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A simple model for reliable prediction of the specific heat release capacity of polymers as an important characteristic of their flammability

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Abstract The heat release capacity (HRC) is the ratio of specific heat release rate by the rate of the temperature rise of a sample polymer during a test. It is an important factor for the determination of fire safety and flame retardancy of polymeric materials because it can help to develop new polymers with desired flame-retardant properties. A simple and reliable model is introduced to predict the HRC of different polymers on the basis of their repeat units that may contain chemical groups/moieties such as methyl, phenyl, carbonyl, ether, amide and ester. It simply requires only molecular structure of repeat unit of a desired polymer without using complex molecular descriptors and computer codes where they need expert users. Model building has been constructed on the basis of the measured HRC of 111 polymers and compared with the predicted results of two group additivity methods. The root-mean-square (RMS) deviation of the new model is 80 J g^{-1} K^{-1}, which is lower than those predicted by two group additivity methods, i.e., 147 and 208 J g^{-1} K^{-1} corresponding to application of group additivity methods for 110 and 101 polymers, respectively. The new method has also been examined for 11 new synthesized polymers that its RMS value is lower than those obtained by group additivity methods.

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Introduction

Determination of fire safety and flame retardancy of polymeric materials is important for the development of new polymers with desired flame-retardant properties. Specific heat release rate (HRR), heat release capacity (HRC) and total heat release (THR) are important parameters to reflect the combustion properties of materials. Microscale combustion calorimeter (MCC) is a small-scale flammability testing technique to screen polymer flammability prior to scale-up, which measures the values of HRR, HRC and THR on the basis of principle of oxygen consumption as well as cone calorimeter to determine the rate and amount of heat during combustion [1]. The thermogravimetric analysis (TG) and derivative TG (DTG) data of polymers are also adopted to assist the assessment of data from the MCC [2]. The HRR is the molecular-level fire response of a burning polymer, which can be obtained through analyzing the oxygen consumed by the complete combustion of the pyrolysis gases during a linear heating program. It can be divided by the rate of the temperature rise of a sample during a test to determine the HRC. However, the HRC appears to be a good predictor of the fire response and flammability of polymers. The HRC is a combination of the thermal stability and combustion properties, which can be obtained by the following equation [3–5]:

$$\mathrm{HRC} = \frac{Q_{\mathrm{c}}^{\circ}(1-\mu)E_{\mathrm{a}}}{eRT_{\mathrm{p}}^{2}} \quad (1)$$

where Q_c° is the heat of complete combustion of the pyrolysis gases; μ is the weight fraction of the solid residue after pyrolysis or burning; E_a is the global activation energy for the single-step mass-loss process or pyrolysis; T_p is the temperature at the peak mass-loss rate in a linear heating program at a constant rate; e is the natural number; and R is the gas constant.

Additive molar group contributions and quantitative structure–property relationships (QSPR) methodology are two different approaches, which have been recently developed for prediction of the HRC [6–9]. The molar group contribution method is an easy approach, which uses additive contribution from a variety of functional groups. This method cannot be applied for prediction of the HRC of those polymers containing a particular functional group where it is missed from the used database of functional groups to build the model. Parandekar et al. [9] used QSPR approaches to predict the HRC as well as total heat release and % char using genetic function algorithms. In contrast to available additive molar group contribution methods, two QSPR models of Parandekar et al. [9] for estimation of the HRC are based on complex/unfamiliar descriptors such as AlogP98 and LUMO–HOMO energy, which require specific computer codes and expert users.

Since searching for new heat- and flame-resistant polymers has attracted considerable research activity during recent years, it is important to develop new approach for prediction of the HRC. The purpose of this work is to introduce a simple and reliable model for the prediction of the HRC of different polymers with their repeat units that are comprised of chemical groups/moieties such as methyl, phenyl, carbonyl, ether, amide and ester. The model is based on a molecular basis for polymer flammability that correlates the HRC test results.

Materials and methods

Experimental data of the HRC for 111 polymers with their repeat units containing chemical groups/moieties such as methyl, phenyl, carbonyl, ether, amide and ester are given in Table 1, which were taken from previous works where these data have been used to provide over 40 different empirical molar group contributions as well as (QSPR) methodology for prediction of the heat release capacity [6–9]. These data were taken as training set for building the new model. Since each new model is frequently tested on some chemicals that were not used in the model building, further an external dataset of 11 polymers compiled from several new experimental studies was considered to compare the new model predictions with molar group contribution methods.

Results and discussion

Development of the new model

Parandekar et al. [9] introduced the following correlations on the basis of complex descriptors for prediction of the HRC:

$$\begin{aligned}\mathrm{HRC} = [&-2.03W(19.93 - \%\mathrm{H}) + 2.76W(\%\mathrm{C} - 87.02)\\ &- 1.05W(\mathrm{AlogP98} - 1.615)\\ &- 8.55W(0.668 - \mathrm{AlogP98})\\ &- 1.12W(12 - R_{\mathrm{bonds}})\\ &- 2.48W(H_{\mathrm{bond\ donor}}) + 5.46]^2\end{aligned} \tag{2}$$

$$\begin{aligned}\mathrm{HRC} = [&67.55W(E_{\mathrm{LUMO-HOMO}} - 0.104) + 0.743\,R_{\mathrm{bonds}}\\ &- 0.647W(R_{\mathrm{bonds}} - 26) + 0.00128\mathrm{VDE}\\ &- 0.00056\mathrm{VDM} - 0.6853Kap + 0.347\%\mathrm{C}\\ &+ 4.38W(\%\mathrm{C} - 90.5) - 0.084\mathrm{MR} + 0.248\mathrm{AC}\\ &+ 5.473W(0.95 - \mathrm{DM})\\ &+ 1.07W(5.372 - \mathrm{S\_sNH_2}) - 15.73]^2\end{aligned} \tag{3}$$

where W is the ramp function; %H is mass percent of hydrogen atoms; %C is mass percent of carbon atoms; AlogP98 is the log of the octanol–water partition coefficient that is calculated from empirical atomic contributions; R_{bonds} is rotatable bonds; $H_{\mathrm{bond\ donor}}$ is hydrogen bond donor; $E_{\mathrm{LUMO-HOMO}}$ is LUMO–HOMO energy (au); VDE is vertex distance/equality; VDM is vertex distance/magnitude; *Kap* is kappa-1; MR is molecular refractivity; AC is atomic composition (total); and DM is dipole moment (au). Equation (2) was generated by genetic function algorithm containing six variables. Meanwhile, Eq. (3) was obtained by using trimer structures including 12 variables where the geometry was optimized with density functional method GGA/PW91 (L56). Although complexity of Eq. (3) is higher than Eq. (2), it provides more reliable predictions. Beside complexity of descriptors, these QSPR models require special computer codes and expert users.

It was indicated that the flash point and the auto-ignition temperature as two flammability characteristics of organic compounds depend on elemental composition and the contribution of some structural parameters, which are related to intra- and intermolecular interactions [10–13]. A careful examination of the HRC of many polymers revealed that the elemental composition as well as the specific structural parameters can be used to construct the new model. Among different elements, the number of carbon, hydrogen, nitrogen, oxygen, chlorine and silicon

Table 1 Comparison of the predicted results of HRC in J g^{-1} K^{-1} for the new model as well as two molar group contributions of Walters and Lyon [6] and Lyon et al. [8] with experimental data

Name	Elemental composition in repeat unit composition	Exp.	New model	Dev	Walters–Lyon	Dev	Lyon et al.	Dev
Polyethylene (PE)	C_2H_4	1676 [7]	1711	35	1285	−391	1029	−647
Polyoxymethylene (POM)	CH_2O	169 [7]	237	68	170	1	850	681
Polypropylene (PP)	C_3H_6	1571 [7]	1617	46	1567	−4	919	−652
Poly(vinyl alcohol) (99%; PVOH)	C_2H_4O	533 [7]	553	20	532	−1	566	33
Poly(ethylene oxide)	C_2H_4O	652 [7]	671	19	495	−157	907	255
Polyisobutylene	C_4H_8	1002 [7]	1025	23	1607	605	823	−179
Poly(vinyl chloride)	C_2H_3Cl	138 [7]	64	−74	138	0	133	−5
Poly(vinylidene fluoride)	$C_2H_2F_2$	311 [7]	280	−31	289	−22	264	−47
Polyacrylamide	C_3H_5NO	104 [7]	156	52	104	0	86	−18
Poly(acrylic acid)	$C_3H_4O_2$	165 [7]	133	−32	21	−144	171	6
Poly(vinyl acetate) (PVAc)	$C_4H_6O_2$	313 [7]	331	18	374	61	431	118
Poly(methacrylic acid)	$C_4H_6O_2$	464 [7]	472	8	299	−165	230	−234
Polychloroprene	C_4H_5Cl	188 [7]	206	18	186	−2	197	9
Poly(tetrafluoroethylene) (PTFE)	C_2F_4	35 [7]	16	−19	36	1	50	15
Poly(methyl methacrylate) (PMMA)	$C_5H_8O_2$	514 [7]	486	−28	553	39	326	−188
Poly(methyl methacrylate) (PMMA)	$C_5H_8O_2$	461 [7]	486	25	553	92	326	−135
Poly(ethyl acrylate)	$C_5H_8O_2$	323 [7]	415	92	484	161	391	68
Polymethacrylamide	$C_4H_7NO_2$	103 [7]	180	77	198	95	126	23
Polystyrene (PS)	C_8H_8	927 [7]	901	−26	554	−373	313	−614
Isotactic polystyrene	C_8H_8	880 [7]	901	21	554	−326	313	−567
Poly(2-vinyl pyridine)	C_7H_7N	612 [7]	580	−32	590	−22	568	−44
Poly(4-vinyl pyridine)	C_7H_7N	568 [7]	580	12	590	22	568	0
Poly(1,4-phenylene sulfide) (PPS)	C_6H_4S	165 [7]	313	148	166	1	194	29
Poly(*n*-vinyl pyrrolidone)	C_6H_9NO	332 [7]	345	13	256	−76	441	109
Polycaprolactam	$C_6H_{11}NO$	487 [7]	492	5	612	125	580	93
Polycaprolactone	$C_6H_{10}O_2$	526 [7]	525	−1	438	−88	513	−13
Poly(ethyl methacrylate)	$C_6H_{10}O_2$	470 [7]	478	8	646	176	412	−58
Poly(ethyl methacrylate)	$C_6H_{10}O_2$	380 [7]	478	98	646	266	412	32
Poly(α-methyl styrene)	C_9H_{10}	730 [7]	734	4	739	9	340	−390
Poly(2,6-dimethyl 1,4-phenyleneoxide) (PPO)	C_8H_8O	409 [7]	424	15	398	−11	404	−5
Poly(4-vinyl phenol)	C_8H_8O	261 [7]	424	163	436	175	317	56
Poly(ethylene maleic anhydride)	$C_6H_6O_3$	138 [7]	197	59	246	108	244	106
Poly(vinyl butyral)	$C_8H_{14}O_2$	806 [7]	828	22	1027	221	813	7
Poly(2-vinyl naphthalene)	$C_{12}H_{10}$	834 [7]	831	−3	732	−102	835	1
Poly(benzoyl 1,4-phenylene)	$C_{13}H_8O$	41 [7]	83	42	153	112	144	103
Poly(ethylene terephthalate) (PET)	$C_{10}H_8O_4$	332 [7]	350	18	−26	−358	140	−192
Poly(ether ketone) (PEK)	$C_{13}H_8O_2$	124 [7]	143	19	122	−2	129	5
Polylaurolactam	$C_{12}H_{23}ON$	743 [7]	790	47	859	116	859	116
Poly(styrene maleic anhydride)	$C_{12}H_{10}O_3$	279 [7]	275	−4	297	18	171	−108
(ABS) Poly(acrylonitrile butadiene styrene)	$C_{15}H_{17}N$	669 [7]	674	5	827	158	267	−402
Poly(1,4-butanediol terephthalate) (PBT)	$C_{12}H_{12}O_4$	474 [7]	445	−29	340	−134	400	−74
Poly(hexamethylene adipamide)	$C_{12}H_{12}O_2N_2$	615 [7]	569	−46	612	−3	607	−8
Polyazomethine	$C_{15}H_9N_3$	36 [7]	97	61	225	189	120	84
Poly(1,4-phenylene ether sulfone) (PES)	$C_{12}H_8O_3S$	115 [7]	85	−30	116	1	114	−1
Poly(*p*-phenylene benzobisoxazole) (PBO)	$C_{14}H_6O_2N_2$	42 [7]	33	−9	38	−4	42	0
Poly(*p*-phenylene terephthalamide)	$C_{14}H_{10}O_2N_2$	302 [7]	132	−170	121	−181	55	−247
Poly(*m*-phenylene isophthalamide)	$C_{14}H_{10}O_2N_2$	52 [7]	132	80	−5	−57	55	3

Table 1 continued

Name	Elemental composition in repeat unit composition	Exp.	New model	Dev	Walters–Lyon	Dev	Lyon et al.	Dev
Poly(ethylene naphthalate) (PEN)	$C_{14}H_{10}O_4$	309 [7]	215	−94	148	−161	321	12
Dicyclopentadienyl bisphenol cyanate ester	$C_{17}H_{17}NO$	493 [7]	393	−100	463	−30	–	–
Polycarbonate of bisphenol A (PC)	$C_{16}H_{14}O_3$	359 [7]	331	−28	176	−183	510	151
Polyphosphazene	$C_{14}H_{14}PNO_3$	204 [7]	133	−71	262	58	–	–
Poly(dichloroethyl diphenyl ether)	$C_{14}H_8OCl_2$	16 [7]	97	81	172	156	15	−1
Cyano-substituted Kevlar	$C_{15}H_9N_3O_2$	54 [7]	40	−14	116	62	94	40
Bisphenol E polycyanurate	$C_{16}H_{12}O_2N_2$	316 [7]	339	23	205	−111	222	−94
Bisphenol A polycyanurate	$C_{17}H_{14}O_2N_2$	283 [7]	377	94	123	−160	430	147
Poly(hexamethylene sebacamide)	$C_{16}H_{30}O_2N_2$	878 [7]	919	41	727	−151	669	−209
Poly(ether ether ketone) (PEEK)	$C_{19}H_{12}O_3$	155 [7]	146	−9	143	−12	170	15
Poly(siloxytetraalkyl biphenylene oxide) (PSA)	$C_{18}H_{18}SiO_2$	119 [7]	119	0	293	174	121	2
Poly(ether ketoneketone) (PEKK)	$C_{20}H_{12}O_3$	96 [7]	140	44	103	7	84	−12
Tetramethyl bisphenol F polycyanurate	$C_{19}H_{18}O_2N_2$	280 [7]	277	−3	276	−4	390	110
Bisphenol C polycarbonate	$C_{15}H_8O_3Cl_2$	29 [7]	49	20	43	14	8	−21
Polybenzimidazole (PBI)	$C_{20}H_{12}N_4$	36 [7]	97	61	36	0	36	0
Poly(hexamethylene dodecane diamide)	$C_{18}H_{34}N_2O_2$	707 [7]	576	−131	769	62	701	−6
Bisphenol C, polycyanurate	$C_{16}H_8O_2Cl_2$	24 [7]	73	49	29	5	22	−2
Bisphenol A epoxy, catalytic cure phenoxy A	$C_{21}H_{24}O_4$	657 [7]	587	−70	473	−184	662	5
Phenolphthalein polycarbonate	$C_{21}H_{12}O_5$	28 [7]	192	164	65	37	146	118
Poly(amide imide) (PAI)	$C_{22}H_{14}O_3N_2$	33 [7]	56	23	20	−13	44	11
Novolac polycyanurate	$C_{23}H_{15}O_3N_3$	122 [7]	130	8	31	−91	207	85
Polyimide (PI)	$C_{22}H_{10}O_5N_2$	25 [7]	60	35	39	14	25	0
Hexafluorobisphenol A polycyanurate	$C_{17}H_8O_2N_2F_6$	32 [7]	7	−25	10	−22	55	23
Bisphenol C epoxy	$C_{20}H_{18}O_4Cl_2$	506 [7]	331	−175	332	−174	270	−236
Bisphenol M polycyanurate	$C_{26}H_{24}O_2N_2$	239 [7]	325	86	235	−4	552	313
Poly(phenyl sulfone)	$C_{24}H_{16}SO_4$	153 [7]	140	−13	182	29	159	6
Bisphenol C polyarylate	$C_{22}H_{12}O_4Cl_2$	21 [7]	99	78	47	26	7	−14
Biphenol phthalonitrile	$C_{28}H_{14}N_4O_2$	15 [7]	90	75	84	69	241	226
Polysulfone of bisphenol A PSF	$C_{27}H_{22}O_4S$	345 [7]	320	−25	231	−114	287	−58
LaRC-1A	$C_{28}H_{14}N_2O_6$	38 [7]	101	63	−39	−77	24	−14
Epoxy novolac, catalytic cure phenoxy N	$C_{10}H_{11}O$	246 [7]	483	237	230	−16	–	–
Bisphenol A phthalonitrile	$C_{31}H_{20}N_4O_2$	40 [7]	163	123	138	98	401	361
Technora	$C_{34}H_{24}N_4O_5$	131 [7]	155	24	112	−19	130	−1
Bisphenol A6F phthalonitrile	$C_{31}H_{14}N_4O_2F_6$	9 [7]	10	1	61	52	159	150
Poly(ether imide) (PEI)	$C_{37}H_{24}O_6N_2$	121 [7]	199	78	61	−60	155	34
Polyester of hydroxybenzoic and hydroxynapthoic acids	$C_{39}H_{22}O_{10}$	164 [7]	80	−84	350	186	130	−34
LaRC-TOR	$C_{44}H_{29}N_4O_3P$	135 [7]	208	73	136	1	–	–
LaRC-CP2	$C_{37}H_{18}N_2O_6F_6$	14 [7]	52	38	31	17	−10	−24
LaRC-CP1	$C_{46}H_{22}N_2O_6F_{12}$	13 [7]	68	55	44	31	−23	−36
PHA-1	$C_{20}O_4N_2H_{14}$	42 [24]	146	104	70	28	278	236
PHA-5	$C_{23}N_2O_3H_{12}$	8 [24]	35	27	−34	−42	–	–
PHA-7	$C_{22}N_2O_4H_{18}$	130 [24]	205	75	222	92	390	260
PHA-11	$C_{44}P_2O_6N_2H_{32}$	210 [24]	124	−86	–	–	–	–
PHA-12	$C_{28}N_2P_2O_{10}H_{32}$	73 [24]	106	33	105	32	–	–
BEDB/4,4′-DDS	$C_{34}H_{32}N_2O_7S$	420 [25]	260	−160	300	120	301	−119
BEDB/3,3′-DDS	$C_{34}H_{32}N_2O_7S$	429 [25]	260	−169	300	129	145	−284
BEDB/m-PDA	$C_{26}H_{28}N_2O_5$	391 [25]	300	−91	295	96	223	−168

Table 1 continued

Name	Elemental composition in repeat unit composition	Exp.	New model	Dev	Walters–Lyon	Dev	Lyon et al.	Dev
BEDB/2,4-DT	$C_{27}H_{30}N_2O_5$	372 [25]	320	−52	367	5	428	56
BEDB/2,6-DT	$C_{27}H_{30}N_2O_5$	530 [25]	320	−210	460	70	428	−102
BEDB/2,3-DT	$C_{27}H_{30}N_2O_5$	326 [25]	320	−6	460	−134	428	102
BEDB/3,4-DT	$C_{27}H_{30}N_2O_5$	415 [25]	320	−95	367	48	428	13
BEDB/4-CmP	$C_{26}H_{27}N_2O_5Cl$	169 [25]	221	52	157	12	181	12
BEDB/5-CmP	$C_{26}H_{27}N_2O_5Cl$	292 [25]	221	−71	157	135	181	−111
BEDB/4-CoP	$C_{26}H_{27}N_2O_5Cl$	389 [25]	221	−168	157	232	216	−173
BEDB/3-3′-DMB	$C_{30}H_{36}N_2O_5$	400 [25]	371	−29	423	−23	369	−31
BEDB/3-3′-DMoB	$C_{30}H_{36}N_2O_7$	288 [25]	326	38	334	−46	394	106
EBPA/DDM	$C_{34}H_{38}N_2O_4$	737 [25]	554	−183	485	252	241	−496
EBPA/DDS	$C_{33}H_{36}N_2O_6S$	513 [25]	484	−29	309	204	149	−364
EBPA/m-PDA	$C_{27}H_{35}N_2O_4$	761 [25]	572	−189	408	353	214	−547
ETBBA/DDM	$C_{34}H_{34}N_2O_4Br_4$	308 [25]	254	−54	177	131	–	–
ETBBA/DDS	$C_{33}H_{32}N_2O_6Br_4S$	443 [25]	215	−228	88	355	–	–
ETBBA/m-PMA	$C_{27}H_{24}Br_4N_4$	238 [25]	226	−12	79	159	–	–
BPA Polyarylate	$C_{22}O_5Cl_2H_{12}$	360 [26]	342	−18	68	−292	29	−331
Chalcone II	$C_{25}O_6H_{18}$	110 [26]	91	−19	105	−5	286	176

atoms is important for prediction of the HRC of a desired polymer. Since the presence of the other elements cannot improve the coefficient of determination (R^2) [14] value, their contributions are zero. Magnitude of R^2 is important for validation of the new correlation because it determines that whether regression accounts for the variation or not. For the value of R^2 equals 1.0, the regression accounts for all of the variations and that the correlation is deterministic. Meanwhile, the value of R^2 equals zero means that the regression accounts for none of the variations [15]. Beside the contribution of the above-mentioned elemental composition, repeat units containing molecular moieties –$(CH_2)_{n\geq 1}$–C(X)(Y)–Z– or –X–Ar–Y– with specific X, Y and Z groups can increase the value of the HRC on the basis of elemental composition. Moreover, the presence of oxygen and carbonyl groups between two aromatic rings as well as –O–P or >CHCO and –OC(O)– in repeat units can decrease the value of the HRC on the basis of elemental composition. Halogen-containing polymers can also act as heat-resistant polymers with the discovery that some chlorinated organic compounds were highly toxic and/or persistent in the environment. Since the contribution of specific groups in molecular moieties depends on the kind of these groups, different values may be considered, which are given in Table 2. On the basis of the training data set, the correlation of the HRC of a desired polymer can be obtained as follows:

$$\begin{aligned}\mathrm{HRC} &= 97.00 \\ &+ \frac{5850n_{\mathrm{H}} - 17532n_{\mathrm{N}} - 7495n_{\mathrm{O}} - 19601n_{\mathrm{Cl}} - 83828n_{\mathrm{Si}}}{\mathrm{MW}_{\text{repeat unit}}} \\ &+ 236.5\mathrm{HRC}_{(\mathrm{CH_2})_n\mathrm{CXYZ,XArY}} - 116.2\mathrm{HRC}_{\mathrm{YXArZ,Hal}}\end{aligned} \quad (4)$$

where HRC is in J g^{-1} K^{-1}; n_{H}, n_{N}, n_{O}, n_{Cl} and n_{Si} are the number of moles of hydrogen, nitrogen, oxygen, chlorine, and silicon atoms per mole of repeat unit, respectively; $\mathrm{MW}_{\text{repeat unit}}$ is the molecular weight of repeat unit in g mol^{-1}; and $\mathrm{HRC}_{(\mathrm{CH_2})_n\mathrm{CXYZ,XArY}}$ and $\mathrm{HRC}_{\mathrm{YXArZ,Hal}}$ are two correcting functions in J g^{-1} K^{-1} for the presence of molecular fragments $-(\mathrm{CH_2})_{n\geq 1}-\mathrm{C(X)(Y)}-\mathrm{Z}-$ or –X–Ar–Y– and Y–X–Ar–Z or halogens (fluorine) in repeat units. The numerical coefficients for n_{H}, n_{N}, n_{O}, n_{Cl} and n_{Si} have units of J mol^{-1} K^{-1}. Since aliphatic polymers such as vinyl-based polymers have higher energy gap than aromatic or unsaturated polymers containing nitrogen and oxygen, the contribution of molecular fragment $-(\mathrm{CH_2})_{n\geq 1}-\mathrm{C(X)(Y)}-\mathrm{Z}-$ in these polymers can increase significantly the value of $\mathrm{HRC}_{(\mathrm{CH_2})_n\mathrm{CXYZ,XArY}}$. As seen in Eq. (1), all coefficients of the number of atoms are negative except the coefficient of n_{H}, which indicate that increasing the values of n_{N}, n_{O}, n_{Cl} and n_{Si} in a desired polymer can decrease the value of the HRC. Since the value of the coefficient n_{H} is smaller than the coefficients of n_{N}, n_{O}, n_{Cl}

Table 2 Values of two correcting functions $HRC_{(CH_2)_nCXYZ,XArY}$ and $HRC_{YXArZ,Hal}$

Molecular fragment in repeat unit	*X*	*Y*	*Z*	$HRC_{(CH_2)_nCXYZ,XArY}$	Example
Predicting $HRC_{(CH_2)_nCXYZ,XArY}$					
$-(CH_2)_{n\geq 1}-C(X)(Y)-Z-$	–H	–H	$-CH_2-$	3.3	Polyethylene (PE)
		–R		2.9	Polypropylene (PP)
		Carbocyclic aromatic without substituent		1.5	Polystyrene (PS)
		Pyridine		1.1	Poly(2-vinyl pyridine)
		–OH		0.4	Poly(vinyl alcohol) (99%; PVOH)
		Cyclic ether		1.1	Poly(vinyl butyral)
		–CN		0.8	Poly(acrylonitrile butadiene styrene) (ABS)
		–H	$-OCH_2-$	0.9	Poly(ethylene oxide)
			–C(O)–NH– or –C(O)O–	0.2	Polycaprolactam
			–OC(O)Ar–O–	0.7	Poly(ethylene terephthalate) (PET)
			$-NH-C(O)-(CH_2)_m-$ C(O)– where $m \leq 8$	1.6	Poly(hexamethylene adipamide)
	–R	–R	$-CH_2-$	0.4	Polyisobutylene
		–COOH		0.6	Poly(methacrylic acid)
		$-COOCH_3$		0.3	Poly(methyl methacrylate) (PMMA)
		Carbocyclic aromatic without substituent		0.6	Poly(α-methyl styrene)
–*X*–Ar–*Y*–	$-C(=CCl_2)-$	–OC(O)–	–	1.1	BPA Polyarylate
	–CRR′–	$-O-CH_2-$ or –O–C=N	–	0.6	EBPA/DDM

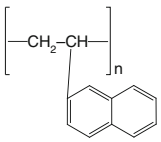
Molecular moiety in repeat unit	*X*	*Y*	*Z*	$HRC_{YXArZ,Hal}$	Example
Estimating $HRC_{YXArZ,Hal}$					
Y–*X*–Ar–*Z*	–CO–	Ar	–	2.0	Poly(benzoyl 1,4-phenylene)
	–O– or the presence simultaneously of both –O– and –CO– (or –SO2– or –SO–) without $-Ar-C(CH_3)_2-Ar-$		–	1.0	Poly(ether ketone) (PEK)
	–O–P	Ar or R	–	1.0	Polyphosphazene
	–	>CHCO	–OC(O)–	1.3	Chalcon II
$-CF_3$ or more than one $-CF_2$	–	–	–	0.7	Poly(tetrafluoroethylene) (PTFE)

and n_{Si}, its contribution in lowering the HRC is minor. The coefficients of electronegative elements n_N and n_{Cl} as well as n_{Si} are much higher than the coefficient of n_O, which indicates increasing n_N, n_{Cl} and n_{Si} is more effective than n_O for reduction in the HRC. Increasing of unsaturation in a new designed heat resistance polymer is one of the appropriate ways for decreasing the value of the HRC because it reduces the value of n_H. Since the addition of relatively small amounts of silicon compounds to various polymeric materials can improve their flame retardancy [16–18], the coefficient of n_{Si} in Eq. (4) has the largest negative value with respect to the coefficients of the other atoms. Thus, introducing silicon element and its groups into monomers of suitable polymers such as epoxy can also improve some other properties of the epoxy resins, such as thermal stability, high resistance to thermal oxidation, low surface energy and low toxicity [19, 20]. It was found that phosphorus-containing compounds or resins have been

demonstrated as effective flame retardants for epoxy resins. As indicated in Table 2, this situation has been considered in the new correlation because the presence of –O–P can decrease the value of the HRC through the contribution of the $HRC_{YXArZ,Hal}$. As indicated in Eq. (4), the effects of halogens for decreasing the value of the HRC appear in two terms: (a) n_{Cl} for chlorine as additive term and (b) $HRC_{YXArZ,Hal}$ for fluorine as non-additive contribution. For those polymers such as biphenol phthalonitrile where $HRC_{(CH_2)_nCXYZ,XArY}$ and $HRC_{YXArZ,Hal}$ have no contribution and $\frac{5850n_H-17532n_N-7495n_O-19601n_{Cl}-83828n_{Si}}{MW_{repeat\ unit}} < 97$, the value of the HRC should be taken 20 J g^{-1} K^{-1}.

The last column of Table 2 indicates the use of two correcting functions in Eq. (4). For example, the value of HRC for poly(2-vinyl naphthalene) is calculated as follows:

Repeating unit:



Elemental composition and $MW_{repeat\ unit}$: $n_H = 10$, $n_N = n_O = n_{Cl} = n_{Si} = 0$ and $MW_{repeat\ unit} = 154.22$ g mol^{-1}.

The various parameters for repeating unit with general molecular fragment $-(\mathbf{CH_2})_{n\geq 1}-\mathbf{C}(X)(Y)-\ Z-$ $n = 1$, $X =$ –H, $Y =$ carbocyclic aromatic without substituent and $Z =$ $–CH_2–$ where as given in Table 2, the value of $HRC_{(CH_2)_nCXYZ,XArY}$ is 1.5 J g^{-1} K^{-1}. Since there is no contribution of $HRC_{YXArZ,Hal}$, the value of $HRC_{YXArZ,Hal} = 0$. Thus, Eq. (4) gives the value of the HRC as:

$$HRC = 97.00 + \frac{5850(10)}{154.22} + 236.5(1.5) = 831\ J\ g^{-1}\ K^{-1}$$

Statistical parameters in new model and their significance

Table 3 shows important statistical parameters of the new model including regression coefficients, standard errors, *t* statistics, *P* values, as well as the upper and lower bounds of a 95% confidence interval. The statistical significance of the regression coefficients in predicting the HRC values can be evaluated on the basis of the above-mentioned statistical parameters as: (1) *standard error*—if the standard error is small relative to each coefficient, its variable is significant; (2) *t statistic*—since it is the ratio of coefficients to their standard errors, higher *t* statistic values correspond to the more significant coefficients [21, 22]; (3) *P value*—it shows the probability that a parameter estimated from the measured data should have the value which was determined. However, the effect of variable is significant and the observed effect is not due to random variations for *P* value of <0.05 [15]. As seen in Table 3, all statistical parameters show that the proposed nine descriptors in Eq. (4) have a highly significant ability to predict the HRC. As shown in Table 1, the predicted results of the new model, Walters and Lyon [6] and Lyon et al. [8], have been compared with experimental data. For several polymers, the group additivity methods of Walters and Lyon [6] and Lyon et al. [8] cannot be used because some particular functional groups in these polymers are absent for these methods. The predictive reliability of the new method has been tested for some new polymers, which are given in Table 4. As seen in Table 4, the results of the model as well as two group additivity

Table 3 Regression coefficients, standard errors, *t* statistics, *P* values and confidence intervals for new model

Variable	Coefficient	SE	*t* statistic	*P* value[a]	Lower bound[b]/95%	Upper bound[c]/95%
Intercept	97.00	31.45	3.08	0.00262	34.62	159.38
$n_H/MW_{repeat\ unit}$	5850	383	15.29	2.98E−28	5091	6609
$n_N/MW_{repeat\ unit}$	−17,532	2490	−7.04	2.21E−10	−22,471	−12,593
$n_O/MW_{repeat\ unit}$	−7495	1352	−5.55	2.28E−07	−10,176	−4815
$n_{Cl}\ MW_{repeat\ unit}$	−19,601	3960	−4.95	2.92E−06	−27,455	−11,746
$n_{Si}/MW_{repeat\ unit}$	−83,828	24,909	−3.37	0.00108	−133,229	−34,427
$HRC_{(CH_2)_nCXYZ,XArY}$	236.5	17.6	13.45	2.05E−24	201.6	271.3
$HRC_{YXArZ,Hal}$	−116.2	24.5	−4.75	6.68E−06	−164.8	−67.7

[a] *P* value = probability of rejecting a true null hypothesis

[b] Lower bound (95%) = lower bond of a 95% confidence interval

[c] Upper bound (95%) = upper bond of a 95% confidence interval

methods of Walters and Lyon [6] and Lyon et al. [8] have also been compared with experimental data. Among eleven polymers given in Table 4, two group additivity methods can be applied only for seven polymers because these methods do not contain some particular functional groups.

Table 5 shows a comparison between further statistical parameters of Eq. (4) and two group additivity methods for model building and the test dataset. Root-mean-squared (RMS) error provides a reliable indication of the fitness of the model, which is independent of the distribution of data points. RMS values should be low and as similar as possible to ensure both the predictive ability (low values) and generalizability (similar values) [23]. Mean absolute deviation (MAD) is also a linear measure of errors that assesses the average size of errors when negative signs are ignored. Statistical parameters RMS, MAD and maximum of errors of these data for different models are given in Table 5. These parameters for new polymers are close to those obtained for training set. Low values of these statistical parameters confirm high reliability of the new model as compared to two available group additivity methods of Walters and Lyon [6] and Lyon et al. [8].

It should also be mentioned that derivation of Eq. (4) was done from an examination of the HRC of different types of polymers given in Table 1 where their repeat units containing chemical groups/moieties by two principal steps as:

1. *Elemental composition:* It was found that the ratios of the number of moles of some atoms (n_H, n_N, n_O, n_{Cl} and n_{Si}) to $MW_{repeat\ unit}$ have important contribution because P values of corresponding coefficients are <0.05 [14].
2. *The presence of some specific molecular fragments:* It is possible to correct large deviations of the predicted results of step 1 through introducing two correcting functions $HRC_{(CH_2)_nCXYZ,XArY}$ and $HRC_{YXArZ,Hal}$ as well as adjusting their coefficients by minimizing RMS error [14].

Figure 1 shows a graphical comparison between the new model and the group additivity methods for all data. As indicated, the predictions of the new model methods exhibit a lower dispersion with respect to both group additivity methods. This is consistent with the fact that the new method has lower RMS values for model building and testing data as compared to group additivity methods. Figure 2 shows the range of absolute errors of the new model ($AE = |HRC_{exp.} - HRC_{pred.}|$) for all 122 data points given in Tables 1 and 4, which indicate high reliability of the new method.

Table 4 Comparison of the predicted results of HRC in J g^{-1} K^{-1} of the new model as well as two molar group contributions of Walters and Lyon [6] and Lyon et al. [8] for some new polymers with the measured values

Name	Elemental composition in repeat unit composition	Exp.	New model	Dev	Walters–Lyon	Dev	Lyon et al.	Dev
BHDB-sulfone (1)	$C_{26}H_{18}O_5S$	120 [27]	134	14	218	98	108	−12
BHDB-sulfoxide (2)	$C_{26}H_{18}O_4S$	66 [27]	157	91	210	144	182	116
BHDB/biphenyl (9)	$C_{25}H_{17}O_{4.5}S$	86 [27]	137	51	333	247	265	179
BHDB/sulfide (10)	$C_{25}H_{17}O_{4.5}S_{1.5}$	138.5 [27]	131	−8	333	195	265	126
PPSU	$C_{24}H_{16}O_4S$	228 [28]	140	−88	182	−46	159	−69
BDHB acrylate	$C_{22}H_{14}O_5$	65 [28]	70	5	39	−26	39	−26
BDHB phosphinate	$C_{20}H_{14}O_4P$	65 [28]	129	64	–	–	–	–
BHDB poly(arylate-co-phosphonate) (1:1)	$C_{42}H_{28}O_9P$	35 [28]	1	−34	–	–	–	–
Polyester carbonate (white)	$C_{37}H_{26}O_{10}$	213 [28]	219	6	126	−87	293	80
Polyester carbonate (gray)	$C_{37}H_{26}O_{10}$	192 [28]	219	27	–	–	–	–
Polyester carbonate (clear)	$C_{37}H_{26}O_{10}$	168 [28]	219	51	–	–	–	–

Table 5 Statistical parameters of the predicted results of HRC in J g^{-1} K^{-1} of the new model as well as two molar group contributions of Walters and Lyon [6] and Lyon et al. [8] for model building and testing

	RMS			MAD			Maximum of errors		
	Equation (4)	Walters–Lyon	Lyon et al.	Equation (4)	Walters–Lyon	Lyon et al.	Equation (4)	Walters–Lyon	Lyon et al.
Model building	80	147	208	58	100	129	237	605	681
Testing	50	141	102	40	120	87	91	247	179

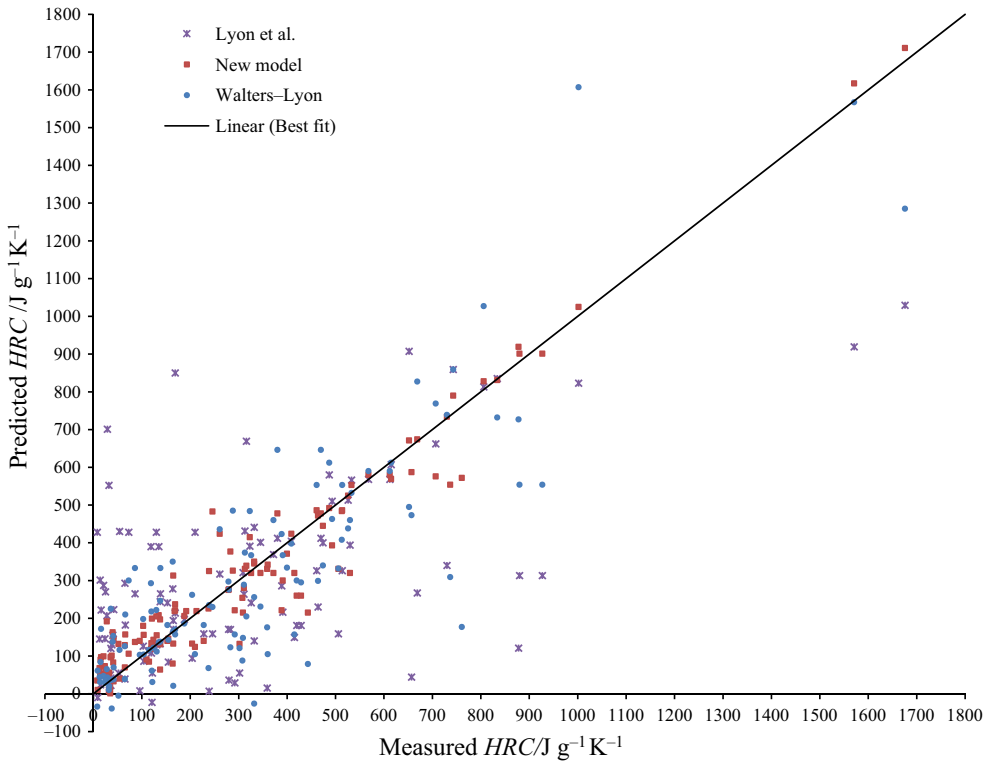


Fig. 1 Predicted results of HRC in J g^{-1} K^{-1} for the new model (122 data) as well as two molar group contributions of Walters and Lyon [6] (117 data) and Lyon et al. [8] (108 data) versus experimental data

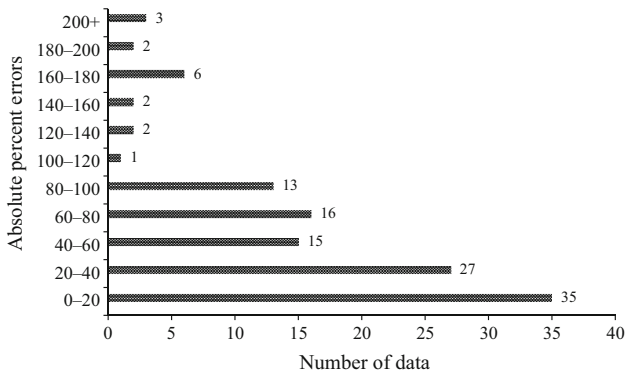


Fig. 2 Range of absolute errors of the new model for all data points (122 data)

Conclusions

A simple and accurate model was developed for prediction of the HRC values of different polymers with their repeat units that are comprised of chemical groups/moieties such as methyl, phenyl, carbonyl, ether, amide and ester. The model is based on the contribution of n_H, n_N, n_O, n_{Cl} and n_{Si} divided by $MW_{repeat\ unit}$ as well as two correcting functions of $HRC_{(CH_2)_nCXYZ,XArY}$ and $HRC_{YXArZ,Hal}$. The predicted results of the new model were compared with the calculated data of two group additivity methods, which confirm higher reliability of the new correlation. The values of $HRC_{(CH_2)_nCXYZ,XArY}$ and $HRC_{YXArZ,Hal}$ beside elemental composition and $MW_{repeat\ unit}$ can be easily obtained from repeat units of polymers.

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