFs with respect to the notching direction (i.e., final crack plane) is crucial. When more SGFs are aligned in the loading direction than transverse to it, higher fracture mechanical parameters are measured. In the former case stress concentration on the ends of SGFs trigger multiple matrix cracking which was schematized by Karger-Kocsis and Friedrich [16]—cf. Fig. 7. On the other hand, when SGFs are laying transverse to the loading direction, i.e., in plane of the final fracture, they do not act as efficient reinforcements [17], resulting in lower G_c and especially K_c data (cf. Fig. 8). Though in our BMCs a random SGF
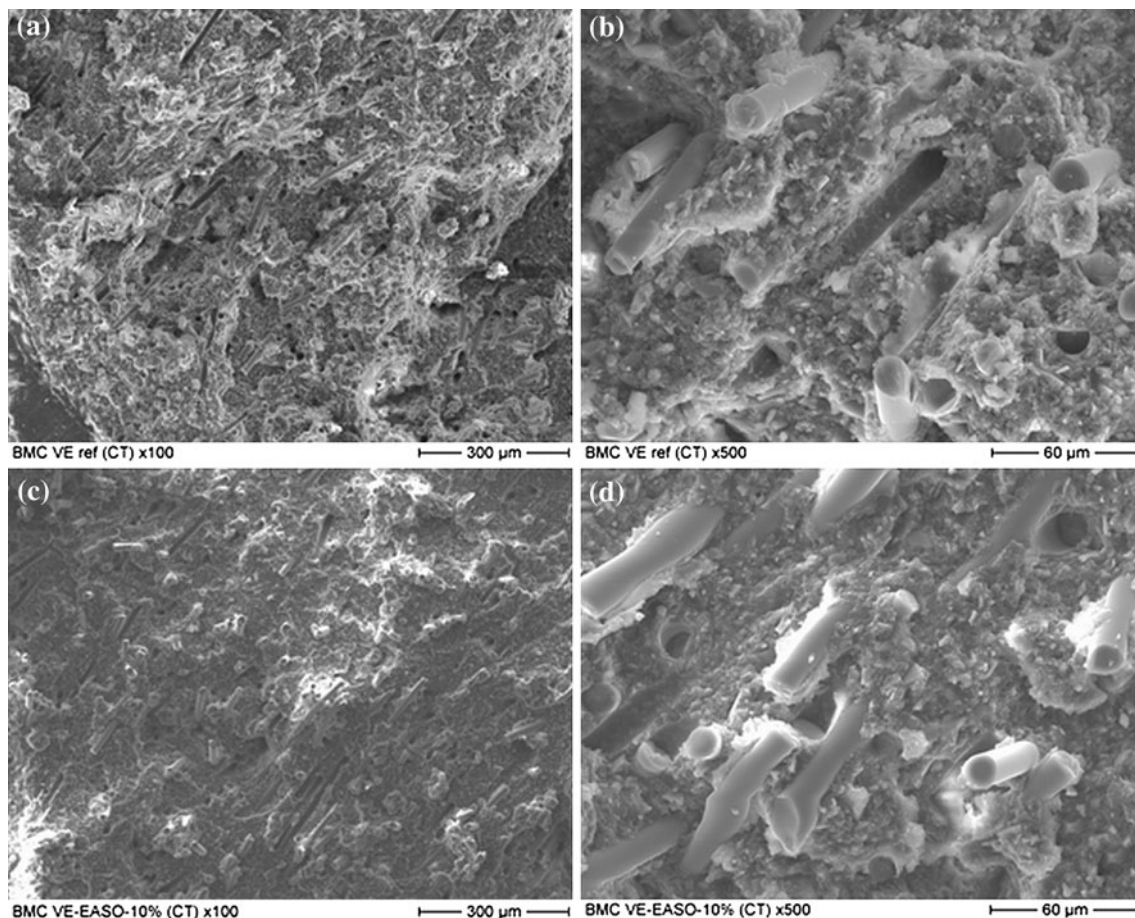
Fig. 7 SEM pictures taken at different magnifications from the fracture surfaces of the CT-specimens cut of the unmodified (**a**, **b**) and with 10 wt% EASO-modified (**c**, **d**) BMCs
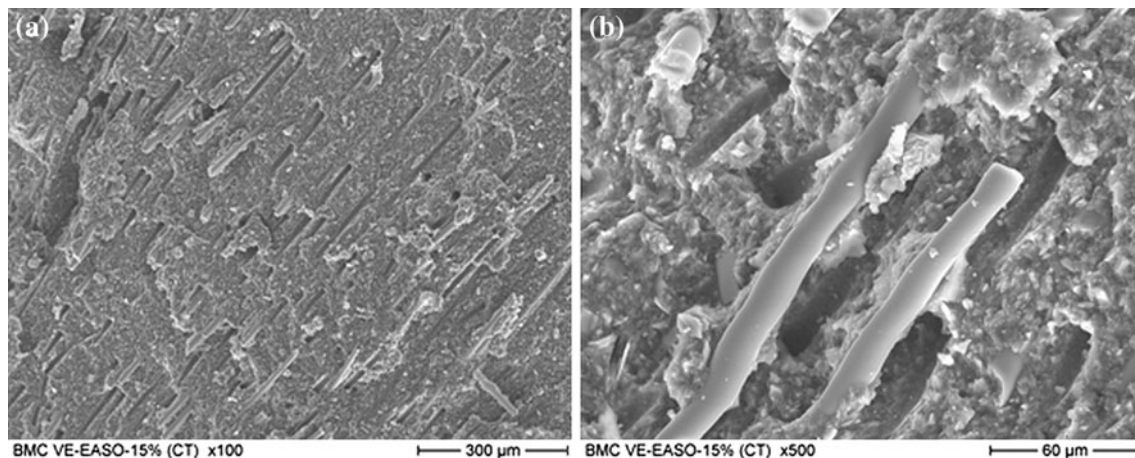
Fig. 8 SEM pictures taken at different magnifications (**a**, **b**) from the fracture surfaces of the CT-specimens cut of BMC VE-EASO 15% showing almost planar fiber orientation

orientation should prevail, this is not always the case due to some the molding-induced alignment.

The effect of PMDI is highlighted in Fig. 9 on the examples of VEUH2-Ref and VEUH2-EASO 5%. Comparing the fracture surfaces of the reference BMC compound without (VE-Ref in Fig. 7b) and with PMDI (cf. Fig. 9a), one can notice that incorporation PMDI caused a better SGF/matrix adhesion. This can be assigned to the reaction between the –OH groups of the GF surface and –NCO of PMDI that affected the interfacial shear strength between the GF and matrix, and thus also the pull-out of the SGF. At the same time, the highly filled VEUH matrix became less prone for multiple brittle cracking (cf. Fig. 9). Instead of that some microductile deformation appeared close to the ends of the SGF which is obviously linked to stress concentration effects. The overall effect of these changes was beneficial on the fracture mechanical parameters as displayed by the related data in Table 1.

Dynamic impact behavior and related failure

The unnotched Charpy impact strength values are also listed in Table 1 for the BMCs investigated. At 5 wt% oil content the impact strength was improved according to ranking: EASO < AELO < AESO. With increasing EASO content the Charpy impact strength was slightly reduced and even at 15 wt% EASO content was comparable with of the BMC VE-Ref. On the other hand, prominent changes with respect to the individual failure events can hardly be resolved on the Charpy fracture surfaces (cf. Fig. 10).

Adding PMDI resulted in some increase in the unnotched Charpy impact strength compared to that of BMC VE-Ref—cf. Table 1. In Fig. 11, the fracture surfaces of VE-EASO 5% and VEUH1-EASO 5% are compared. One can notice that PMDI incorporation "compacted" the filled matrix which became thus less prone for multiple matrix cracking. The latter is an efficient energy absorbing
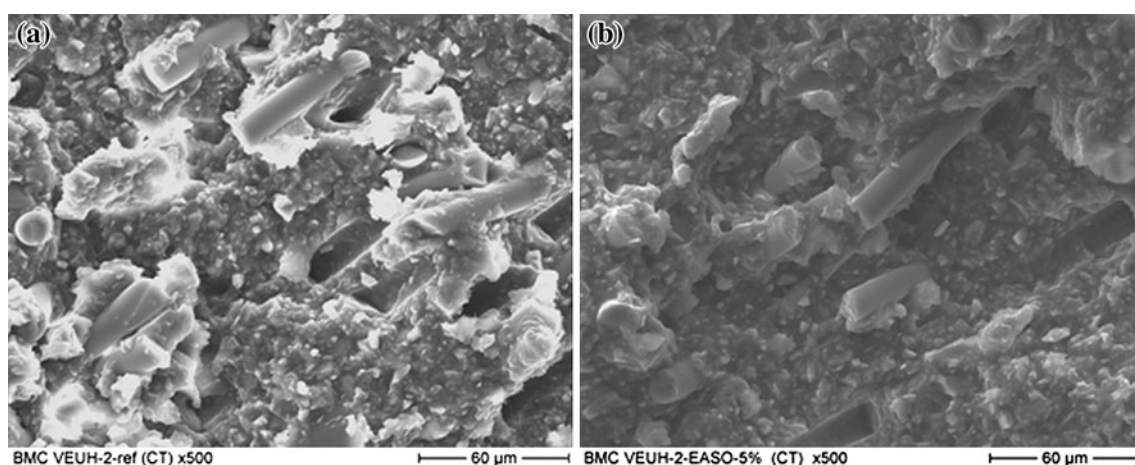
Fig. 9 SEM pictures taken from the fracture surfaces of the CT-specimens cut of the PMDI-modified BMC (VEUH2-Ref; **a**) and its 5 wt% EASO containing version (VEUH2-EASO 5%; **b**)
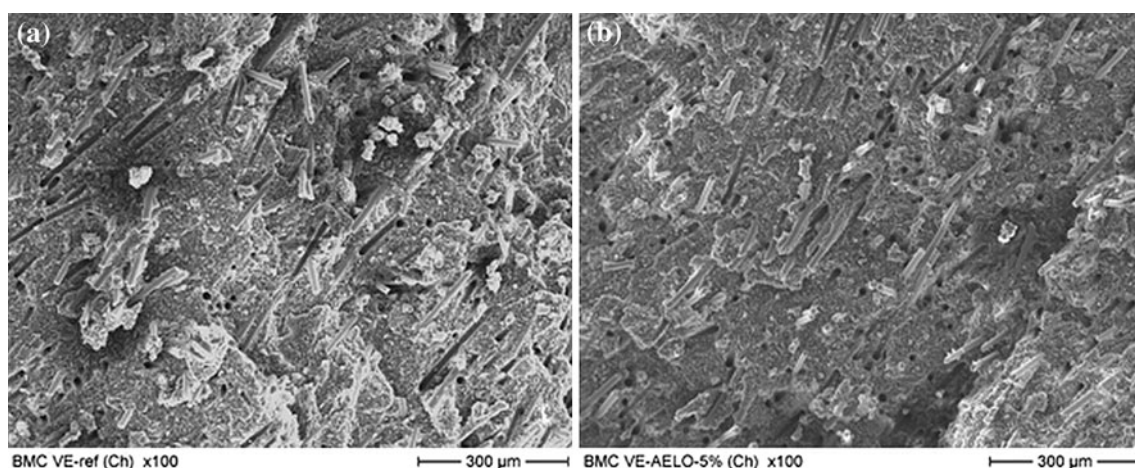
Fig. 10 SEM pictures taken from the fracture surfaces of Charpy specimens cut of the unmodified (a) and with 5 wt% AELO-modified BMC (b)
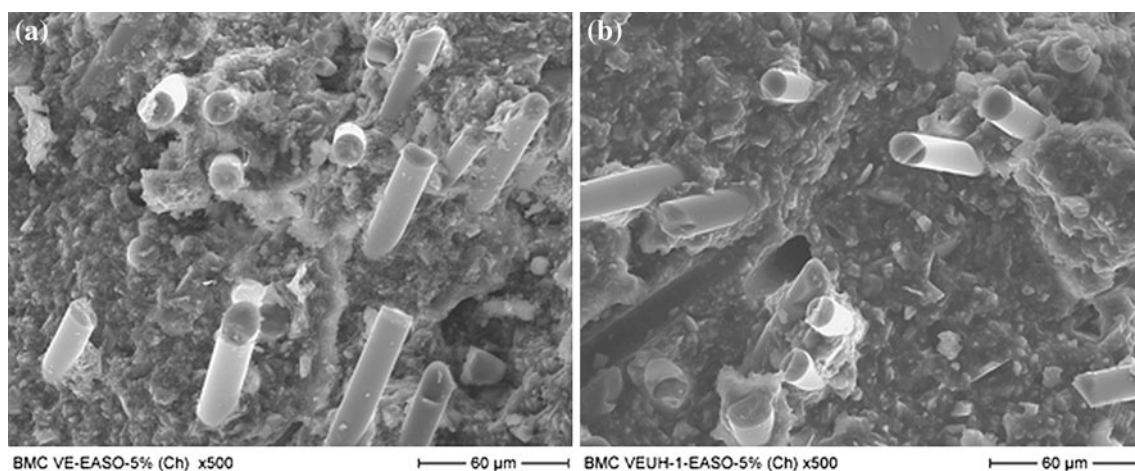
Fig. 11 SEM pictures taken from the fracture surfaces of Charpy specimens cut of the BMC VE-EASO 5% (a) and VEUH1-EASO 5% (b)

mechanism and thus lowered Charpy impact strength was expected. Apparently, the fiber related events (fracture and pull-out) owing to the improved GF/matrix adhesion compensated this matrix-related change because the related Charpy data are practically identical (cf. Table 1).

It is noteworthy that the effect of PMDI under dynamic (Charpy) and static loading (CT) on the related fracture characteristics is quite similar.

Thermogravimetric behavior

Selected TGA curves of the BMCs investigated are displayed in Figs. 12 and 13. Find that their thermal degradation occurred in two steps. The first step with a maximum degradation rate at 320 °C and yielding a weight loss of ca. 25 wt% represents the degradation of the VE matrix. This value is in line with the information of the BMC producer (see above). Further, plant oil modification

affected only this degradation step. With increasing EASO content the weight loss of the BMC compounds increased accordingly (cf. Fig. 12). The second step showing an inflexion point at temperature of 750 °C reflects the decompositions of carbonate minerals, used as fillers, in the BMC compound. Assuming that this filler is solely $CaCO_3$, the amount of the latter in the BMC recipe can be estimated for ∼20 wt%. Based on this estimate the kaolin content may be at ∼36 wt%. The residue at $T = 900$ °C is in the range of ∼53–55 wt%, which is well matched with the total amount of GF and kaolin in the parent BMC formulation.

Similar to EASO the hybridization of BMC with PMDI reduced the onset of the degradation of VEUH2-Ref that occurred somewhat earlier in the temperature scale compared to the VE-Ref (cf. Fig. 13). The thermal stability of the VEUH-based BMCs is less influenced by increasing amount of PMDI. On the other hand, the final residue at
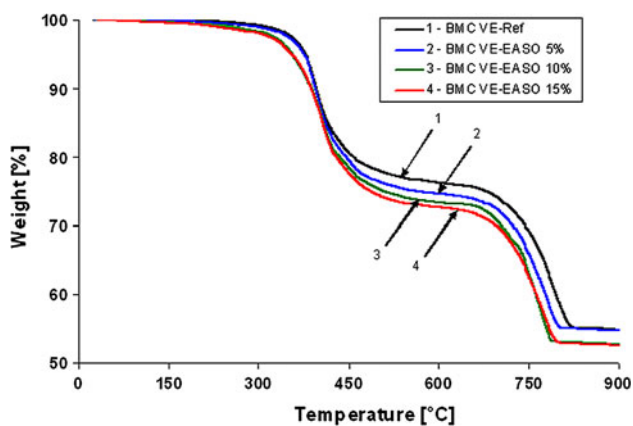
Fig. 12 TGA curves of BMC compounds modified with different EASO amount
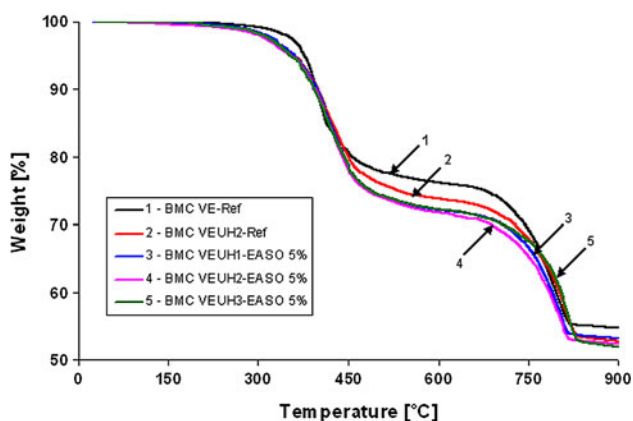
Fig. 13 TGA curves of VE and VEUH reference (VE-Ref and VEUH2-Ref, respectively) and the 5 wt% EASO containing VEUH-based BMC compounds with various amount of PMDI. *Designations* PMDI/VE (without styrene) weight ratio in VEUH1:0.6/1; VEUH2: 0.65/1, and VEUH3:0.7/1

900 °C of VEUH type BMCs was reduced compared to that of BMC VE-Ref reflecting the dilution of the matrix formulation by PMDI.

Conclusion

This article was dedicated to check the effects of dilution of VE resin-based BMCs with AESO and AELO. These functionalized oils were added up to 15 wt% in the parent BMC compound. In addition, PMDI was used as further modifier. Modification with the plant oils, up to 10 wt%, was associated with a moderate reduction of the stiffness (*E* modulus) of the BMCs in the glassy state. By contrast, a large drop in the *E* modulus was noticed for the BMC after PMDI modification. The latter was traced—beside of dilution of the resin matrix—to a reaction of –NCO with the crystal water of kaolin. Kaolin was present as major filler—apart of chalk and glass fiber—in the BMC recipe.

On the other hand, the glass transition temperature of the BMCs was markedly enhanced via the hybridization with PMDI ("urethane hybridization"—UH). The static fracture mechanical parameters were slightly improved with increasing amount of both the plant oil and PMDI. The Charpy impact strength was more sensitive to the oil than to the PMDI modification. The thermal degradation of the functionalized plant oil and PMDI-modified BMC compounds started earlier but did not change profoundly the degradation behavior later on. The results suggest that caution is required when "greening" a BMC recipe through adding functionalized plant oils. Hybridization with PMDI seems to be a promising tool to compensate the reduction in the stiffness, and even to enhance the glass transition temperature, provided that the recipe does not contain hydrated fillers.

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