DACOMAT

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DACOMAT - Damage Controlled Composite Materials

Interim LCA and LCCA report based upon technology selection and modelled processes

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Introduction

According to the project timetable the development of the improved vinyl ester resin and the optimised glass fibre sizing system is due to be completed by M12. The development of the vinyl ester resin system is an activity in Task 2.2 and based upon the outcome of this task, one to three of the best candidates will be selected for further study. From the fibre sizing optimisation study in Task 2.3, 10 variations will be selected for study in Task 2.4. The resin and sizing optimisation study in Task 2.4 will run from M13 until M24 and modification studies of the lamina interface are not due to be completed until M30. Hence D6.2 is an interim report, since the final decisions have not at this stage been made regarding the optimised DACOMAT system. This report provides some background of the environmental impacts associated with the materials choices for the components that could be used in the DACOMAT system in order to support the final selection process.

Based upon the inventory data linked to the final formulation of the optimised systems and comparison of that data with the current state of the art, it should be possible to determine the differences in LCA and LCCA between the state of the art and the optimised systems. However, at this stage of the project, there is no single candidate that has been selected for the final optimised DACOMAT system and the purpose of this interim report is to conduct a sensitivity analysis to determine what the major impacts will be from the different inputs and also to provide some guidance regarding the choice of materials for the optimisation process.

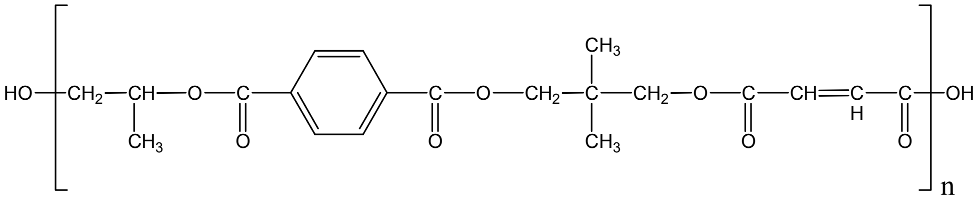
Components in the New System

This section discusses the different parts that will contribute to the resin system and discusses how the environmental impact of these components is altered by making different choices regarding the composition.

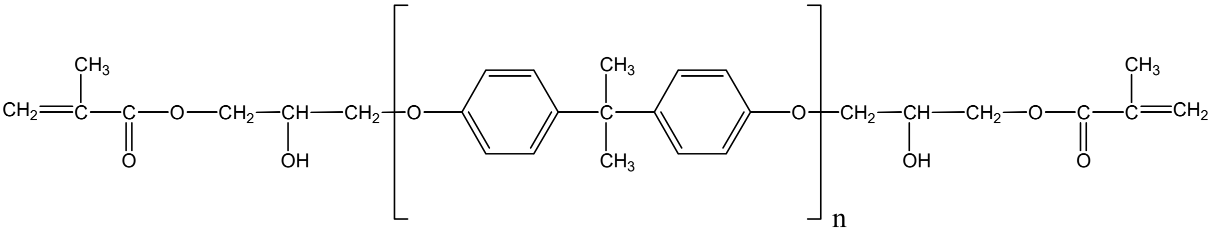
Vinyl Ester Resin

Vinyl ester resins (VERs) are high performance unsaturated resins derived from the reaction of epoxy resins with unsaturated carboxylic acids. They were first commercialised by the Shell Chemical Company in 1965 under the trade name Epocryl. VERs are often used instead of unsaturated polyester resins (UPRs) because UPRs have unreacted double bonds and ester groups present in the backbone, which are susceptible to chemical degradation, whereas VERs only have ester groups present at the terminal ends of the backbone. Although VERs are more expensive that UPRs, they are widely used because of their low water sorption, low curing shrinkage and good chemical resistance compared with UPRs. Neat VERs have a high viscosity and they are used with diluents (reactive, or non-reactive) to provide useful viscosity levels and to enhance reactivity to control the cross-link density and tailor the mechanical properties of the cured resin. The properties of the resin depend upon the backbone chain termination chemical group (methacrylate, or acrylate), the quantity and identity of the co-reactant and the molecular weight of the backbone. Acrylate backbone-terminated VERs are more susceptible to hydrolysis compared with methacrylate VERs. Examples of a VER and a UPR are shown in Figure 1.

Because the reactive double bonds are at the chain ends, the cross-link density of VERs tends to be lower than a standard UPR, which produces materials with higher failure strains and better impact properties.



Unsaturated polyester resin



Vinyl ester resin based upon bis-phenol A epoxy

Figure 1: An unsaturated polyester resin and a vinyl ester resin

The epoxy backbone can be formed of a bis-phenol A diglycidyl ether (Fig. 1), or an epoxy phenol novolac (Fig. 2). Most commercial VERs are derived from bis-phenol A backbones, whereas the more brittle novolac-based resins tend to be confined to specialised uses, where better thermal, or chemical resistance is required.

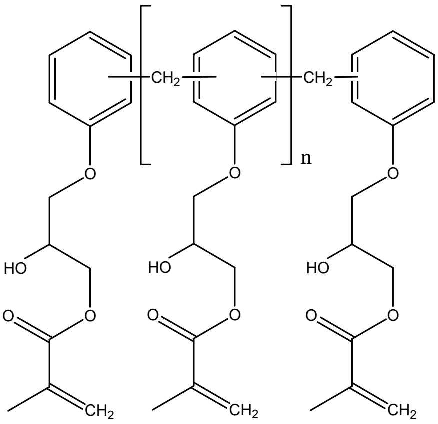


Figure 2: Novolac backbone

The most commonly used reactive diluent is styrene (30-50% by weight). The styrene content can be reduced by adding other reactive monomers, such as vinyl toluene, vinyl acetate, or methyl methacrylate, as well as difunctional vinyl monomers, such as diacrylates and dimethacrylates. Unreacted bisphenol A can also be used as co-reactor to decrease viscosity and increase ductility of the cured resin. Toughened VERs can be prepared by adding carboxyl-terminated butadiene-acrylonitrile copolymers.

The GWP and embodied energy data for the different potential components of a vinyl ester resin are given in Appendix A.

The composition of the vinyl ester resin listed in Ecoinvent is shown below.

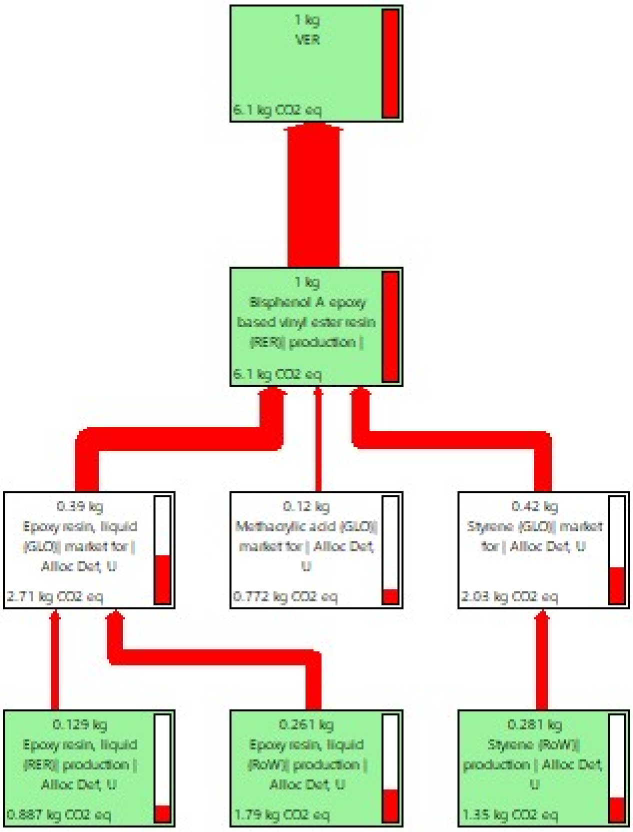


FIGURE 1: VINYL ESTER RESIN GWP IMPACT

The Ecoinvent and EuCIA baseline, or default value for VER is based upon a mix of 0.39 kg epoxy resin, 0.12 kg methacrylic acid and 0.42 kg styrene. Methacrylic acid, styrene and epoxy resin are all listed in the Ecoinvent database.

The three major impacts in the environmental profile of VER arise from variations in the ratio of epoxy resin/methacrylic acid/styrene.

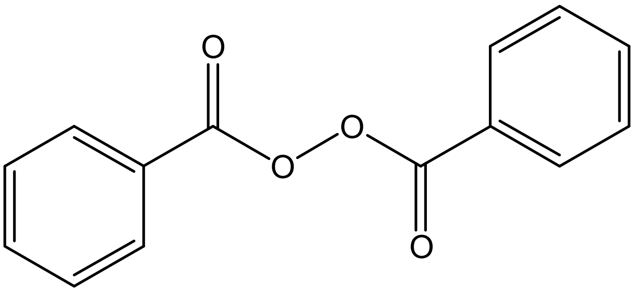
Carboxy-terminated butadiene acrylonitrile copolymer is not listed in Ecoinvent, but acrylonitrile-butadiene-styrene copolymer is and this is considered a reasonable proxy. The GWP and embodied energy values for this are listed in Appendix A.

Free-radical Initiators

The resin is mixed with an activator (an organic peroxide, such as benzoyl peroxide for thermally-cured resins, or methyl ethyl ketone peroxide, tertiary butyl peroxybenzoate, or cumene peroxide for room temperature curing), possibly in combination with a redox initiator, such as cobalt naphthenate. Depending upon the rate of curing required, initiator can be added at 1 to 3 parts per hundred resin (1-3 phr).

No free-radical initiators are listed in Ecoinvent and the only way of estimating the GWP and embodied energy and other environmental data is to create models. The calculated GWP and embodied energy values are listed in Appendix B.

Benzoyl peroxide (BPO) (CAS: 94-36-0)



BPO is not listed in Ecoinvent and there is no published LCA on this chemical. Benzoyl peroxide is produced by the reaction of benzoyl chloride with hydrogen peroxide.

$$2\ C_6H_5COCl + H_2O_2 + 2\ NaOH \rightarrow (C_6H_5CO)_2O_2 + 2\ NaCl + 2\ H_2O$$

Hydrogen peroxide and sodium hydroxide are listed in Ecoinvent, but benzoyl chloride is not.

Benzoyl chloride is produced by the reaction of benzotrichloride with water.

$$C_6H_5CCl_3 + H_2O \rightarrow C_6H_5COCl + 2\ HCl$$

Although benzotrichloride ($C_6H_5CCl_3$) is not listed in Ecoinvent, benzal chloride ($C_6H_5CHCl_2$) is, and this is considered a reasonable proxy for benzotrichloride.

The quantities of each feedstock required to manufacture one mole of benzoyl peroxide are shown below in Table 1.

TABLE 1: ENVIRONMENTAL IMPACTS OF FEEDSTOCKS FOR BENZOYL PEROXIDE

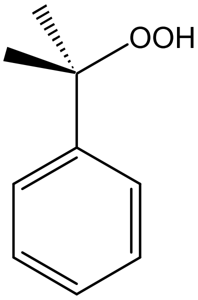
Material	Mol. Wt.	Moles	GWP (kg CO_2e/kg)	EE (MJ/kg)
Benzal chloride	161	2	2.3	63
Hydrogen peroxide	34	1	1.0	20
Sodium hydroxide	40	2	1.3	18
Water	18	2	3.77×10^{-4}	7.0×10^{-3}

This model takes no account of any process energy involved, waste disposal, etc., but is the best that can be done under the circumstances. Based on these inputs, the model gives a GWP of 3.6 kg CO_2e and an embodied energy of 93 MJ, per kg of benzoyl peroxide.

Cobalt naphthenate (CAS: 61789-51-3)

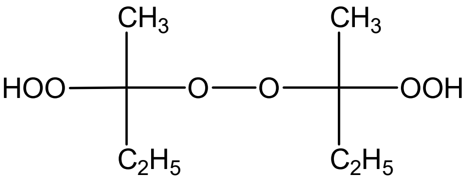
There is no entry in Ecoinvent for cobalt naphthenate. Naphthenic acids are a variable mixture of cyclopentyl and cyclohexyl carboxylic acids with a range of molecular weights, which are removed by distillation during the refining process. There is no entry for naphthenic acids in Ecoinvent. Cobalt metal is listed in the Ecoinvent database.

Cumene hydroperoxide (CAS: 80-15-9)



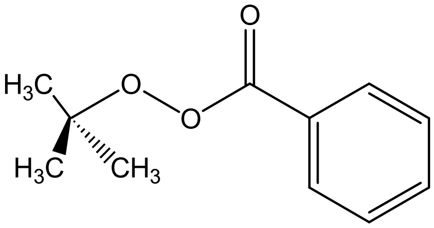
Cumene hydroperoxide is formed as an intermediate during the cumene process, in which benzene and propylene are reacted together in the presence of air to form phenol and acetone. There is an entry in Ecoinvent for cumene (2.5 kg CO_2e and 80 MJ per kg) and this is considered to be an acceptable proxy for cumene peroxide.

Methyl ethyl ketone peroxide (MEKP) (1338-23-4)

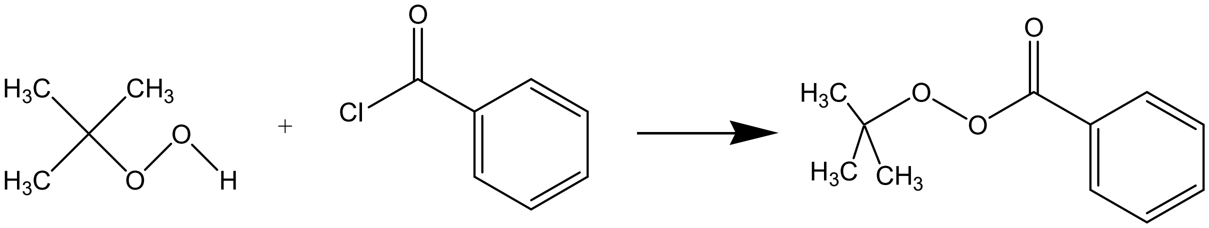


Synthesised by reacting methyl ethyl ketone with hydrogen peroxide. There is an entry in Ecoinvent for methyl ethyl ketone (1.8 kg CO_2e, 60 MJ per kg) and it is considered that this is a reasonable proxy for MEKP.

Tertiary butyl peroxybenzoate (CAS: 614-45-9)



Synthesised by the reaction of *tertiary*-butyl hydroperoxide with benzoyl chloride.



t-butyl hydroperoxide and benzoyl chloride are not listed in the Ecoinvent database. Benzoyl chloride is synthesised by the reaction of thionyl chloride with benzoic acid – both of which are listed in Ecoinvent. *Tertiary*-butyl hydroperoxide is prepared by the reaction of hydrogen peroxide with isobutylene or *tertiary*-butyl alcohol (neither of which are listed in Ecoinvent). Based on the availability of information, it was decided to use benzoic acid as a proxy for tertiary butyl peroxy benzoate.

Glass Fibre

The environmental impact associated with glass fibre production was reviewed in D6.1. The data from the recent GlassFibreEurope (GFE) study is reproduced in Appendix C, along with data from other sources. The GWP and embodied energy associated with the production of glass fibre assembled rovings from the GFE data have been used as the default values for this study.

Sizing agents are added to the glass fibres to reduce damage during processing and to improve the bond between the fibre surface and the matrix. The sizing agent on the glass fibre is typically added at 0.5-0.6% by fibre weight. Many glass fibre sizing agents are tri-alkoxy silane-based. With one pendant organic group which reacts with the matrix. This organic group can have amino, epoxy, vinyl, or methacryl reactive groups. There is one entry in the Ecoinvent database for an alkoxy silane (TEOS, tetraethyl ortho silicate), which is herein used as a proxy. The environmental data for TEOS is shown in Appendix D. With a weight of 0.5% based on the fibre, the GWP impact is 0.0255 kg CO_2e per kg of fibre and the embodied energy is 0.545 MJ per kg.

DACOMAT composite analysis

Global warming potential

The final recipe for the DACOMAT composite has not yet been decided and the purpose of this preliminary report is to provide information about the environmental burdens associated with different material options. It is known that the DACOMAT composite will be based upon a VER and that that there will changes made to the composition of the VER and the sizing agents. The reinforcement will be glass fibre. Gel coats and fillers are not included. The effect of changing the composition of the VER, by altering the weight fraction of epoxy to styrene, or epoxy to methacrylic acid on GWP is shown in Fig. 2. Below.

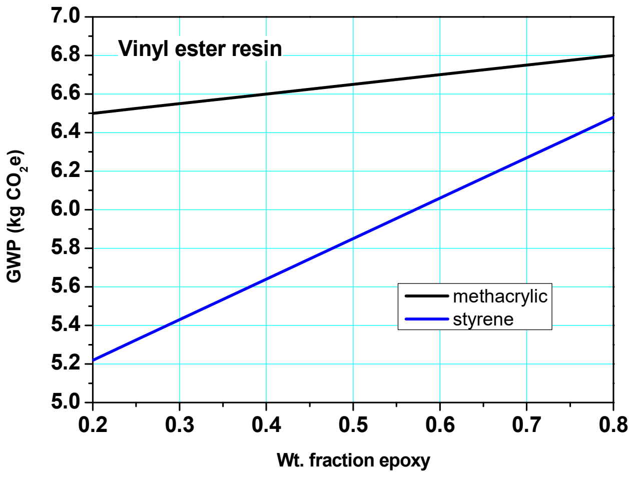


FIGURE 2: EFFECT OF CHANGING THE WEIGHT FRACTION OF EPOXY RESIN ON THE GWP OF 1 KG OF VINYL ESTER RESIN WITH METHACRYLIC ACID, OR STYRENE DILUENT

The change in GWP as a result of altering the styrene/methacrylic acid ratio is shown in Figure 3.

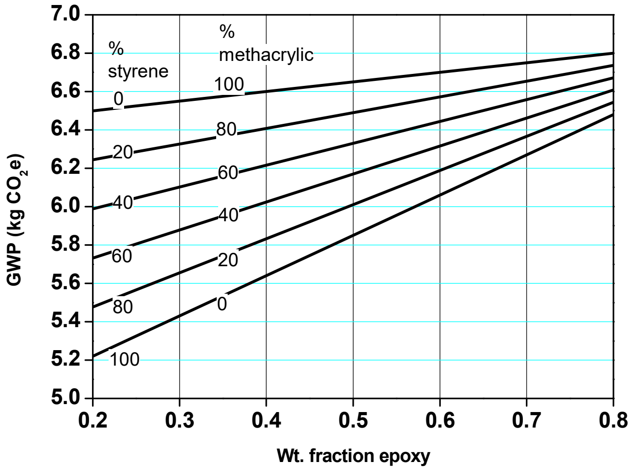


FIGURE 3: SENSITIVITY OF GWP IMPACT OF 1 KG VINYL ESTER RESIN TO VARIATIONS IN THE RATIO OF STYRENE TO METHACRYLIC ACID

The relationship between GWP of the resin system, based upon the type and quantity of initiator is shown in Table 2.

TABLE 2: GWP IMPACT OF INITIATORS AT DIFFERENT CONCENTRATIONS (KG CO_{2E} PER KG OF RESIN)

Initiator	1 phr	2 phr	3 phr
Benzoyl peroxide	0.036	0.072	0.108
Cobalt napthanoate	0.106	0.212	0.318
Cumene hydroperoxide	0.025	0.050	0.075
Methyl ethyl ketone peroxide	0.018	0.036	0.054
t-butyl peroxy benzoate	0.015	0.030	0.045

This shows that changing the initiator, or the composition of the initiator has only a minor effect upon the GWP impact of the resin system. A typical initiator system for VER consists of a mixture of cumene hydroperoxide and *t*-butyl benzoate and this has been used as the standard for this analysis at a ratio of 1:1 and 3 phr (=0.06 kg CO_2e per kg of resin).

An analysis of the effect of adding acrylonitrile- butadiene-styrene (ABS) copolymer upon the GWP impact of the resin is shown in Figure 4. A range of 5.6-6.6 kg CO_{2*}e per kg of VER is assumed and the ABS is added between 0-10% by weight, based on VER. The results are shown for 1 kg of the resin system (VER plus ABS).

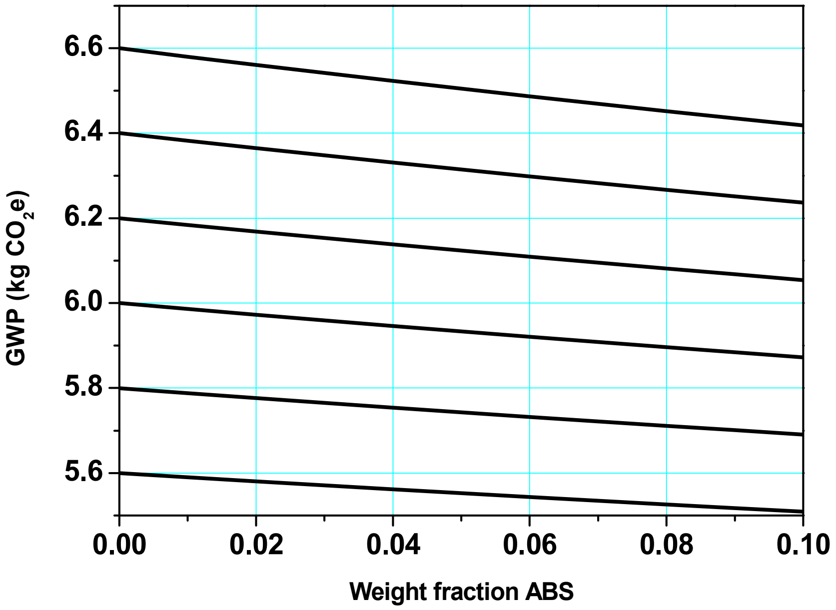


FIGURE 4: EFFECT OF ADDITION OF ABS COPOLYMER UPON THE GWP OF THE RESIN SYSTEM (PER KG)

The GWP impact for 1 kg of the DACOMAT composite is shown below in Figure 5, using the GWP data for assembled rovings and data for the VER ranging from 5.6-6.6 kg CO_2e per kg of resin system. The fibre weight fraction is varied from 0-1.0. The impacts associated with the coupling agent and initiator are not included in this calculation because their contributions to the overall GWP are not significant, compared with changes in the ratio of styrene to methacrylic acid, or incorporation of ABS.

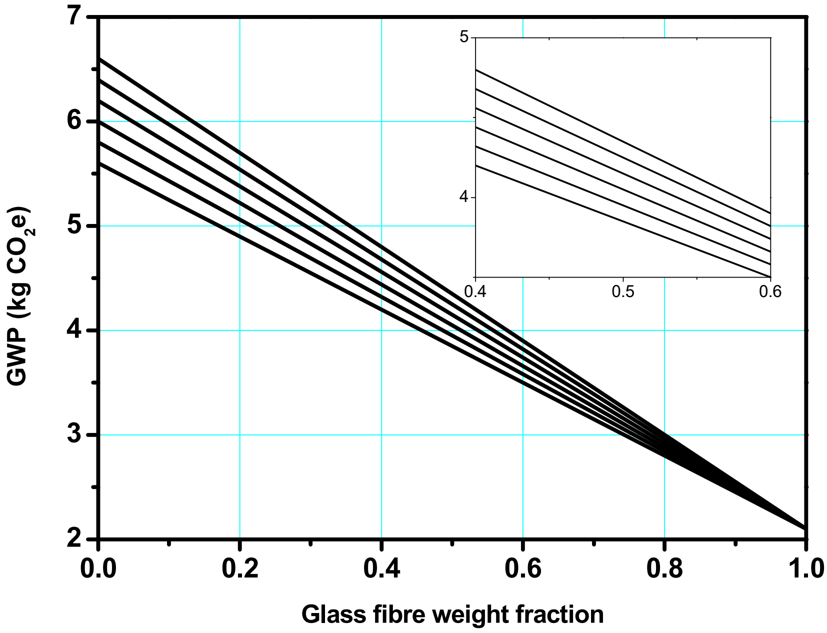


FIGURE 5: GWP FOR THE DACOMAT COMPOSITE SYSTEM FOR A RANGE OF GWP VALUES FOR THE VINYL ESTER RESIN SYSTEM AND FOR DIFFERENT GLASS FIBRE WEIGHT FRACTIONS

The same data is shown in relationship to the glass fibre volume fraction in Figure 6. This is based upon an assumed density of 2.56 g cm^{-3} for the fibre and 1.8 g cm^{-3} for the VER.

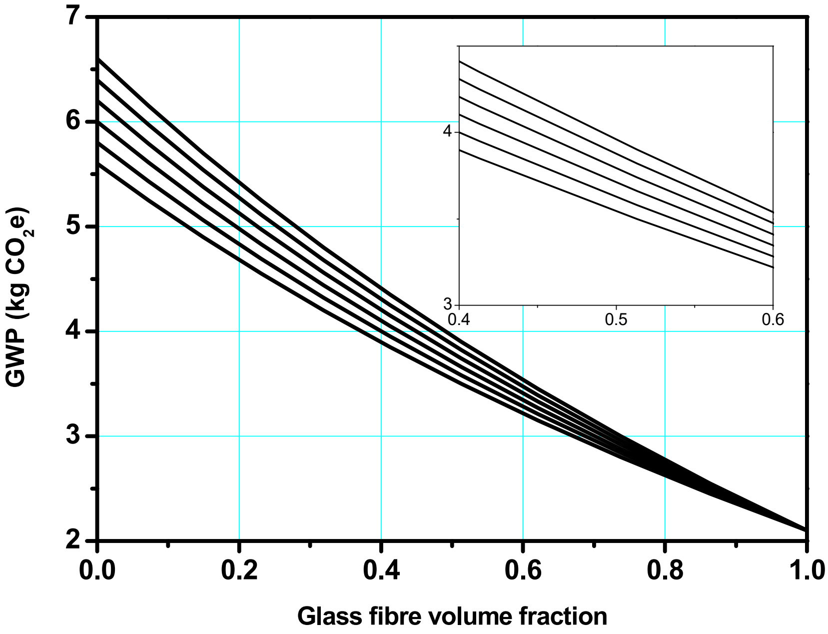


FIGURE 6: VARIATION OF GWP WITH GLASS FIBRE VOLUME FRACTION

Embodied energy

The variation in the ratio of styrene to methacrylic acid upon the embodied energy of the vinyl ester resin system is shown in Figure 7.

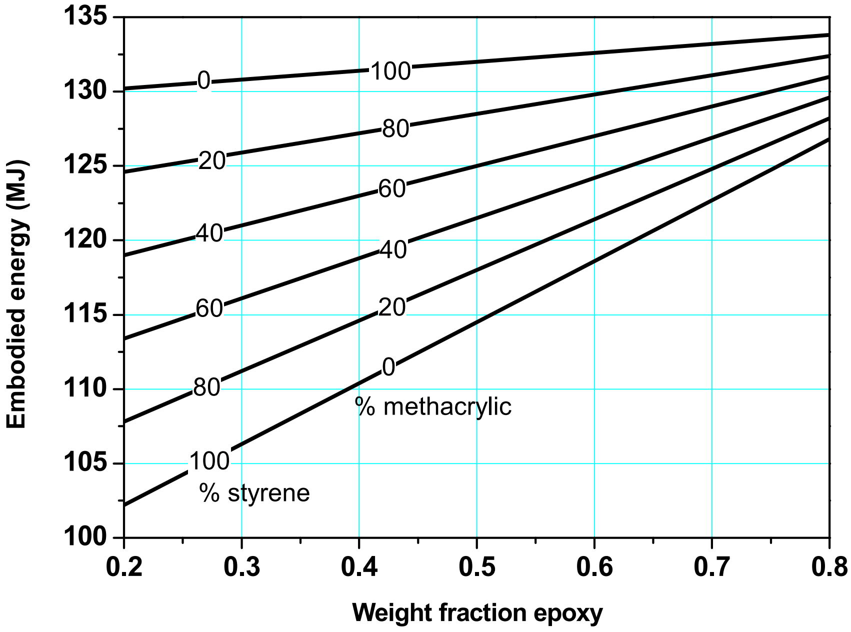


FIGURE 7: EMBODIED ENERGY PER KG OF VINYL ESTER RESIN WITH CHANGES IN THE EPOXY, STYRENE AND METHACRYLIC ACID CONTENT

An analysis of the embodied energy associated with initiators at different concentrations was undertaken and the results are shown in Table 3.

TABLE 3: EMBODIED ENERGY OF INITIATORS AT DIFFERENT CONCENTRATIONS (MJ PER KG OF RESIN)

Initiator	**1 phr**	**2 phr**	**3 phr**
Benzoyl peroxide	0.93	1.86	2.79
Cobalt napthanoate	1.31	2.62	3.93
Cumene hydroperoxide	0.8	1.6	2.4
Methyl ethyl ketone peroxide	0.6	1.2	1.8
t-butyl peroxy benzoate	0.42	0.84	1.26

The typical VER initiator gives has an embodied energy of 1.8 MJ per kg of resin.

The variation of embodied energy with different levels of addition of ABS is shown in Figure 7.

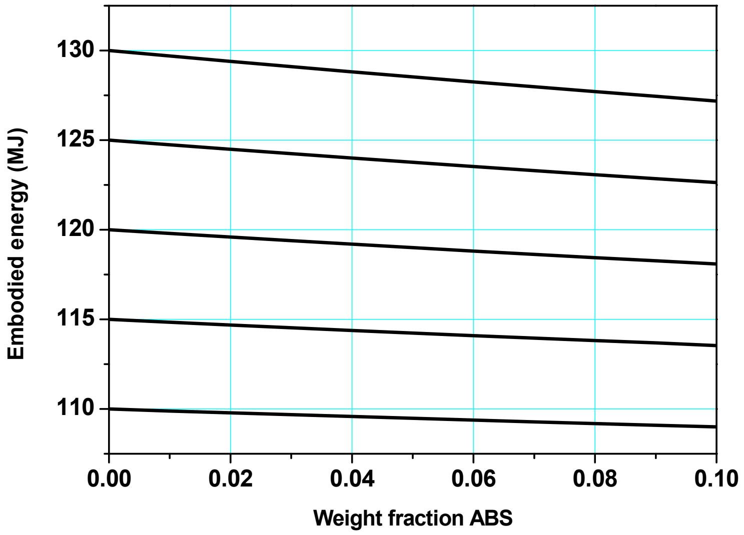


FIGURE 7: VARIATION OF EMBODIED ENERGY PER KG OF RESIN SYSTEM WITH ADDITION OF ABS

The embodied energy associated with the production of 1 kg of the DACOMAT composite system for a range of fibre weight fractions is shown below in Figure 8. A range in embodied energy from 110 to 130 MJ/kg for the resin system has been used.

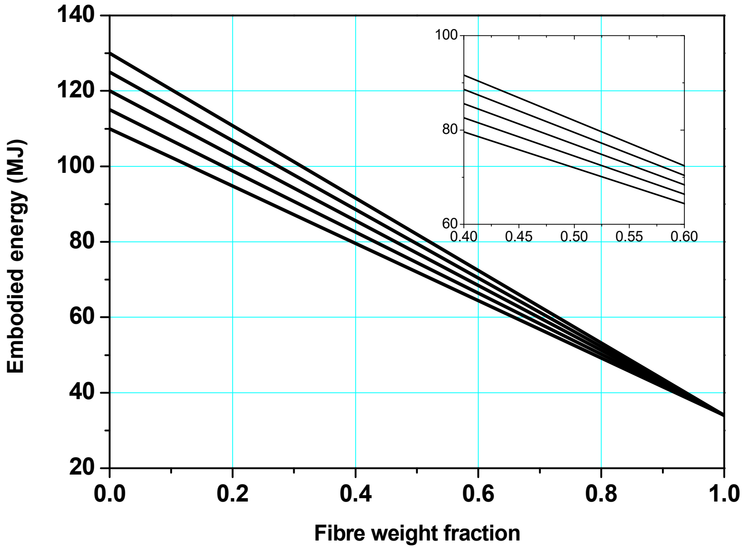


FIGURE 8: VARIATION IN EMBODIED ENERGY PER KG OF DACOMAT COMPOSITE SYSTEM FOR A VARIATION IN FIBRE WEIGHT FRACTION AND DIFFERENT RESIN EMBODIED ENERGIES

The variation in embodied energy with different glass fibre volume fractions is shown in Figure 9.

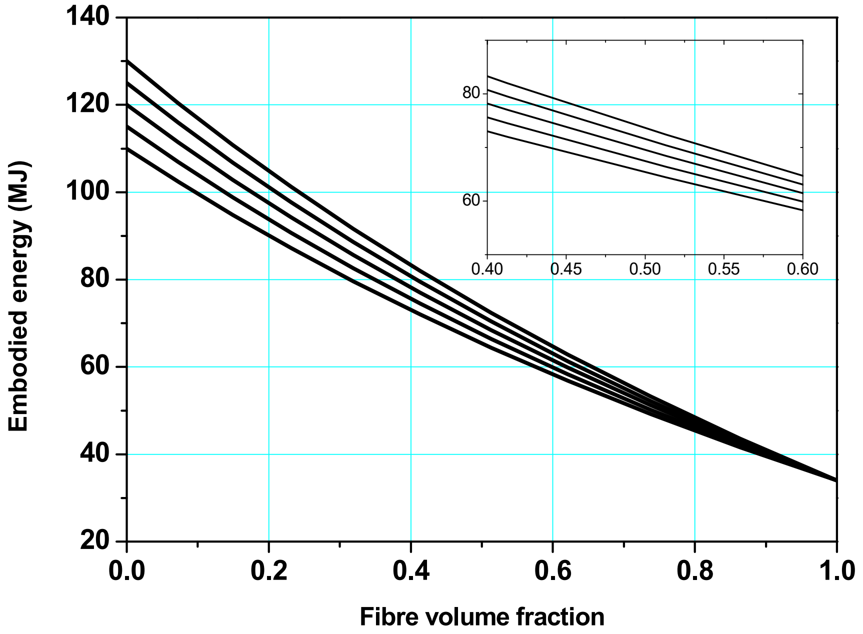


FIGURE 9: VARIATION IN EMBODIED ENERGY WITH DIFFERENT FIBRE VOLUME FRACTIONS FOR THE DACOMAT COMPOSITE SYSTEM

The contribution of the different components to the GWP of the potential DACOMAT composite systems are shown in Figure 10, for a fibre volume fraction of 0.5 and an assumed GWP of 5.2 kg CO_2e/kg and an embodied energy of 110 MJ/kg for the resin.

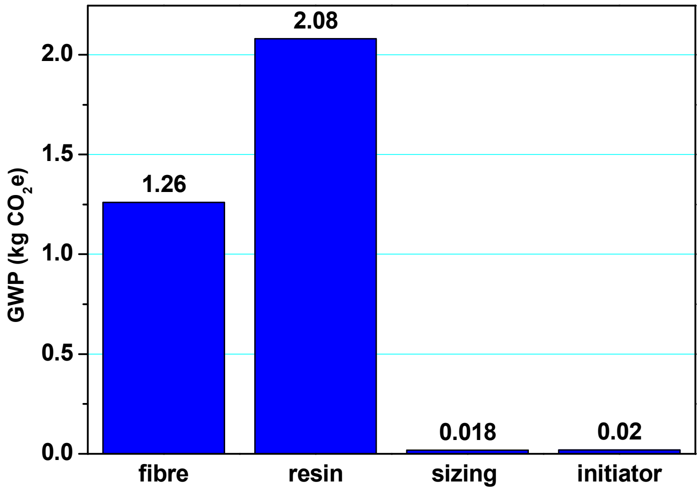


FIGURE 10: CONTRIBUTION TO THE GWP IMPACT OF THE DACOMAT COMPOSITE FROM THE DIFFERENT COMPONENTS

The contribution of the different components to the embodied energy of the potential DACOMAT composite systems are shown in Figure 11.

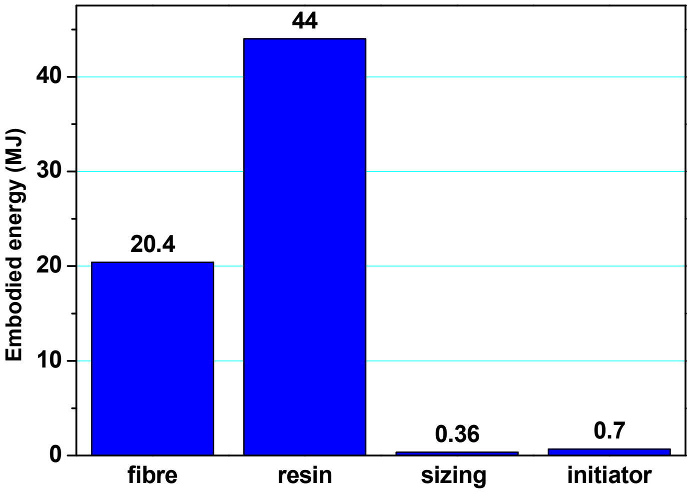


FIGURE 11: CONTRIBUTION TO THE EMBODIED ENERGY OF THE DACOMAT COMPOSITE FROM THE DIFFERENT COMPONENTS

The potential contribution from fibre sizing agents is low, at 0.4 MJ per kg of composite (0.6%). It is therefore proposed not to include the impact associated with sizing agents, in accordance with guidance given in EN15804 (Section 6.3.5).

‘In case of insufficient input data or data gaps for a unit process, the cut-off criteria shall be 1 % of renewable and non-renewable primary energy usage and 1 % of the total mass input of that unit process. The total of neglected input flows per module, e.g. per module A1-A3, A4-A5, B1-B5, B6-B7, C1-C4 and module D shall be a maximum of 5 % of energy usage and mass.’

The contribution from the initiator is 1% of the total embodied energy of the DACOMAT composite and this is also excluded from the study.

Assuming the same fibre system is used in a DACOMAT composite and the state-of-the-art system, the only factor that needs to be taken into account is the resin system.

Conclusions

The sensitivity analysis has shown that the resin is the main component that affects the LCA of the DACOMAT composite system, compared with the industry standard. The sizing agent and the choice of initiator have a minimal influence. The styrene/methacrylic acid/epoxy ratio has an influence upon the resin environmental burdens and the resin represents approximately double the impact of the glass fibre. Once the resin formulation is finalised, the final LCA will be calculated and this will be compared with an industry-standard system.

APPENDIX A: Environmental data vinyl ester resin

Chemical (1 kg)	GWP (kg CO_2e)	EE (MJ)	Source
Acrylic acid	2.4	64-65	Ecoinvent
Acrylonitrile-butadiene-styrene copolymer	4.6	99	Ecoinvent
Adipic acid	22.8-23.3	125-129	Ecoinvent
Bisphenol A	2.5	80	Plastics Europe
Bisphenol A	5.3	136-139	Ecoinvent
Epichlorohydrin	1.0-3.6	23.9-52.3	Ecoinvent
Epoxy resin	6.9	135	Ecoinvent
Epoxy resin	8.1	137	Plastics Europe
Methacrylic acid	6.4-7.3	129-131	Ecoinvent
Methyl methacrylate	6.9	122	Ecoinvent
Styrene	4.5-4.8	92-94	Ecoinvent
Styrene	3.1	83	Plastics Europe
Vinyl ester resin	6.1	122	Ecoinvent
Vinyl ester resin	6.0	122	EuCIA

APPENDIX B: Environmental data initiators (per kg)

Chemical	GWP (kg CO_2e)	EE (MJ)	Source
Benzoyl peroxide	3.6	93	DACOMAT (calculated)
Cobalt napthanoate	10.6	131	Ecoinvent (cobalt)
Cumene hydroperoxide	2.5	80	Ecoinvent (cumene)
Methyl ethyl ketone peroxide	1.8	60	Ecoinvent (methyl ethyl ketone)
t-butyl peroxy benzoate	1.5	42	Ecoinvent (benzoic acid)

Appendix C: Environmental data glass fibre

Fibre type	GWP (kg CO_2e/kg)	EE (MJ/kg)	Source
Dry chopped strands	1.4	28	GFE
Wet chopped strands	1.2	24	GFE
Rovings	1.3	25	GFE
Assembled rovings	2.1	34	GFE
Mats	1.8	41	GFE
	2.2	32	EuCIA
	1.4	28	Bath ICE
	1.3-2.6	21-37	Ecoinvent

Appendix D: Environmental data sizing agents

Chemical	GWP (kg CO_2e/kg)	EE (MJ/kg)	Source
Tetraethyl orthosilicate	5.1	109	Ecoinvent

References

EN 15804: 2012+A1:2013, incorporating corrigendum February 2014 ‘Sustainability of construction works – Environmental product declarations – Core rules for the product category construction products. CEN, Brussels.